

SYNTHESIS OF METHYL METHACRYLATE (MMA) VIA C₂-CARBOXYLATION AND C₃-CONDENSATION REACTIONS

Makarand R. Gogate¹, James J. Spivey¹, Joseph R. Zoeller², Richard D. Colberg²,
Gerald N. Choi³, and Samuel S. Tam⁴

¹Research Triangle Institute, P.O. Box 12194, Research Triangle Park, NC 27709-2194

²Eastman Chemical Company, P.O. Box 1972, Kingsport, TN 37662-5150

³Bechtel, P.O. Box 193965, San Francisco, CA 94119-3965

⁴Bechtel, P.O. Box 2166, Houston, TX 77252-2166

KEYWORDS: Ethylene Carbonylation, Formaldehyde Condensation, MMA.

INTRODUCTION

The most widely practiced commercial technology for the synthesis of methacrylic acid (MAA) and methyl methacrylate (MMA) is the acetone cyanohydrin (ACH) process. The ACH process requires handling of large quantities of extremely toxic and hazardous hydrogen cyanide and generates copious amounts of ammonium sulfate wastes which are either discarded or reclaimed at substantial cost. The ACH technology is thus environmentally and economically untenable for new expansions. There is a strong drive within the chemical industry for an alternate coal-based process (Gogate et al., 1997; Spivey et al., 1995a, 1996). The process proposed here (Figure 1) is based on C₂-hydrocarbonylation reactions using CO generated from coal and C₃-Condensation reactions (Spivey et al., 1995b) and consists of three steps: Step 1—ethylene carbonylation, Step 2—formaldehyde condensation, and Step 3—esterification of MAA produced in Step 2 to MMA. Steps 1 and 2 present technical challenges for successful commercial demonstration and are the focus of this paper.

The research presented in this paper on Step 1 elucidates the development of a homogeneous catalyst for propionate synthesis and research on Step 2 delineates the development of an acid-base catalyst for condensation of formaldehyde with propionates. Additionally, results of a preliminary economic analysis comparing the product value of MMA via six different commercial or near-commercial routes is presented.

EXPERIMENTAL

Ethylene Carbonylation

To allow the measurement of experimental rates of ethylene carbonylation to propionates, a 2-L Hastelloy[®]-C overhead stirred autoclave was fitted with a high-pressure condenser and a dip tube for removing samples during the reaction. During a typical run, 5.81 g (0.022 mol) of Mo(CO)₆, 15.5 g (0.040 mol) of tetrabutyl phosphonium iodide, 109.2 g (0.700 mol) ethyl iodide, 81 g (4.5 mol) of H₂O, and 450 g (7.5 mol) of acetic acid (as an internal standard and solvent) were added to the autoclave. The autoclave was then pressure-tested with nitrogen at 68.0 atm and a gas purge was established through the reactor at 3 mol/h. The nitrogen was vented, and autoclave was then pressurized to 23.8 atm with 5 percent hydrogen in carbon monoxide, and subsequently heated to 160 °C. Upon reaching the temperature, the pressure was raised to 51.0 atm using a gas mixture consisting of 6 percent hydrogen, 47 percent CO, and 47 percent ethylene, maintaining the 3 mol/h gas purge. Liquid samples were removed every 30 min from the reactor for the first 5 hours after the steady state was reached, and analyzed for ethyl iodide, ethyl propionate, acetic acid, and propionic acid, using a Hewlett Packard 5890 Gas Chromatograph (GC) containing a 25 m (0.25 - mm ID, 0.25 μm film) Quadrex 007 FFAP capillary column, with p-xylene as the internal standard. Gas samples were also removed every 60 min for first 5 h, to ensure that the gas composition was uniform. All trace materials were detected by a gas chromatograph (GC) / mass spectrometer (MS).

Condensation Catalysis

The condensation catalysts were tested in a continuous fixed-bed microreactor system. The nominal flow rates of propionic acid, formaldehyde, and nitrogen were kept at 75, 15, and 220 mmol/h. The feed was prepared by dissolving trioxane (solid trimer of formaldehyde) into propionic acid in a ca. 5:1 mole ratio, and fed into a preheater maintained at 300 °C, using a syringe pump (ATI Orion SAGE M361). The vaporized feed was passed over a catalyst charge, located centrally in a 6-mm ID x 356-mm L SS316 reactor tube. The catalyst charge (of a 16-30 mesh nominal size fraction) was held in place by glass wool and glass beads. Thermocouples mounted directly at the entrance and exit of catalyst bed provided temperature control and readout. Both the preheater and the reactor

were mounted horizontally in Lindberg furnaces (Blue M, Model #TF55035A). The product vapors containing methacrylic acid, water, propionic acid, and diethyl ketone were cooled and collected in a impinger contained in an ice bath. The product gases were collected in a Tedlar Bag. The liquid products were analyzed over a fused silica capillary column (30 m x 0.32 mm ID) with a 0.25 μm film thickness of DB-FFAP, using a flame ionization detector (FID) using a HP 5890 gas chromatograph (GC). The gas samples were analyzed using a fixed-volume loop injection onto a Poropak[®]T/Molecular Sieve (MS) 5 \AA columns, with a column isolation sequence, using a thermal conductivity detector (TCD).

The catalysts were characterized for their surface area, pore volume, and surface acid-base properties. The surface and pore volume determinations were made on a Quantachrome NOVA 100 BET-N₂ surface area analyzer. The acid-base properties were measured on an Altamira AM1-100 catalyst characterization system. The NH₃-adsorption was carried out with a 10 percent NH₃-N₂ gas mixture (25 mL/min) for 30 min at 50 °C. The desorption was carried out from 50 to 550 °C, at 10 °C/min. The evolved gases were continuously monitored using a thermal conductivity detector (TCD). For surface basicity measurements, an identical time, temperature, and flow profile was followed, with a 10 percent CO₂-N₂ gas mixture as the treatment gas.

RESULTS AND DISCUSSION

Ethylene Carbonylation.

General Description of the Catalyst. Although homogeneous catalysts for this reaction are well known (Samel et al., 1993), commercial application has been limited to a highly toxic and volatile Ni(CO)₄ catalyst operating at high pressures (>180 atm) and high temperatures (>270 °C) (Bertleff, 1986; Samel et al., 1993) to produce propionic acid. Processes operating at lower pressures and temperatures generally require expensive catalysts such as Rh, Ir, or Pd and none have been employed commercially (Bertleff, 1986; Colquhoun et al., 1991; Forster et al., 1981; Mullen, 1980; Pino et al., 1977). Although Cr group metals have been used in combination with known carbonylation catalysts such as Co, Ni, Rh, and Ir, they have not been shown to have significant catalytic activity in isolation. In the study reported here, a halide-stabilized Mo(CO)₆ homogeneous catalyst is used at 130 to 170 °C and 350 to 750 psig.

The results of batch experiments comparing the observed order of reactivity for the Group 6 metals shows that Mo >> W > Cr and that the halide employed may be either Br or I. Substitution of bromine for iodine only leads to a small change (~25 percent decrease) in reaction rate, suggesting an electron transfer process (Huber et al., 1995). When the process is operated with a catalyst composed of Bu₄PI, Mo(CO)₆, and EtI, the Mo catalyzed carbonylation of ethylene to propionic anhydride at a nearly linear rate with time, until a 75- to 85-percent conversion of the propionic acid is achieved, at which point the reaction begins to slow markedly. A typical reaction profile for this process appears in Figure 2.

Effect of Temperature, Determination of Activation Parameters. The effect of temperature was measured in batch experiments between 130 and 170 °C using identical levels of gas and catalyst components throughout the full range of temperatures. The apparent activation energy (E_{app}) was 39.3 kcal/mol. The rate expression is:

$$k = \frac{\text{Rate} \cdot [P_{\text{H}_2}]^{\text{app}}}{[\text{Mo}(\text{CO})_6]^{n_{\text{Mo}}} [\text{EtI}]^{n_{\text{EtI}}} [\text{I}^-]}$$

The enthalpy of activation (ΔH^\ddagger) and entropy of activation (ΔS^\ddagger) were determined from the Eyring plot: $[\ln(k/T) \text{ vs. } (1/T)]$. ΔH^\ddagger was found to be +38.4 kcal/mol and ΔS^\ddagger was estimated to be +40 cal/mol/K. These activation parameters suggest a rate-determining step involving the dissociation of the Mo-CO bond in Mo(CO)₆ (Ehlers and Frenking, 1993, 1994).

Kinetic Effects of Reactants. To measure kinetic effects due to ethylene, CO, and hydrogen, a continuously gas purged autoclave with a liquid sampling loop was used. Using this apparatus, the partial pressure of each reactant could be varied independently. The effects of hydrogen and ethylene were uneventful and increasing partial pressures of these two reactants did not show any discernible increase in the reaction rate. It was therefore concluded that the reaction is zero order with respect to hydrogen and ethylene. Increasing the partial pressure of CO led to a decreased reaction rate and the measured reaction order was found to be -1.2. This inverse and complex dependence of reaction order in CO suggests that the overall mechanism involves a step which is inhibited by CO. To study the effect of Mo(CO)₆, EtI, and Bu₄I levels on reaction rate, the partial

pressures of CO, hydrogen, and ethylene were kept constant, with CO levels controlled very accurately at 23.8 atm. While the reaction order in Bu₄I was first order, the experimentally measured reaction orders for both Mo(CO)₆ and EtI were both approximately 1/2 order, indicating a likely free-radical type reaction mechanism. Based on these reaction order measurements, a predictive rate equation was proposed.

Condensation Catalysis

The condensation of formaldehyde with propionic acid is catalyzed by acid-base catalysts, as shown in Figure 3 (Gogate et al., 1997). The catalyst development effort has focused on developing a stable, selective, and active condensation catalyst for this reaction. Fixed-bed microreactor studies of more than 80 potential catalytic materials have shown that Group V metals (V, Nb, and Ta) are active condensation catalysts and that niobium catalysts are the most active.

The results show that the 20 percent Nb/SiO₂ is the most active catalyst. However, the catalyst deactivates. The long-term deactivation of a 10 percent Nb/SiO₂, V-Si-P 1:10:2.8, and 10 percent Ta/SiO₂ are shown in Figure 4. The deactivation of these catalysts has been correlated with the strength and distribution of the acid and base sites on the catalyst. There appears to be an optimum balance between these sites that is necessary to promote the condensation reaction. Figure 4 shows that an oxidative treatment of the deactivated catalyst partially restores the activity. Work is under way to minimize deactivation.

Economics of the Overall Process

An economic analysis was carried out by Eastman and Bechtel based on the results on the 20 percent Nb/SiO₂ catalyst at 300 °C, 2 atm, flow rates of propionic acid: formaldehyde:nitrogen 72:16:200 mmol/h, 5 g catalyst charge (0.7- to 1.1-mm size fraction), and a volume hourly space velocity of 1,080 cm³/g cat·h. Reaction kinetics are assumed to be first order in formaldehyde, in order to remove the effects of excess nitrogen diluent and excess HOPr. This process was compared to five commercial (or, near commercial) technologies for MMA manufacture:

- Conventional ACH-based process (Rohm & Haas),
- (New) Mitsubishi Gas Chemical (MGC) ACH-based process,
- *i*-butylene oxidation process (Lucky, Japan Methacrylic),
- *t*-butanol oxidation process (Kyodo, Mitsubishi Rayon), and
- Propyne carbonylation (Shell, ICI).

A comparison of production cost (or, product value) was carried out for these six routes, based on a 250 Mlb/year plant (except for the propyne carbonylation process, for which a 100 Mlb/year capacity is assumed due to the very limited worldwide supply of propyne). To account for catalyst deactivation, the process design includes parallel fixed-bed reactors.

The product value comparison for the RTI-Eastman-Bechtel HOPr/MeOH route with five commercial routes (Figure 5) shows that the RTI-Eastman-Bechtel three-step process at 52¢/lb MMA is competitive with all commercial technologies for MMA manufacture, except propyne carbonylation (at 44¢/lb). [The current selling price for MMA is roughly 75¢/lb.] However, the propyne carbonylation technology suffers from limited raw material supply. Both the conventional ACH and MGC ACH-based processes (at 73¢/lb and 70¢/lb MMA, respectively) are more costly than the RTI-Eastman-Bechtel three-step route, as is the *i*-butylene oxidation route (at 59¢/lb). In the United States, the *i*-butylene route suffers from competing raw material demands for methyl tert-butyl ether (MTBE) plants. The *t*-Butanol oxidation process at 55¢/lb MMA appears quite competitive with the RTI-Eastman-Bechtel three-step process.

CONCLUSIONS

The carbonylation of olefins, particularly ethylene, with a halide-promoted Mo catalyst represents the efficient process using a Cr-group metal as the active catalyst. Detailed mechanistic analysis indicates that the reaction likely proceeds via a free radical mechanism, which is initiated by a rate limiting dissociation of CO from Mo(CO)₆. The precise propionate derivative obtained depends on the nature of the nucleophile, and the process for propionic acid uses steam. If present in too large a quantity (alcohol for methyl propionate process, or water for propionic acid process), the nucleophilic component can inhibit the reaction, by competing with the EtI for the vacant coordination site of Mo(CO)₆. The condensation of propionate derivatives with formaldehyde is a synthetic route to MAA and MMA. The reaction mechanism suggests that both acid and base properties are required and a definitive balance of acid and base site strengths is perhaps needed for an active, selective, and stable catalyst. As a result of screening over 80 catalytic materials, a 20%

$\text{Nb}_2\text{O}_5/\text{SiO}_2$ catalyst is found to give optimum performance, although catalyst deactivation is ubiquitous on this and other catalysts. Detailed XPS/ESCA/XRD studies prove that carbon deposits in nodular form on the active Nb_2O_5 sites, thereby limiting accessibility of an Nb_2O_5 site to the reactants. Based on the XPS/ESCA study of a regenerated catalyst (using oxidative regeneration), a reaction-regeneration cycle study on the 20% $\text{Nb}_2\text{O}_5/\text{SiO}_2$ is planned, which may alleviate the catalyst deactivation pattern. A preliminary economic evaluation of the RTI-Eastman-Behcetel three-step methanol process consisting of external formaldehyde generation, condensation of formaldehyde with propionic acid, and external esterification of resulting methacrylic acid with methanol to form MMA shows that for a 250 Mlb/yr product and 10 percent rate of return on investment, the product value of RTI-Eastman-Behcetel three-step route at 52¢/lb is cost-competitive with known commercial and near commercial technologies for MMA manufacture, except propyne carbonylation, which suffers from limited raw material supply. Further research on condensation catalysis, particularly in enhancing catalyst longevity is under way.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the support of this research, by the U.S. Department of Energy / Federal Energy Technology Center (DOE/FETC), through Contract No. DE-AC22-94PC065. The authors are also indebted to DOE Project Officer, Dr. Richard E. Tischer, for his support and guidance.

REFERENCES

- Bertleff, W. 1986. Carbonylation. In: *Ullman's Encyclopedia of Industrial Chemistry*, 5th edn., Vol. A5, VCH Publishers, New York, NY, p. 223.
- Colquhoun, H.M., D.J. Thompson, and M.V. Twigg. 1991. *Carbonylation-Direct Synthesis of Carbonyl Compounds*, Plenum Press, New York, NY, pp. 102-106; 119-130.
- ChemSystems. 1996. Methacrylic Acid/Methacrylates, PEP Report 94/95-3.
- Forster, D., A. Hershman, and D.E. Morris. 1981. *Catalysis Rev.-Sci. Eng.*, 23, p. 89.
- Gogate, M.R., J.J. Spivey, and J.R. Zoeller. 1997. "Synthesis of methyl methacrylate by vapor phase condensation of formaldehyde with propionate derivatives", *Catal. Today*, 36(3), pp. 243-254.
- Gogate, M.R., J.J. Spivey, J.R. Zoeller, R.D. Colberg, S.S. Tam, and G.N. Choi. 1997. "Novel Catalysts for Environmentally Friendly Synthesis of Methyl Methacrylate." *Ind. Eng. Chem. Res.*, 36, pp. 4600.
- Huber, T.A., D.H. Macartney and M.C. Baird. 1995. *Organometals*, 14, p. 592.
- McKetta, J.J., ed. 1989. *Encyclopedia of Chemical Processing and Design*. Vol. 30.
- Mullen, A. 1980. In J. Falbe (Ed.), *New Syntheses with Carbon Monoxide*, Springer, Berlin, pp. 275-286.
- Pino, P., F. Piacenti, and M. Bianchi. 1977. In: *Organic Syntheses via Metal Carbonyls*, 1st edn., Wender and P. Pino, Vol. 2, Wiley, New York, NY, pp. 233-296.
- Samel, U.R., W. Kohler, A.O. Gamer, and U. Keuser. 1993. "Propionic Acid and Derivatives." In *Ullman's Encyclopedia of Industrial Chemistry*, 5th edn., Vol. A22, VCH Publishers, New York, NY, p. 223.
- Spivey, J.J., M.R. Gogate, B.W.L. Jang, E.D. Middlemas, J.R. Zoeller, S.S. Tam and G.N. Choi. 1995a. "Synthesis of Methyl Methacrylate from Coal-Derived Syngas", In *Proceedings of the Contractors' Review Meeting on Coal Liquefaction and Gas Conversion*, U.S. DOE/PETC, Pittsburgh, PA, pp. 385-395.
- Spivey, J.J., M.R. Gogate, B.W.L. Jang, E.D. Middlemas, J.R. Zoeller, S.S. Tam, and G.N. Choi. 1995b. "A New Route to Acrylates and Methacrylates from Syngas." Presented at the World Environmental Congress, London, Ontario.
- Spivey, J.J., M.R. Gogate, J.R. Zoeller, R.D. Colberg, G.N. Choi, S.S. Tam, R.E. Tischer, R.D. Srivastara. 1996. "Novel Syngas-based Process for Methyl Methacrylate." In *Proceedings of the Thirteenth Annual International Pittsburgh Coal Conference*, Volume 1, pp. 559-564, The University of Pittsburgh, Pittsburgh, PA.
- SRI. 1993. Methacrylic Acid and Esters, PEP Report 11D, Section 8.

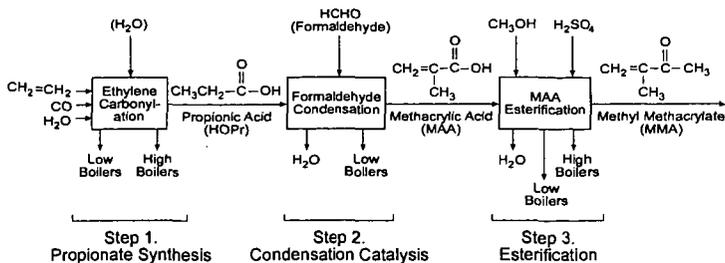
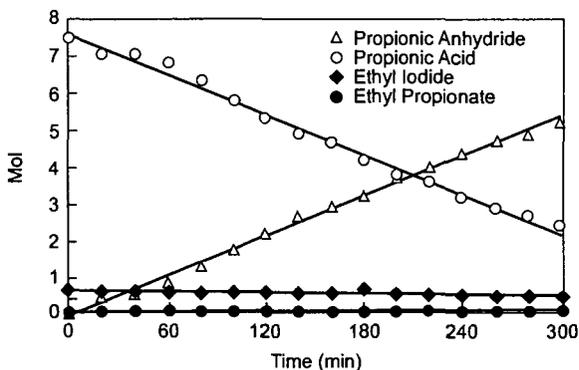


Figure 1. RTI-Eastman-Bechtel three-step HOPr/MeOH-based MMA process (with external formaldehyde feed).



Initial composition: EtI, 0.7 mol; EtCOOH, 7.5 mol; Mo(CO)₆, 22 mmol; Bu₄PI, 40 mmol. Conditions: 160 °C, 55 atm. Gas compositions: 5% H₂, 50% C₂H₄, 45% CO.

Figure 2. Reaction profile for the carbonylation of ethylene to propionic anhydride.

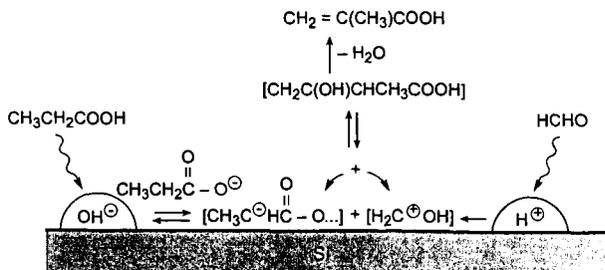
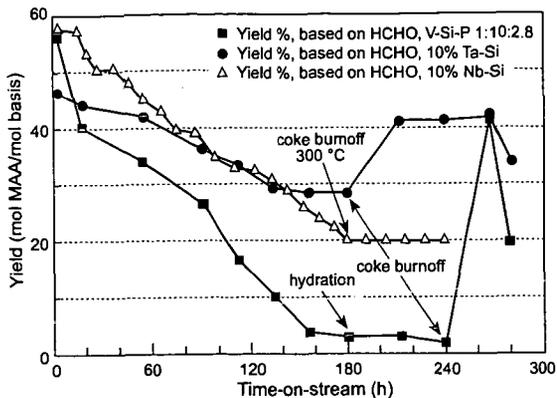


Figure 3. Representative mechanism for propionic acid and formaldehyde.



Experimental Conditions V-Si-P, Ta-Si

For V-Si-P, Ta-Si: 300 °C, 2 atm, 15 g cat. charge, 41:17:220 mmol/h
 PAA:HCHO:Nitrogen, 290 cm³/g cat-h

For Nb/Si: 300 °C, 2 atm, 5 g cat. charge, 72:16:220 mmol/h
 PA:HCHO:Nitrogen, 1080 cm³/g cat-h

Figure 4. Long-term activity check on V-Si-P 1:10:2.8, 10% Ta-Si, and 10% Nb-Si catalysts.

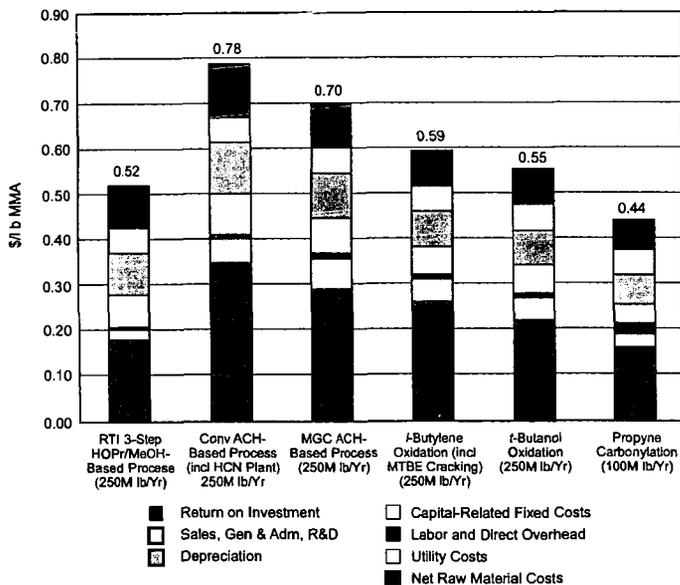


Figure 5. MMA processes, product value comparison (10% ROI).

STUDY OF PETROLEUM COKE USED AS REDUCING AGENT IN IRON ORES PROCESSING

Jun M. Lee, Jeffrey G. Rolle, James J. Baker

A. J. Edmond Co., 1530 West 16th Street, Long Beach CA 90813

Marcos de Albuquerque Contrucci, Edmar Saul Marcheze

TECNORED LTDA, Rua Georges Smirnow 305/306 Bairro Boa Vista

CEP 89206-740, Joinville, SC Brasil

James W. Ramming

Tecnored Technologies Incorporated, 100 First Stamford Place, Stamford, CT 06902

Keywords: petroleum coke, iron ores reduction

ABSTRACT

A petroleum coke with a high sulfur content (approximately 7.0 wt %) was tested as reducing agent in iron ores processing. Proprietary TECNORED pellets were prepared by blending of iron ore fines, petroleum coke fines and other additives (binders, fluxing agents, etc.) through a wet-pelletizing process. A pilot-scale reaction system was assembled for the reaction performance study with the petroleum coke and TECNORED pellets, which consists of a packed-bed Inconel reactor with temperature controller and programmer, air, argon and nitrogen gas supply system, effluent product gas sampling system, and gas analyzers. Five screening tests were recently performed and experimental results are presented.

INTRODUCTION

Production of petroleum cokes steadily increased by 51% during the past decade, expecting continuous increase in the coming years, primarily due to declining quality of crude oils [1]. Green petroleum cokes are mostly used as utility fuels (about 73% for fuel grade), and as feedstocks (about 27%) for further upgrading calcination. The calcined petroleum cokes are used in production of specialty products such as aluminum anodes, graphite electrodes, titanium oxide pigments, recarburized ductile irons, etc.

In addition green petroleum coke was often used as an additive in metallurgical coke making, depending on its availability in the market at lower prices than those of coking coals [2]. The performance of metallurgical coke, produced from coking coal blends containing petroleum coke, was successfully tested in several blast furnaces. The maximum limit of petroleum coke in a coal blend for acceptable coke quality was reported to be 5 wt % in Japan. However, elsewhere a higher limit (20 or 40 wt %) was reported. Several properties of coal blends such as particle size, rheological properties, volatile matter and total carbon content are important affecting quality of metallurgical coke. Various instrumental and analytical methods and techniques can be found in the literature to be used to characterize petroleum cokes and coal blends.

TECNORED Process Background and Description

The proprietary TECNORED process (developed by the TECNORED in Brazil) utilizes self-reducing pellets composed of tiny particles of iron ore and petroleum coke, and generating infinite reaction sites, enhances reaction rates of iron ore reduction by more than ten times (residence time 0.5 vs. 6 to 8 hours) [3]. The pellet consists of 70 to 75 wt % iron ore fines, 15 to 20 wt % coke fines and 5 to 10 wt % binders and fluxes, respectively. The process can use 100% petroleum coke without blending with coal or any blends of petroleum coke and coal.

In conventional commercial blast furnace processes [4,5,6], two main reduction steps are involved, requiring 1 to 2 hours residence time for each reduction zone, zone converting wustite ($\text{Fe}_{0.947}$) to solid iron (Fe_s) and zone converting Fe_2O_3 to Fe_3O_4 and further to $\text{Fe}_{0.947}$. Fusion and slagging zones add more residence time after completion of reaction, totaling 5 to 8 hours. Gas residence times are in the order of only 1 second and hence good gas and solid contact is required for efficient operation.

In contrast, the TECNORED process has many advantages in processing iron ores:

- Diversified low-cost raw materials and fuels
 - low-grade iron-ore fines with 60 to 64% Fe
 - low-cost reductant fines with non-coking coals, cokes, petroleum cokes, etc.
 - low-cost binders
 - low-cost solid fuels with non-coking lumps, petroleum cokes, semi-cokes, etc.

- full recycling of all dust and fines
- Low-cost and low-investment pelletizing process
 - cold curing in open air yards
 - grinding of coal fines only to minus 140 mesh
 - grinding of ores, if any, only to minus 100 mesh
 - no hot-firing of pellets
 - green pellets with enough strength to bulk handling
- High productivity and energy efficiency in TECNORED furnace
 - 30 to 40 minutes residence time against 6 to 8 hours in blast furnaces
 - no Boudouard reaction on solid fuels due to side feeders
 - CO burning in the upper shaft to heat up and pre-reduce pellets
 - pellets drying in the silos by hot-blast stack off-gases
 - low power requirements due to low shaft height (2-3 m), low-pressure blast and lower elevation of the charge
 - use of blast partially cold
 - cheap top-gas available, if desired
- Low investment TECNORED furnace
 - multi-mode atmosphere concept on a single-vessel unit
 - compact shaft-furnace design with classical units of hot blast, gas cleaning and centrifugal blowers, making even blast furnace conversion possible
 - small working volume due to high productivity
 - no dosing of charge required
 - flow of charge regulated by melting rate solely through the blast
 - simple process control

Summary of Pilot-Scale Tests

The pilot-scale plant tests were performed during July 21-22, 1997 at the Kaiser's Mead Works laboratory of an aluminum smelter, located at Spokane, Washington. Five gas sampling runs were successfully completed as planned by the A. J. Edmond Company (primary contractor - test planning and coordinator), the Kaiser laboratory (subcontractor - testing reactor set-up and operator), and the Am Test-Air Quality, LLC (subcontractor for gas sampling and analysis). Highlights of sampling activities are summarized as follows:

- (1) Nitrogen oxides (NO_x) of five gas samples collected in Tedlar bags were analyzed on-site using a chemiluminescent analyzer, Thermo Environmental Instrument Model 42H, performing the EPA Method 7E. In addition, carbon dioxide (CO₂), carbon monoxide (CO) and oxygen (O₂) were analyzed on-site, performing the EPA Method 3A for CO₂ and O₂, and the EPA Method 10 for CO, respectively.
- (2) Five gas samples for GC/MS analysis of CO, CO₂, H₂ (hydrogen), CH₄ (methane), C_nH_m (speciated volatile organic compounds-VOC), SO₂ (sulfur dioxide), H₂S (hydrogen sulfide), COS (carbonyl sulfide) and N₂ (nitrogen), were collected in 6-L evacuated SUMMA stainless steel canisters. The sample canisters were transported next day to the Atmospheric Analysis and Consulting, Inc. laboratory in Ventura, California, for immediate analysis of gas samples, performing the EPA Method TO-14.
- (3) Five gas samples were withdrawn through a sampling probe. Analysis samples were collected passing through the sampling train device, for IC analysis of Cl₂. The collected samples were transported to the Am Test laboratory, Redmond, Washington, for immediate analysis performing the EPA Method 26.

Details of the experimental procedure for each test are described in the following sections.

RUN OBJECTIVES

The objective of this study is to perform pilot-scale process simulation and variable testing using petroleum coke as a reducing agent of iron ore under operating conditions of a commercial blast furnace process. Specific detail objectives of three Tests A, B and C performed for this study with a petroleum coke and/or iron ore pellets are listed below.

- Test A: To perform a chemical analysis of volatile matter produced from petroleum coke heated at 950 °C for 10 min under non-oxidizing conditions (argon atmosphere) as defined in the ASTM Method D 3175, or equivalent.
- Test B: To perform a chemical analysis of effluent gases produced from combustion of petroleum coke through the injection of air at the base of

the packed column, which is controlled at 1000 °C of the effluent gas temperature.

Test C: To perform chemical analyses of effluent gases produced at three different effluent gas temperatures (500, 900, and 1100 °C, respectively), which are resulting from operation of a column of TECNORED pellets (iron ore blended with petroleum coke) under internally self-generated reduction atmosphere. The column operation is controlled under neutral and non-pressurized argon atmosphere. In addition, to analyze solids product (sintered and clogged pellets) remained in the reactor after heating beyond 1200 °C for composition of carbon, sulfur, and residual FeO present in both metal and slag, which are separated by heating.

EXPERIMENTAL PROCEDURES

Materials Tested

Petroleum coke, a testing sample derived from a refinery located in Texas, with high sulfur content of 7.0 wt %. Approximately 5 kg of sponge/shot coke (60/40 mixture) was prepared with ¼" to ½" (6 to 13 mm) particle sizes by A. J. Edmond Company. The volatile matter content present in this coke was 10.0 wt %.

TECNORED pellets (iron ore blended with the coke fines) were made in Joinville, Brazil and forwarded by courier to A. J. Edmond Co. Approximately 15 kg of TECNORED pellets were prepared with 7.5 wt % moisture content and 3.4-6.4 mm particle sizes.

Reaction System

A schematic diagram of the reaction system of the pilot-scale plant is shown in Figure 1. The reaction system consists of argon cylinder, compressed air supply, nitrogen cylinder, pressure regulators, gas mass flow meter and control valves, preheating zone, reactor with temperature controller and programmer, sampling probes and analyzers for Cl₂, NO_x, and other gases (CO, CO₂, H₂, CH₄, C_nH_m (VOC), SO₂, H₂S, COS and N₂). The packed column reactor was made of a 3"φ x 48"H Inconel tube connected at the top to the stainless-steel sampling vent tube (3"φ x 24"H) with three sampling ports. At the mid-point inside the reactor a nickel-chromium screen (16 mesh, #24 wire size) welded to the wall to support the loading of petroleum coke and TECNORED pellets.

Effluent Gas Analyses

The Am Test-Air Quality, LLC (a subcontract service laboratory), Preston, WA performed on-site effluent gas analyses and sampling. Total five grab samples were collected and analyzed as required in this study, employing the analytical methods as described in Section INTRODUCTION, Summary of Pilot-Scale Tests.

Run Procedures

Tests A, B and C were performed under operating conditions closely simulating commercial blast furnace processes, as required by the client, CAEMI International and TECNORED. A 3" Inconel vertical reactor tube was placed in a 3" tube furnace capable of being controlled at 1200 °C of the reaction temperature. The control thermocouple was located at the mid-point outside surface of reactor tube. The effluent gas temperature at the top of reaction zone was not determined, but estimated to be similar within several degrees of this control temperature, based on previous experience with the heating furnace used. The temperature controller was effectively programmed to reach a target temperature within an hour in order to be ready for the next test planned as soon as possible. Effluent gas stream was naturally cooled without condenser through the sampling vent tube before reaching gas sampling probes. The effluent gas temperature at the sampling probe location was periodically measured using a portable thermometer during each test, and ranged from 100 to 350 °C. During the first Run 1, pre-tests were conducted for an integrity check of the reaction system, gas sampling and instrumental analyses, and other pertinent experimental parameters such as temperature, flow rate, etc.

RUN 2 - TEST A

A representative sample of a petroleum coke with 7 wt % sulfur content (approximately 5 kg) was prepared using ASTM Practice D 346 in the range of particle size from ¼" to ½" (6 to 13 mm), and stored in an air tight sample bag until needed for the test. The moisture content of the coke was approximately 0.21 wt %. The reaction test steps were:

- (1) Approximately 312.6 g of the petroleum coke sample was charged into the reactor. The packed-bed height was approximately 4-5".

- (2) Initially the nitrogen gas flow was on for 30 min at 5 liter/min to purge out the reaction system. Then the gas flow switched to argon.
- (3) The argon gas flow slowly increased to 17 liter/min (1000 ± 10 liter/hr). The inlet argon gas pressure to the reactor was set at 70-75 psig.
- (4) The reactor heating furnace was turned on, and the reactor temperature was rapidly increased to 400 °C in 6 min. No sampling was conducted during this preheating period.
- (5) Sampling began at 400 °C and continued heating-up of the reactor from 400 to 950 °C. Three sampling probes were installed and total sampling rate was set at 6.2 liter/min; 4 for NO_x analysis, 2 for Cl₂ analysis, and 0.2 liter/min for GC/MS analysis, respectively.
- (6) The reactor temperature maintained at 950 °C for additional 5 min, and during this period sampling continued. Total sampling time (or reaction time) was 25 min.
- (7) After completion of the gas sampling, the argon gas flow valve and reactor heating furnace were turned off, and the gas flow switched back to nitrogen. Opened the heater when the temperature lowered several hundred degrees and allowed the reactor to cool down.
- (8) Solids product remained in the reactor was easily removed without any visible deposits on the wall, when the reactor was sufficiently cooled down, and the reactor was cleaned thoroughly for preparation of the next test.

The material balance showed approximately 9.3 wt % of the petroleum coke converted to volatile matter.

RUN 3 - TEST B

The reaction test steps were:

- (1) Approximately 302.3 g of the petroleum coke sample was charged into the reactor. The packed-bed height was approximately 4-5".
- (2) Initially the nitrogen gas flow was on for 30 min at 7.5 liter/min to purge out the reaction system. Then the gas flow switched to compressed air.
- (3) The air gas flow was set at low rates, 7.5-8.3 liter/min, in order to closely observe the reactor exotherm. *Note: This lower air flow rate employed was primarily due to the safety consideration of equipment limitation, that is, the Inconel reactor should operate below 1260 °C (maximum operating temperature for Inconel material). The planned air flow rate estimated for complete combustion was 17 liter/min.*
- (4) At the same time the reactor heating furnace was turned on, and the reactor temperature was slowly increased to 920 °C. No sampling was conducted during this preheating period.
- (5) Sampling began at 920 °C and continued heating-up of the reactor from 920 to 1000 °C. Three sampling probes were installed and total sampling rate was set at 5.1 liter/min; 4 for NO_x analysis, 1 for Cl₂ analysis, and 0.1 liter/min for GC/MS analysis, respectively.
- (6) The reactor temperature maintained at 1000-1015 °C for additional 56 min, and during this period sampling continued. The air flow rate was adjusted in the range of 6 to 9.4 liter/min in order to control the reactor exotherm during this period.
- (7) After completion of the gas sampling, the air gas flow valve and reactor heating furnace were turned off, and the gas flow switched back to nitrogen. Opened the heater when the temperature lowered several hundred degrees and allowed the reactor to cool down.
- (8) Solids product remained in the reactor was easily removed without any visible deposits on the wall, when the reactor was sufficiently cooled down, and the reactor was cleaned thoroughly for preparation of the next test.

The material balance showed approximately 27.5 wt % of the petroleum coke combusted and converted to various product gases. This low conversion is partly attributed to the oxygen-deficient reaction condition employed in this test with the lower air flow, 6-9.4 liter/min, than 17 liter/min (planned target and estimated stoichiometric flow for complete conversion), and/or partly attributed to possible low reactivity of petroleum coke with air. *Note: The lower oxygen flow (air flow) was employed primarily due to the equipment limitation of Inconel material as discussed in the above (3). This would significantly affect the effluent product composition, resulting in lower content of CO, CO₂, and SO₂.*

RUN 4, 5 AND 6 - TEST C

A representative sample of TECNORED pellets (iron ore blended with coke fines) with 7.5 wt % moisture content was prepared (approximately 15 kg) in the range of particle size from 3.4 to 6.4 mm, and was stored in an air tight sample container until needed for the test. The reaction test steps were:

- (1) Approximately 1200 g of the TECNORED pellets sample was overnight dried in an oven at 100 °C and was charged into the reactor. The packed-bed height was approximately 4-5".
- (2) Initially the nitrogen gas flow was on for 30 min at 15 liter/min to purge out the reaction system. Then the gas flow switched to argon.
- (3) The argon flow was set at 6.9 liter/min. This gas flow was above the sampling rate set in the following (5), <5.1 liter/min.
- (4) At the same time the reactor heating furnace was turned on, and the reactor temperature was rapidly increased to 500 °C in 12 min. No sampling was conducted during this preheating period.
- (5) Sampling began at 500 °C and continued for 60 min with the reactor temperature maintained at 500 °C. Three sampling probes were installed and total sampling rate was set at <5.1 liter/min; <4 for NO_x analysis, 1 for Cl₂ analysis, and 0.1 liter/min for GC/MS analysis, respectively.
- (6) After completion of the gas sampling at 500 °C, three sampling probes were reinstalled, and then the reactor temperature was again rapidly increased to 900 °C. No sampling was conducted during this second preheating period. The argon gas flow rate was set at 6.7 liter/min.
- (7) Sampling began at 900 °C and continued for 30 min with the reactor temperature maintained at 900 °C. Sampling rates were the same as before at 500 °C.
- (8) After completion of the gas sampling at 900 °C, three sampling probes were reinstalled, filters were replaced, and then the reactor temperature was again rapidly increased to 1100 °C. No sampling was conducted during this third preheating period (about 37 min consumed). The argon gas flow rate was set at 6.7 liter/min.
- (9) Sampling began at 1100 °C and continued for 20 min with the reactor temperature maintained at 1100 °C. Sampling rates were the same as before at 900 °C.
- (10) After completion of the gas sampling at 1100 °C, sampling devices were removed, sampling ports were blocked, and then the reactor temperature was again rapidly increased to 1200 °C. No sampling was conducted during this fourth preheating period. The argon gas flow rate was the same as before.
- (11) Without sampling the reactor temperature was maintained at 1200 °C for 60 min before ending the Test C.
- (12) The argon gas flow valve and reactor heating furnace were turned off, and the gas flow switched back to nitrogen. Opened the heater when the temperature lowered several hundred degrees and allowed the reactor to cool down.

During the heating-up period to 1200 °C for the pre-melt and slag-off test, trickling and slipping-down noise was noticed inside the reactor tube. It appeared that the wire-mesh screen welded to the reactor wall (for support of pellets and petroleum coke loading inside the reactor) was loosened and fell down to the bottom section of the reactor. The test was not successfully completed for further analysis of solids remained.

RESULTS AND DISCUSSION

Table 1 summarizes analysis results of gas samples collected for this study. Some of Runs 4 to 6 results are proprietary data. Therefore, ratio values of N₂, CO, CO₂ and H₂ compositions were calculated for comparison. Run 5 data were used as basis.

Devolatilization and Pyrolysis of Petroleum Coke under Argon Atmosphere

A study of pyrolysis of petroleum cokes under nitrogen inert atmosphere showed that the volatile matter significantly released in the plastic range of a given coal (400-500 °C) [2]. Maximum evolution of volatile matter (about 40 to 49% of total) was observed in the range of 500-750 °C, and then the volatile matter release decreased in the range of 750-1000 °C. Based on this literature information, in Run 2 - Test A gas sampling was performed for 25 min in the temperature range of 400-950 °C. The weight loss determined after the test showed 9.3 wt %,

similar to the volatile matter content (10.0 wt %) determined by ISO 562, which is equivalent to ASTM Method D 3175.

The gas analysis data for Run 2 – Test A at 400-950 °C (in Table 1) shows that the effluent product gas consists of H₂, CH₄, CO₂ and CO. In addition a significant amount of H₂S is present in the gas sample produced primarily due to the high sulfur content of the petroleum coke (7.0 wt %) tested for this study. Other trace gases are NO_x, C_nH_m (VOC), and insignificant amounts of Cl₂ and SO₂ plus COS.

Combustion of Petroleum Coke with Air Flow

During the start-up (heating-up) period in Run 3 – Test B, the oxygen deficient reaction condition was employed as mentioned in Section RUN 3 – TEST B, in order to control highly exothermic reaction (combustion), $C + O_2 \rightarrow CO_2$, occurring below 930 °C (1200 K) [4]. When the reaction temperature reaches above 930 °C, the controlling reaction changes to highly endothermic reaction (gasification), $CO_2 + C \rightarrow CO$. The low flow rates of air, 6-9.4 liter/min, coupled with slow heating-up of the reactor enabled to closely control the reactor exotherm. The estimated stoichiometric flow of air for complete conversion was 17 liter/min. Without increasing the flow rate of air for complete conversion, gas sampling started at 920 °C when the governing reaction changes from combustion to gasification and continued for 60 min at 1000-1015 °C (most of time).

The material balance showed approximately 27.5 wt % of the petroleum coke combusted and converted to various product gases. This low conversion is partly attributed to the oxygen-deficient reaction condition employed in this test with the lower flow rate of air, and/or partly attributed to possible low reactivity of petroleum coke with air. The low conversion would significantly affect the effluent gas product composition, resulting in low content of CO, CO₂, and SO₂. The on-site gas analysis data showed an insignificant amount of O₂, 0.2%, present in the gas sample, indicating most of oxygen in the air converted to oxides and depleted in the reaction zone.

The gas analysis data for Run 2 – Test B at 1000-1015 °C (in Table 1) shows that the nitrogen-free effluent product gas consists of H₂, CH₄, CO₂ and CO. A significantly reduced amount of H₂S is present in the gas sample, and the SO₂ plus COS content significantly increased by oxidation, compared to the result of Run 2 – Test A. Other trace gases are NO_x, C_nH_m (VOC), and insignificant amount of Cl₂.

The combustion reaction with air produced much higher amounts of CO₂ and CO, while reducing CH₄ composition, compared to the result of Run 2 – Test A. The high hydrogen content observed suggests a possibility of pyrolysis reaction still present under the oxygen deficient condition. The reactor temperature profile was not measured in this study, which might provide better understanding of reaction mechanism.

TECNORED Pellets Reduction under Argon Atmosphere

In Runs 4 to 6 – Test C, TECNORED pellets were processed under argon atmosphere at three different reaction temperatures, 500, 900 and 1100 °C, sequentially. Ratio values were used for comparison of proprietary data (compositions of N₂, CO, CO₂ and H₂). Other gas composition data are reported as measured (carrier gas-free basis) in Table 1.

Run 6 at 1100 °C shows the highest CO composition in the gas sample among three runs, indicating that a significant gasification reaction occurs above 930 °C with TECNORED pellets present. The CO content is several times higher than the CO₂ content at this condition. This suggests that gasification is the controlling reaction, $CO_2 + C \rightarrow CO$, and TECNORED pellets generate self-reducing environment.

In Run 5 at 900 °C, the CO content is similar to the CO₂ content. Both combustion and gasification are competing and important at this temperature. Again this indicates that TECNORED pellets generate self-reducing environment.

Relatively small, insignificant amounts of CO and CO₂ were observed at the lower reaction temperature of 500 °C. A small degree of devolatilization might be mainly happening at this temperature without presence of self-generated combustion and gasification reactions.

Other trace gases produced at 900-1100 °C are CH₄, H₂S, SO₂ plus COS, NO_x, C_nH_m (VOC), and insignificant amount of Cl₂.

SUMMARY

Five screening tests with high sulfur petroleum coke and TECNORED pellets were successfully completed under process conditions of iron ores reduction. Effluent product gas analyses suggest that:

- TECNORED pellets generate self-reducing environment for iron ores processing at 900-1100 °C.
- The high CO production at 1100 °C with TECNORED pellets provides an evidence of gasification reaction controlling at this temperature.
- Minimum or insignificant amounts of trace gases (H₂S, SO₂ plus COS, NO_x, C_nH_m (VOC) and Cl₂) were produced at 900-1100 °C with TECNORED pellets.
- TECNORED pellets effectively reduce sulfur compounds emission in the gas stream through internal scavenging actions with addition of additives in the pellets, even though a high-sulfur petroleum coke fines (7 wt %) was used in pelletizing.
- Reactivity of petroleum coke under combustion and gasification condition seems significant and sufficient enough in its application for iron ores processing.

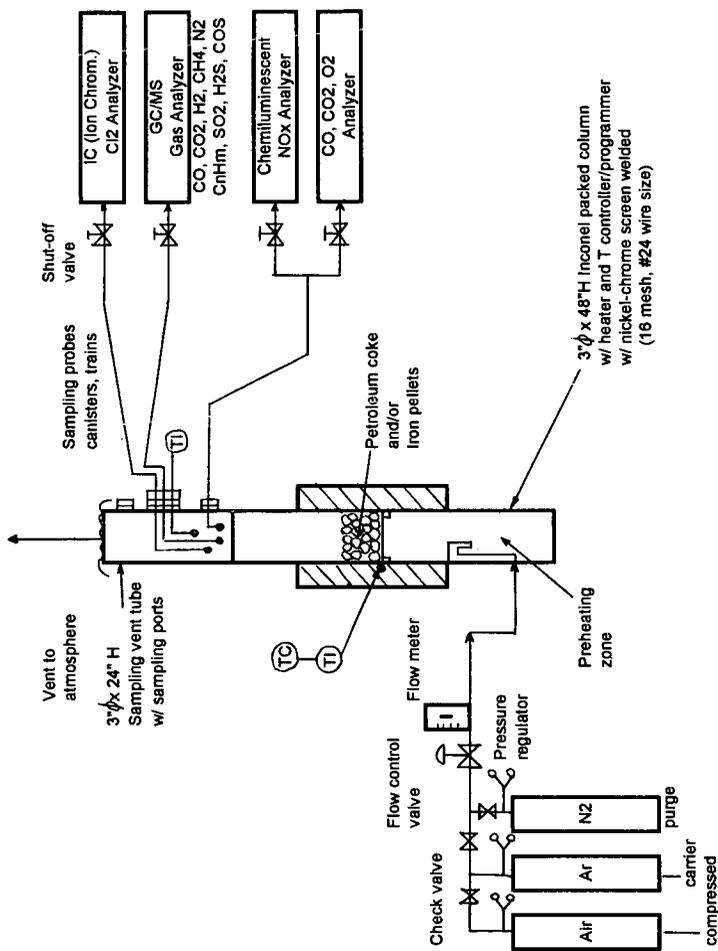
ACKNOWLEDGMENT

The project was sponsored by North Star Steel and Tecnored Technologies, Stamford, Connecticut and TECNORED LTDA, Joinville-SC, Brazil. Messrs. Mark Wyborne and Randy Czikall, Kaiser laboratory, Spokane, WA, are acknowledged for their participation and efforts in testing reactor set-up at the Kaiser laboratory and successful operation of the reactor. Mrs. Karen Kumke, A. J. Edmond Company, Texas City, TX, provided the petroleum coke sample used for this study.

REFERENCES

1. J. M. Lee, J. J. Baker, R. Llerena, J. G. Rolle, 214th American Chemical Society National Meeting, Las Vegas, Preprints of Symposia, Division of Fuel Chemistry, Vol. 42, No. 3, 844-853 (1997).
2. J. A. Menendez, et. al., *Energy & Fuels*, Vol. 10, No. 6, 1996, 1262-1268.
3. J. W. Ramming, M. Contrucci, E. Marcheze, TECNORED process data published (1997).
4. J. G. Peacey, *The Iron Blast Furnace: Theory and Practice* (1979).
5. McGraw-Hill Encyclopedia of Science and Technology, 7th Ed., 423 (1992).
6. Kerk-Othmer Encyclopedia of Chemical Technology, Volume 9, 7th Ed., 829 (1995).

Figure 1. SCHEMATIC DIAGRAM OF REACTION SYSTEM



**Table 1. EFFLUENT PRODUCT GAS ANALYSES
(Carrier Gas-Free Basis)**

Based on argon (carrier gas)-free in Runs 2, 4 to 6, & nitrogen-free in Run 3.

	Run 2 <u>Test A</u>	Run 3 <u>Test B</u>	Run 4 <u>Test C</u>	Run 5 <u>Test C</u>	Run 6 <u>Test C</u>
<u>Operating Conditions</u>					
Reaction temperature (°C)	400-950	1000-1015	500	900	1100
Reaction/sampling time (min)	25	60	60	30	20
<u>Raw material charge (gr)</u>					
Petroleum coke	312.6	302.3	—	—	—
TECNORED pellets (dried)	—	—	1200 ^a	1200 ^a	1200 ^a
<u>Gas flow (L/min)</u>					
Argon (carrier gas)	17	—	6.9	6.7	6.7
Air (reactant gas)	—	6-9.4	—	—	—
<u>Effluent Gas Composition (vol %)</u>					
			<i>Relative ratio to Run 5 data^b</i>		
N ₂ (nitrogen)	—	—	2.1	1	0.7-1.0
CO (carbon monoxide)	<0.1-1.2	8.5	<0.01	1	2.9
CO ₂ (carbon dioxide)	<0.1-2.1	15-24	0.0-0.5	1	0.9
H ₂ (hydrogen)	—	—	1	1	0.6-0.8
CH ₄ (methane)					
C _n H _m (C ₂ -C ₆ hydrocarbons)					
C _n H _m (VOC) (ppmv)					
(volatile organic compounds)					
H ₂ S (hydrogen sulfide) (ppmv)					
SO ₂ (sulfur dioxide) plus					
COS (carbonyl sulfide) (ppmv)					
NO _x (nitrogen oxides) (ppmv)					
Cl ₂ (chlorine) (ppmv)					
Undetermined (H ₂ O, etc.)					

NOTE: Most of data were determined using GC/MS analysis of SUMMA canister samples

a Initially charged in Run 4, and Runs 5 and 6 continued without replacement.

b Ratio values of some of Runs 4 to 6 results (proprietary) were used for comparison.

MIXING ELEMENT RADIANT TUBE (MERT) OFFERS NEW CONCEPT FOR ETHYLENE STEAM CRACKING PROCESS

T.Torigoe, H. Hamada, M. Inui, A. Yoshitake, KUBOTA CORPORATION,
Hirakata-shi Osaka 573, Japan

Keywords: Ethylene, Thermal Cracking, Mixing

ABSTRACT

Mixing Element Radiant Tube (MERT) is a centrifugal cast cracking tube with a spiral element protuberate inside of it. The concept of the mixing the feed gas is introduced in the ethylene steam cracking technology for the first time. The mixing the feed gas in the tube appears to afford homogeneity in gas temperature which provides minimizing under and over cracking and consequently maximizing proper cracking volume. This means that higher yield of ethylene and/or propylene with lower coking rate can be expected. Moreover, effective heating with breaking boundary film by mixing flow provides reducing tube metal temperatures which result in extending tube life. The concept of MERT and its verification test is described.

INTRODUCTION

In a petrochemical industry, olefins such as ethylene or propylene is produced from hydrocarbon by thermal cracking process. In the process, cracking tubes are used in several types of coils. The feed gas, typically naphtha or ethane and steam gas, flows inside of the cracking tube at high velocity. The tube is heated at high temperature from the outside of the tube - within a pyrolysis furnace. During the passage of the feed gas throughout the coils, it is thermally cracked into ethylene, propylene, and so on (see Fig. 1).

There have been a lot of developments in ethylene pyrolysis furnace to increase capacity, improve yield and thermal efficiency and reduce downtime for maintenance and decoking along with material developments ⁽¹⁾⁽²⁾ and improvement in tube size and shape ⁽³⁾.

MERT or mixing element radiant tube, is a centrifugal cast cracking tube with a spiral mixing element on the inside diameter (see Fig. 2), and provides new concept for improving steam cracking process.

By the mixing of the feed gas:

1. Homogeneous heating can be achieved.
2. The feed gas flow inside of the tube, can be effectively heated thus breaking the boundary film which act as an insulator effecting heat transfer at the metal gas interface.

Homogeneous heating of the feed gas inside the tube can minimize both under and over cracking as well as maximizing proper cracking volume. Therefore it is reasonable to assume that a) ethylene and/or propylene yield can be increased and b) coking can be reduced.

In order to verify the effect of the mixing element, computational fluid dynamic (CFD) analysis was applied to both smooth tube (Bare Tube) and MERT using hot air. As shown in Fig. 3, homogeneous heating of the gas inside of the tube can be expected in MERT. The advantage of homogeneous heating of the feed gas is illustrated in Fig. 4.

Effective heating can provide an energy saving and reduce tube metal temperature which is normally related to coking rate. Therefore tube life can be extended, run length can be extended because of lower coking rate, and firing can be increased as much as the temperature drop as well as production increase without sacrificing tube life.

Based on this new concept of cracking tube, MERT was developed to apply to commercial ethylene cracker.

The material used for MERT is KHR45A(43Ni-31Cr-Nb,Si,Ti) which is superior grade of conventional HP alloys for the mother tube and KHR45A mod. for the element. The element in the MERT is well integrated to the mother tube, and has excellent properties of carburization resistance, thermal shock resistance, and anti-coking.

This paper mainly described the performance of the MERT both in pilot test plant and commercial plant.

EXPERIMENTAL

Experimental 1

In general, internal protrusions in the cracking tube have been considered a cause of coking due to stagnation of the feed gas where over cracking might occur⁽⁴⁾. The MERT element is designed in a spiral shape to produce a "swirl flow", thus eliminating stagnation of the feed gas(see Fig. 5). The visualization tests were performed to confirm the "swirl flow" in each tube size and element angle(see Fig. 6).

In the design of the element, pressure drop (ΔP) and heat transfer coefficient should be taken into account. As shown in Fig. 7, the heat transfer coefficient and pressure drop was measured by air test. The air supplied from a blower is controlled in the flow rate by the air damper. And the tests were carried out within the range of the Reynolds Number between 2.5×10^4 and 2×10^5 . The heat was supplied from hot water or well controlled electric heater from outside of the pipe. Inlet temperature and outlet temperature were measured by thermocouples. Then the heat transfer coefficients of the boundary film were calculated.

In the same way, the pressure drop was measured from the measurement of the pressure difference between inlet and outlet pressure.

These measurements were performed on both bare pipe and MERT in each test.

The pressure drop and boundary film heat transfer coefficient depend on both element angle and fluid velocity. In order to apply MERT technology practically in an ethylene furnace, these data should be made available.

Experimental 2

In order to verify the concept of MERT described in Fig. 4, pilot plant tests were performed.

As shown in Fig. 8, the tube used in this test was 2 inch O.D. and 1.5 inch I.D. and 3.6 M in length. The element angle in MERT was 30° and element height was 2.5mm. The furnace used in this test had electric heater separated in three zone which were independently controlled. The feed gas flows from top to bottom. The composition of the naphtha used is shown in Table 1. The steam to feed ratio was 0.5 for naphtha and 0.3 for ethane respectively. The system of the pilot plant was quite similar to that of commercial plant.

The product was immediately quenched just after the outlet of the tube and the product yield was analyzed by G.C. The coking amount was measured by the analysis of CO and CO₂ as well as the measurement of the temperature during de-coking.

Experimental 3

In order to verify the performance of the MERT tubes, they are testing in commercial plants. Fig. 9 shows an example of the result of U coil furnace. The MERT tubes were installed in one quadrant of the furnace in two types of modes, applied MERT to both inlet and outlet tubes and to only outlet.

The pressure drop, Tube Metal Temperature(TMT), and feed increase was measured throughout the run length.

RESULTS AND DISCUSSIONS

The heat transfer coefficient of MERT is, however it is depend on tube size, the element angle and height, and velocity of the gas, normally 20 to 50 % higher than that of smooth tube (Bare tube) while its increasing of heat transfer area is only around 1%.

So it is expected that TMT must be lower than that of bare tube under the same firing condition.

In the pilot plant test using naphtha as a feedstock, when the temperature was adjusted at the same TMT, the feed rate of the MERT could be increased by 40%. And under the same TMT, coking rate of MERT was about 50% lower than that of bare tube. Moreover both ethylene and propylene yield was increased by MERT(see Table 2 - test 1).

When the feed rate was adjusted at the same, TMT of MERT was 24°C lower than that of bare tube. In this condition, coking rate of MERT was around 50% lower and ethylene and propylene yield was also increased in MERT.(See Table 2-test 2).

The test data shown in Table 2 is under the P/E ratio of 0.45 which is severe condition. The tests were carried out in the range of P/E ratio from 0.45 to 0.70, and the same tendency, especially the increasing of the yields was observed in all tests.

In ethane test (see Table 3), when the conversion was adjusted at the same of 65%, the TMT of MERT was 56 °C lower than that of bare. And ethylene yield could be increased by 3%. When the selectivity was adjusted at the same level, ethane conversion of MERT should be raised up. Even in this condition, the TMT of MERT was 25°C lower than that of bare tube.

In this case, the ethylene yield was 8% higher than that of bare. The test result also suggested that coking rate of MERT was much less than that of bare.

Based on these pilot plant tests, it can be said that the concept described in Fig. 4 was somewhat occurred in actual furnace.

Because no catastrophic coking problem was reported in commercial plants where MERT tubes were preliminary installed, MERT performance tests in commercial plants were started. Firstly MERT test was performed in U coil furnace in 1997. In the test operation, the TMT of MERT was found to be approximately 50F lower than that of the other bare tubes in the same furnace. This may suggest that if the firing could be increased as much as the temperature drop of MERT, the capacity could be increased by 33% without sacrificing tube life. Due to efficient heating by MERT, the feed rate of MERT section was 2 to 3% higher than the average value of Bare section under the same firing condition. The most remarkable point was that the pressure drop increasing rate of MERT was 2/3 of that of bare tubes. This may suggest the MERT has less coking rate than the bare tubes and can extend run length by 50%.

CONCLUSION

Through the above mentioned tests, it is found MERT has mixing effect and has following advantages.

Higher capacity, Extend tube life(Low TMT), Extend run length(low coking rate)

The yield improvement is now studying in commercial furnace tests and computer simulation. Because ethylene cracking tubes are used in several types of coils⁽²⁾⁽³⁾, several factors such as the coil arrangement, the length of MERT, the position installed should be taken into account in the adequate application of MERT to commercial plants. The MERT has a internal protrusion which may cause for higher friction factor which is related to higher pressure drop. The higher the pressure drop, the longer the residence time which may cause for decreasing yield. The mixing effect in MERT should overcome the pressure drop effect.

It was reported that thousands of chemical reactions might be occurred in the hydrocarbon thermal cracking process⁽⁵⁾, and these decompositions might be endothermic reactions. In order to estimate the mixing effect, theoretically and experimental approach should be required.

REFERENCES

- (1) Steanson B. Parks, C.M. Schillmoller, AIChE 1995 Spring Paper 24b
- (2) F.W. Tsai, S.C. Che, R.G. Minet, Hydrocarbon Processing, August 1985 p41-47
- (3) J.V. Albano, K.M. Sundaram, M.J. Maddock, Energy Progress, 1988 Vol.8, No.3 P160
- (4) Hirata, 123rd Committee Report, JSPS, 1981, Vol 22, No.3
- (5) E. Ranzi, M. Dente, S. Plerucci, G. Bardi, Ing. Eng. Fundam., 1983, 22. 132-139

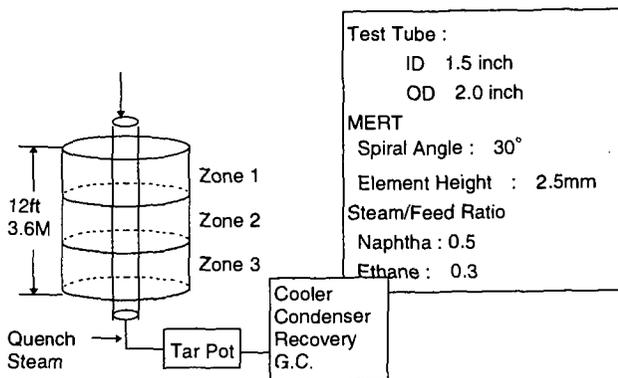


Fig. 8 Pyrolysis Pilot Plant Test

Table 1 Naphtha Composition (wt%)

Paraffins	28.06	C4's	P	0.06	C7's	P	5.36	C9's	P	0.23
Isoparaffins	34.70		I	0.07		I	8.69		I	0.29
Aromatics	11.35	C5's	P	12.24		A	5.56		A	0.00
Naphthens	23.96		I	13.21		N	11.38		N	0.03
Olefins	0.68		N	0.40		O	0.40	C10's	P	0.00
		C6's	P	9.09	C8's	P	1.07		I	0.16
			I	6.85		I	5.43		N	0.02
			A	0.75		A	5.04	C12's	N	0.00
			N	11.51		N	0.63		A	0.00
			O	0.00		O	0.28	C15's	P	0.00
									I	0.00

Table 2 Prototype Test of MERT (Naphtha) P/E : 0.45

Test 1			Test 2		
	MERT	Bare		MERT	Bare
Ethylene Yield (wt%)	27.6	25.3	Ethylene Yield (wt%)	27.6	25.5
Propylene Yield (wt%)	12.4	11.4	Propylene Yield (wt%)	12.4	11.6
Feed Rate (kg/h)	12.0	8.4	Feed Rate (kg/h)	12.0	12.0
TMT (°C)	892	892	TMT (°C)	892	916
Coking Rate (g/h)	0.68	1.34	Coking Rate (g/h)	0.68	1.47

Table 3 Prototype Test of MERT (Ethane)

Test 1			Test 2		
	MERT	Bare		MERT	Bare
Ethylene Yield (wt%)	52	49	Ethylene Yield (wt%)	57	49
Ethane Conversion(%)	65	65	Ethane Conversion(%)	75	65
Ethylene Selectivity(%)	80	75	Ethylene Selectivity(%)	76	75
TMT (°C)	1003	1059	TMT (°C)	1034	1059

Test 3		
	MERT	Bare
Coking Rate (g/h)	1.3	3.3
TMT (°C)	1034	1059

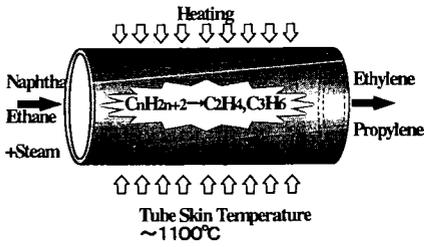


Fig. 1 Cracking Tube



Fig. 2 Cross Sectional Overview of MERT

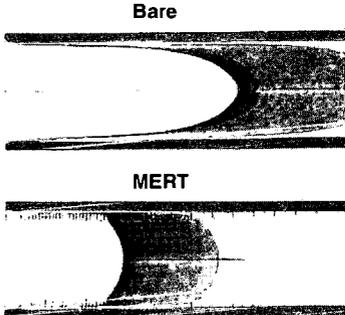


Fig. 3 Analysis of Fluid Temperature

Adequate Temperature Zone for Proper Cracking

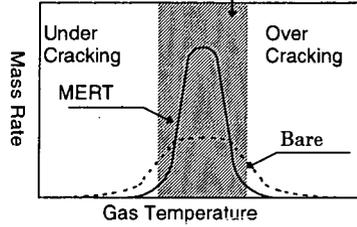


Fig. 4 Homogeneous Chemical Reaction in Tube

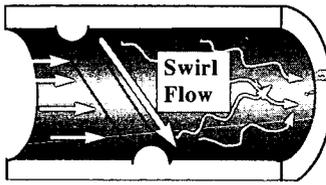


Fig. 5 Swirl Flow

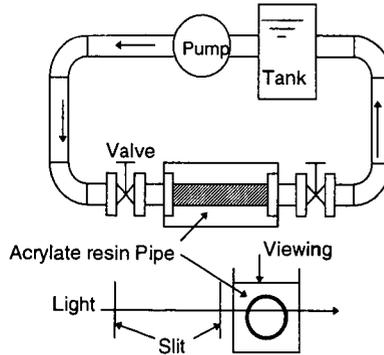


Fig. 6 Visualization Test by Water Flow

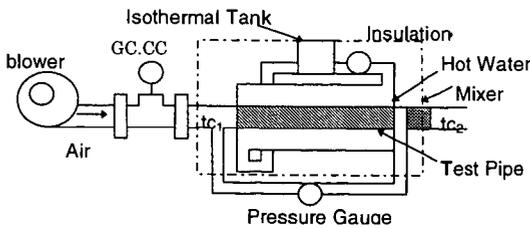


Fig. 7 Heat Transfer Coefficient and Pressure Drop Measurement Apparatus

CHARACTERIZATION OF GREEN AND CALCINED COKE PROPERTIES USED FOR ALUMINUM ANODE-GRADE CARBON

Jun M. Lee, James J. Baker, Jeffrey G. Rolle, Robert Llerena,
A. J. Edmond Co.

1530 West 16th Street, Long Beach, CA 90813

Keywords: petroleum coke, calcine, aluminum anode carbon

ABSTRACT

Various properties of green (raw) and calcined petroleum cokes were analyzed and evaluated for use in aluminum anode-grade carbon. Petroleum cokes for this characterization study include different cokes produced from several refineries in U.S. and in other regions of the world such as China, Indonesia, Brazil, Argentine and Kuwait. Coke properties evaluated are: moisture, volatile carbon matter (VCM), ash, fixed carbon (FC) (by difference), sulfur, carbon, hydrogen, nitrogen, oxygen (by difference), metals (Si, Fe, V, Al, Ca, Na, Cr), calorific value, real density (RD), vibrated bulk density (VBD), size distribution, etc. Some of recent analysis results with these petroleum cokes are compared and presented.

INTRODUCTION

Export quality of petroleum cokes was evaluated and discussed at the ACS Las Vegas Meeting (September 7-11, 1997), based on recent analysis results from calcined petroleum coke produced for aluminum anode-grade and green (raw) coke used in calcination [1]. Production of petroleum cokes steadily increased by 51% during the past decade, expecting continuous increase in the coming years, primarily due to declining quality of crude oils. Exports to foreign countries are a major market for the U. S. coking industry and were 66% of the annual production (78,430 tons/cd) in 1993. Green petroleum cokes are mostly used as utility fuels (about 73% for fuel grade), and as feedstocks (about 27%) for further upgrading calcination. The calcined petroleum cokes are used in production of specialty products: 71% for aluminum anode-grade, 9% for graphite electrodes, needle-grade, 8% for titanium dioxide pigments, 6% for recarburized ductile iron products, and 6% for others (chlorine, phosphorous, silicon carbide, calcium carbide, etc.).

Petroleum cokes are produced at refineries using three different types of coking processes: delayed, fluid, and flexicoking. The delayed coker is mostly used at forty-nine U.S. refineries processing total 1.57 mm b/sd [2]. The other fluid coker and flexicoker are less utilized at a relatively smaller capacity (seven refineries and 0.2 mm b/sd). Coke products from a delayed coker are classified as shot, sponge, (sometimes honeycomb), or needle coke depending on their chemical and physical characteristics. Shot coke (almost always sold as fuel) is hard, having spherical form, and physically produced through precipitating asphaltenes; sponge coke (mostly used for anode-grade) is dull and black, having porous, amorphous structure, and is considered as a mixture of shot and needle cokes; and needle coke (not used in anode production) is silver-gray, having crystalline broken needle structure, and chemically produced through cross linking of condensed aromatic hydrocarbons during coking reactions [3,4]. Most of fluid coke does not enter the anode pool and flexicoke has never been used in aluminum smelting.

The objective of this study is to evaluate various properties of green (raw) and calcined petroleum cokes used in aluminum anode-grade carbon, comparing different cokes produced from several refineries in U.S. and in other countries such as China, Indonesia, Brazil, Argentine and Kuwait.

COKE, ANODE PROPERTIES, AND CARBON CONSUMPTION

Rolle and Hoang [5] investigated the impact of metal impurities, vanadium and sodium, on the air reactivity of cokes and anodes. Vanadium has less impact on air reactivity than previously published and sodium is approximately five times more leveraging than vanadium on both coke and anode air reactivity.

Casada, Rolle, et. al. [6] reported the influence of nickel on reduction cell anodes. Nickel alone does not significantly effect anode air or CO₂ reactivity, but including anode butt material increased CO₂ reactivity.

Leach, et. al. [7] evaluated calcined coke and anode core properties to predict carbon consumption and anode performance in aluminum reduction cells. Calcined cokes having a range

of properties can produce quality prebake anodes that yield low, stable carbon consumption. Their specific findings are:

- o Highly efficient modern prebake potlines can allow larger variability of carbon properties.
- o A strong correlation exists between the coke V content and anode air reactivity, while no correlation between coke air reactivity and anode air reactivity residue (ARR) was evident. To lower anode air reactivity (increase the ARR), reduce the coke V concentration.
- o A strong correlation exists between the anode Na content and anode carboxy reactivity residue (CRR), while a weaker correlation exists between the coke carboxy reactivity and anode CRR. The carboxy reactivity of the anode can be minimized by lowering the anode Na content through the use of cleaner butts and purer coke.
- o A strong correlation between coke grain stability and anode flexural strength was identified.

A desired range of calcined coke air reactivity based on the ignition temperature is 0.05-0.30 %/minute, and airburning increases near 0.30 %/minute [7]. A grain stability range of 75-85% is desirable with values below 75% causing substantially lower anode strength and thermal shock resistance. A substantial reduction in carbon consumption (a 12% decrease in eight years) was achieved and reported by de Mori by applying the correlation formula published by Fisher, et. al. that incorporates baked anode properties, potroom operations parameters, and a cell factor to predict carbon consumption.

$$PAC = C + 334/CE + 1.2 (BT-960) - 1.5(ARR) - 1.7(CRR) + 9.3(AP) + 8(TC)$$

, where PAC is predicted anode consumption; C, cell factor; CE, current efficiency; BT, bath temperature; ARR, air reactivity residue; CRR, carboxy reactivity residue; AP, air permeability; and TC, thermal conductivity.

With 100% efficiency, the amount of carbon required would be 0.334 kg/kg of aluminum [4]. Actual net carbon consumption is in the range of 0.44 to 0.5 kg C/kg Al.

Eidet et. al. [8] studied effects of iron and sulfur on the air and CO₂ reactivity of calcined cokes. Excess carbon consumption (0.02 to 0.15 kg C/kg Al in prebake cells) in the aluminum electrolysis is caused by the oxidation of the anodes by air and CO₂, catalyzed by many different inorganic impurities present in the carbon anode materials. Iron catalyzes both O₂ combustion and CO₂ gasification of carbon. Sulfur is inactive in and do not have a significant effect on both reactions. Sulfur inhibits iron catalytic reactions.

Vogt and Ries [9] investigated the effect of anode desulfurization on baking by varying temperature and soak time. The best baking furnaces can achieve a uniform baking temperature (typically 1100-1150 deg C) with a variation of +/-25 deg C. Average anode baking temperature has been increased to near 1200 deg C with a soak time of 56 hours. Desulfurization during the baking can cause high air, CO₂ reactivities and permeability with abnormally low sulfur levels (<2.0% S as compared to >2.3% normal). Optimum baking temperature exists at a given soak time, and the porosity created by the loss of sulfur ultimately contributes to poorer reactivity behavior due to increased active sites available for oxidant molecules to attack carbon surface.

During calcining, green cokes with low sulfur less than 2% typically produce a calcined product having 90% of the green coke's sulfur level; cokes with high sulfur up to 5% calcine to about 85% of the original sulfur level. The remaining sulfur in the calcined coke is liberated during the smelting process. A critical temperature was identified in a laboratory calcining study investigating desulfurization, corresponding the initial release of sulfur and the creation of micropore volume (pore diameters <0.1 mm). The critical temperature was found to be coke specific and ranged from 1300 deg C for the high sulfur coke and 1500 deg C for the low sulfur coke.

TYPICAL PROPERTIES OF ALUMINUM ANODE-GRADE CALCINED COKE

Green (raw) petroleum coke is produced as a by-product in the refinery crude oil processing and primarily used in anode manufacture because of its low ash content. In general, coke is considered more valuable if it has low sulfur content, high bulk density, and metals content [4]. Sulfur emissions are an environmental liability in aluminum manufacturing. V and Ni (chemically bonded

to hydrocarbons) and Na (dissolved as sodium chloride in water which is entrained with the crude oil) catalyze anode oxidation accelerating anode consumption and are ingot impurities. Two other variables affecting anode performance are density and sizing. Higher density cokes enhance anode properties and most coke users desire a product which is at least 30 wt % plus No. 4 Tyler mesh.

Calcination process basically removes volatile matter, hydrogen and some of sulfur present in green cokes as a result increasing density and electrical conductivity suitable for use of carbon anodes in aluminum production. Typical ranges of calcined coke properties for aluminum anode-grade specifications are listed in the following [4,10-13]:

Property	Green	Calcined
wt% S	2.5	2.5 (1.7-3.0)
wt% ash	0.25	0.30 (0.1-0.3)
ppm V	150	200 (165-350)
ppm Ni	150	200(120-350)
wt% Si	0.02	0.02
wt% VM	10-12	<0.25
resistivity, microomega-m		950
real density, g/cu-cm		2.06
bulk density, g/cu-cm		0.80
coefficient of thermal expansion per deg C		2 x 10 to -6

SAMPLING AND PREPARATION

Representative samples of petroleum cokes for this study have been obtained from various refineries in U.S., China, Indonesia, Brazil, Argentine and Kuwait. Green (raw) cokes were produced in the delayed coking process and calcined using laboratory furnaces. Laboratory samples are prepared for coke properties analysis following the procedures and principles in handling listed in the ASTM Methods D 346, D 2013 and D 2234.

ANALYTICAL METHODS USED

Laboratory test methods using various advanced analytical instruments are described in the Quality Assurance Manual of the A. J. Edmond Company. Primary analytical methods used for this study are summarized as follows:

Purpose	ASTM Method	Instrument
metals	D5600	ICP-AES
sulfur	D4239	LECO
CHN	D5373	LECO
Btu	D3286	PARR
moisture	D3173	
volatile	ISO562	
ash	D4422,D3174	
VBD	D4292	
RD	D2638	Micrometrics AccuPyc 1330
sieve	D5709,D293	

RESULTS AND DISCUSSION

Table 1 summarizes analysis results of typical properties of green (raw) and calcined petroleum cokes used for aluminum anode-grade carbon. Export qualities of calcined cokes at U.S. West Coast ports are also included in the last two columns of Table 1 (Continued). Proximate, ultimate analysis, metals content, sizing, calorific value, RD and VBD were determined in this study and are compared.

Laboratory Calcination Results

Ratios of calcined to green coke property value as percentage are listed in Table 1 to evaluate laboratory calcination. Calcination basically removed VCM, hydrogen, and some of sulfur and nitrogen present in green cokes. As a result ash, FC and carbon contents increased, while calorific value decreased. Loss or gain of each coke property value after calcination are compared in the following.

Property	Loss, %	Gain, %
VCM	95.4-97.6	
Hydrogen	96.9-99.4	
Sulfur	8-13	(0-1% gain with three samples)
Nitrogen	25-46	
Ash		9-46 (0-10% loss with three samples)
FC		9-13
Carbon		5-6
Btu/lb	9-11	

Ash ratio of calcined to green coke significantly varies from 10% loss to 46% gain, showing analytical errors associated with low ash content of cokes studied (0.05-0.36 wt %).

Sulfur Content

Sulfur content of petroleum cokes analyzed for this study varies in the range of 0.46 to 3.21 wt %. Chinese, Brazilian and Indonesian cokes have a low sulfur content of 0.5 to 0.8 wt %, while cokes from Kuwait and several refineries in U.S. (USA1, USA3, USA4, LV and LB) have a high sulfur content of 2.2 to 3.2 wt %. Cokes from Argentina and a refinery in U.S. (USA2) have a medium sulfur content of 1.0 to 1.5 wt %. Aluminum smelter sulfur restrictions are regional, and locally regulated to meet environmental emission standards, depending upon industrial, urban or rural area [14]. In Europe and Scandinavia, a coke sulfur limit of 2% maximum is frequently imposed locally; and for new smelters in North America and Australia, the sulfur limit is 3% maximum. Latin America, South Asia and Africa generally have few restrictions on sulfur levels in calcined coke. To lower sulfur content of coke (which is projected to significantly increase to 5% in future), residual oil hydro-desulfurization or thermal desulfurization of petroleum coke may become an important, viable process.

Ash and Metals Content

Ash content of petroleum cokes analyzed for this study ranges from 0.05 to 0.36 wt %. Calcined cokes from Kuwait, Brazil and several refineries in U.S. (USA1, LV and LB) show a low ash content of 0.07 to 0.13 wt %, while calcined cokes from Indonesia, USA2 and USA3 have a high ash content ranging from 0.29 to 0.35 wt %. A medium level of ash content, 0.17 to 0.19 wt %, is indicated with calcined cokes from China, Argentina and USA4.

V, Ni and Na metal impurities catalyze oxidation and gasification reactions of carbon in the aluminum smelting process resulting in a higher carbon consumption. Studies performed with various V and Na concentrations indicated a strong correlation with air and carboxy reactivity, but with Ni results were less conclusive. Other metals most likely stay with aluminum ingot as impurities and may affect coke quality parameters.

Chinese, Argentina and Indonesian calcined cokes have a low V content of 24 to 81 ppm; 228-257 ppm with Brazilian, Kuwait and USA4; and a high V content of 300 to 607 ppm is observed with calcined cokes from several refineries in U.S. (USA1, USA2, USA3, LV and LB).

A Ni content less than 200 ppm (ranging from 118 to 194 ppm) is shown with Argentina, Kuwait, USA1, USA4, LV and LB calcined cokes. Other calcined cokes have a high Ni content of 215 to 592 ppm.

Na content of calcined cokes studied varies less in the range of 21 to 140 ppm compared to V and Ni content.

Real Density and Vibrated Bulk Density

Real density of calcined cokes is in the range of 2.057 to 2.076, and all are acceptable for aluminum smelting. Vibrated bulk density of calcined cokes varies in the range of 0.672 to 0.922 g/cm³, indicating significant differences in size distribution among calcined cokes studied.

Size Distribution

Larger than 4 mesh size fraction of calcined cokes varies ranging from 22.9 to 53.7 wt %. Depending on buyer and producing refinery, as listed in Table 1 (Continued), export specification for this fraction can be >32% or >55%. Less than 200 mesh size fraction of these cokes is in the range of 0.2 to 0.6 wt %, meeting export specification.

SUMMARY

Various green (raw) and calcined cokes were analyzed and evaluated for application in production of aluminum anode-grade carbon. Typical coke property data are obtained from nine green and

eleven calcined cokes produced in several different regions of the world (U.S., China, Argentine, Indonesia, Brazil and Kuwait). Important coke quality parameters for these cokes are tabulated and compared, primarily focused on sulfur content, ash and metals (V, Ni, Na) content, density and size distribution. Coke quality significantly varies and is regional in nature depending upon quality specifications dictated by buyer and/or producing refinery.

ACKNOWLEDGMENT

RAIN Calcining Limited, Hyderabad, India, sponsored this project.

REFERENCES

1. J. M. Lee, J. J. Baker, R. Llerena, J. G. Rolle, 214th ACS National Meeting, Las Vegas, Preprints of Symposia, Division of Fuel Chemistry, Vol. 42, No. 3, 844-853 (1997).
2. E. J. Swain, Oil & Gas Journal, Jan. 2, 1995, 33-39; Jan. 9, 1995, 37-42.
3. N. P. Lieberman, Oil & Gas Journal, Mar. 27, 1989, 67-69.
4. R. E. Dymond and B. H. Spector, Light Metal Age, Feb., 1992, 34-38.
5. J. G. Rolle and Y. K. Hoang, Light Metals 1995, 741-744, 124th TMS Annual Meeting, Las Vegas, Feb. 12-16.
6. M. R. Casada, J. G. Rolle, et. al., Light Metals 1997, 489-495, 126th TMS Annual Meeting, Orlando, FL, Feb. 9-13.
7. C. T. Leach, et. al., Light Metals 1997, 481-488, 126th TMS Annual Meeting, Orlando, FL, Feb. 9-13.
8. T. Eidet, et. al., Light Metals 1997, 511-517, 126th TMS Annual Meeting, Orlando, FL, Feb. 9-13.
9. F. Vogt and K. Ries, Light Metals 1995, 691-700, 124th TMS Annual Meeting, Las Vegas, Feb. 12-16.
10. W. M. Goldberger, et. al., Petroleum Derived-Carbons, ACS Symposium Series 303, 1986, Ch. 15, 200-214, (Edited by J. D. Bacha, et. al.).
11. Ullmann's Encyclopedia of Industrial Chemistry, Volume A20 and A27 (1986).
12. E. J. Swain, Oil & Gas Journal, May 20, 1991, 49-52.
13. Kerk-Othmer Encyclopedia of Chemical Technology, Volume 4, 4th Ed., Carbon, 956 (1992).
14. M. F. Vogt, et. al., JOM, July 1990, 33-35.

Table 1. TYPICAL PROPERTIES OF GREEN AND CALCINED COKES USED FOR ALUMINUM ANODE-GRADE CARBON

Origin Type	China		Argentina		Indonesia		Brazil		Kuwait	
	Green	Calicina	Green	Calicina	Green	Calicina	Green	Calicina	Green	Calicina
(as-received)										
Moisture, wt%	1.2		7.2		5.7		5.1			0.9
(dry-basis)										
Proximate, wt%										
VCM	9.90	0.27	11.74	0.28	11.07	0.28	10.09	0.29	8.46	0.28
Ash	0.15	0.21	0.19	0.36	0.33	0.11	0.11	0.11	0.05	0.07
FC	89.95	99.56	88.05	89.53	88.57	99.39	89.80	99.60	91.37	99.65
Ultimate, wt%										
Sulfur	0.68	0.66	1.45	1.46	0.53	0.46	0.79	0.73	3.21	3.14
Carbon	92.10	97.52	91.09	96.89	92.22	97.87	91.95	97.46	91.55	96.05
Hydrogen	3.73	3.10	3.61	0.09	3.94	0.11	3.63	0.05	3.43	0.08
Nitrogen	2.30	1.85	2.08	1.37	1.63	1.23	2.63	1.65	1.05	0.66
Oxygen	1.04	0.00	1.58	0.00	1.32	0.00	0.89	0.00	0.59	0.00
Analysis, ppm										
Sulfur	87	124	98	73	472	579	42	20	7	9
Iron	98	106	256	268	93	184	197	99	16	51
Vanadium	31	51	81	5	24	201	257	184	257	118
Nickel	256	279	117	134	144	238	176	215	86	118
Aluminum	88	85	43	83	48	95	13	9	3	15
Calcium	87	95	123	130	48	73	8	9	5	3
Sodium	63	59	110	96	91	124	51	61	15	21
Chromium	1.1	1.2	0.5	1.4	0	0.8	1.5	1.5	0.3	0.3
Btu/lb	15603	14089	15660	13997	15665	14156	15454	14087	15664	13889
RD, g/cm ³	2.066		2.068			2.071			2.075	
VBD, g/cm ³	0.823		0.765			0.672			0.810	
Size, wt%										
+20 mm	21.2		10.3		10.3		13.7		38.0	
-6 mm	51.1		70.6		72.5		65.7		24.7	
+4 mesh										
+8 mesh		37.7		28.2		31.8		22.9		53.7
+16 mesh		52.6		44.7		49.8		35.7		68.0
+30 mesh		6.4		6.5		3.4		11.8		5.3
+60 mesh		1.4		3.9		1.7		7.3		3.1
+100 mesh		0.3		0.5		0.3		0.6		0.3
+200 mesh										
Ratio of Calicina to Green, %										
VCM		2.7		2.4		2.5		2.9		3.3
Ash		109		90		92		100		140
FC		109		113		112		111		109
Sulfur		100		101		87		92		98
Carbon		105		106		106		106		105
Hydrogen		0.6		2.5		1.4		2.8		2.3
Nitrogen		60		66		75		63		64
Btu/lb		90		89		90		91		89

Table 1 (Continued). TYPICAL PROPERTIES OF GREEN AND CALCINED COKES USED FOR ALUMINUM ANODE-GRADE CARBON

Type	USA1-CA		USA2-CA		USA3-CA		USA4-LA		LV-WA		LB-CA	
	Green	Calcine	Green	Calcine	Green	Calcine	Green	Calcine	Green	Calcine	Green	Calcine
(as-received)												
Moisture, wt% (dry-basis)	4.2		2.6		9.2		6.4		0.03	0.1		
Proximate, wt%												
VCM	8.90	0.26	11.02	0.29	11.18	0.51	10.54	0.27	0.1	0.1		
Ash	0.11	0.12	0.28	0.35	0.22	0.29	0.13	0.19	0.1	0.13		
FC	90.99	99.62	88.70	99.36	88.60	99.20	89.33	99.54	99.8	99.77		
Ultimate, wt%												
Sulfur	2.96	2.95	1.10	1.02	2.42	2.20	2.81	2.65	2.8	2.85		
Carbon	91.20	96.03	91.27	96.59	90.68	96.32	91.02	96.22				
Hydrogen	3.56	0.02	3.83	0.12	3.79	0.04	3.70	0.04				
Nitrogen	1.47	0.88	3.39	1.92	1.80	1.15	1.67	0.90				
Oxygen	0.70	0.00	0.13	0.00	1.09	0.00	0.67	0.00				
Major, ppm												
Silicon	23	22	60	87	156	130	22	20	30	20		
Vanadium	28	45	202	272	211	291	83	105	50	75		
Niobium	321	365	504	607	284	338	229	228	300	385		
Nickel	137	198	488	592	238	300	190	194	125	160		
Aluminum	10	18	28	61	131	211	14	27				
Calcium	18	13	127	140	44	52	89	156	15	30		
Sodium	32	31	133	140	37	67	79	89	30	35		
Chromium	0.5	0.5	1.9	1.9	0.7	0.7	0.1	0.1				
Btu/lb	15600	13991	15539	13929	15612	14030	15633	13946				
RD, g/cm ³		2.068		2.065		2.057		2.076	2.07	2.07		
VBD, g/cm ³		0.823		0.922		0.758		0.744	0.89	0.87		
Size, wt%												
+20 mm	20.5		33.0		19.2		6.2					
+6 mm	50.1		34.3		53.7		65.5					
+4 mesh		44.7		29.1		32.0		33.4	32	55		
+8 mesh		58.2		46.3		50.0		47.9	70	70		
+50 mesh		8.0		1.8		5.1		10.9	8	8		
+70 mesh		4.8		0.9		2.7		7.1	3.3	3.3		
+200 mesh		0.3		0.2		0.4		0.6	0.6	0.3		
Ratio of Calcine to Green, %												
VCM		2.9		2.6		4.6		2.6				
Ash		109		125		132		146				
FC		109		112		112		111				
Sulfur		109		93		91		94				
Carbon		105		106		106		106				
Nitrogen		0.6		3.1		1.1		1.1				
Btu/lb		90		90		90		89				

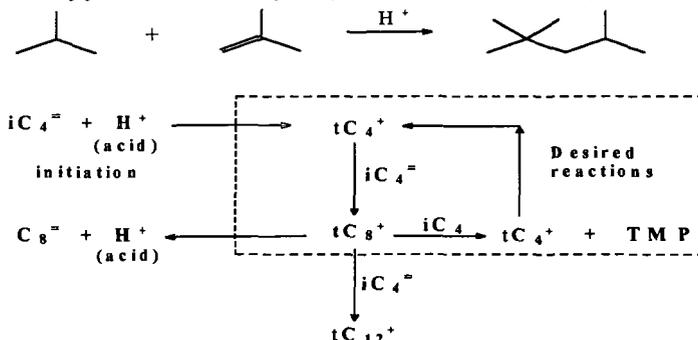
ALKYLATION OF ISOBUTANE AND BUTENES OVER ANION-MODIFIED ZIRCONIUM OXIDE CATALYSTS.

Xin Xiao, Jianmin Chen[†], Shuguang Zhang, John W. Tierney and Irving Wender*
 Department of Chemical and Petroleum Engineering, 1249 Benedum Hall,
 University of Pittsburgh, Pittsburgh, PA 15261

Keywords: alkylation, solid acid catalyst, anion-modified zirconium oxide

Introduction Alkylation of isobutane with butenes is an important industrial process for the production of iso-octane and its isomers, i.e., trimethylpentanes (TMPs). The product, called alkylate, has a high octane number (90-94 RON), low vapor pressure (RVP), no aromatics or olefins. It is a preferred blending stock for reformulated gasoline. The production of alkylate in the US should exhibit steady growth through the year 2000 [1] and will top 900,000 b/d in 1997 [1], about 13 vol% of the US gasoline pool [2]. Two types of commercial processes are now in operation: one based on HF, the other on H₂SO₄. There are considerable environmental concerns about the use of the toxic HF and sulfuric acid presents problems of corrosion and disposal of spent catalysts. Efforts are being made to use HF in a way to reduce its volatility [3]. It is recognized that alkylate production by use of an environmentally benign solid acid catalyst is highly desirable [4-8]. Work on the chemistry and technology of C₄ alkylation before 1993 has been reviewed [9]. A recent symposium was held on the use of solid acid catalysts and processes [10]; none have been commercialized as yet. Major problems for solid catalyst alkylation are short catalyst life time and low selectivity to TMP.

Rao [2] has written a reaction pathway for the isobutane-isobutene alkylation:



Two major undesirable reactions usually occur: competitive side reactions leading to formation of octenes rather than TMPs; and consecutive side reactions leading to higher (C₁₂ and C₁₆) hydrocarbons. To obtain a high selectivity to alkylate, a low olefin concentration must be maintained in the reaction zone; high isobutane to olefin feed ratios and high olefin conversions are necessary. In commercial alkylation processes, the feed isobutane/butenes ratios (external ratio) are typically 5-8 for the H₂SO₄ process and 10-14 for the HF process. Due to high olefin conversion inside the reactor, the internal isobutane/butenes ratios are much higher. However, this ratio is difficult to maintain on a solid catalyst surface because olefin adsorption is much stronger than paraffin adsorption. This may explain a difficulty of the alkylation process over solid catalysts.

Recently, new types of anion-modified metal oxides have drawn increasing attention [11-13]. Metal-promoted ZrO₂/SO₄ and ZrO₂/WO₃ are strong solid acids with activity for hydrocracking and hydroisomerization of hexadecane, polyethylene and Fischer-Tropsch waxes at relatively mild reaction conditions [14-16]. Initial activity has been demonstrated over ZrO₂/SO₄ catalyst for alkylation reaction [7, 17]. In this work we investigated the alkylation chemistry and deactivation behavior over two Pt-promoted anion-modified metal oxide catalysts, Pt/ZrO₂/SO₄ (PtSZ) and Pt/ZrO₂/WO₃ on Al₂O₃ support (PtWZ-Al₂O₃).

Experimental Section

Feed mixture preparation. Isobutane (i-C₄H₁₀, 99.7%; C₃H₈, 0.3%) was obtained from Praxair. A mixture containing isobutene (i-C₄H₈, 8%; i-C₄H₁₀, 91%; C₂H₆, 1%) and a mixture containing cis-2-butene (cis-2-C₄H₈, 20%; i-C₄H₁₀, 80%) were obtained from Air Products. All three are in steel cylinders with dip tubes. Various ratios of isobutane/butene were made by mixing into a

*Correspondence author. [†]Current address: Department of Environmental Science & Engineering, Fudan University, Shanghai 200433, China.

500ml steel container kept at dry ice temperature. Before loading of each component, connecting tubes were purged with the feed component to remove air. The steel container with its contents was weighed each time after a component was put in. The final composition of the mixture was calculated and verified by GC.

Catalyst Synthesis. The solid catalysts PtSZ and PtWZ-Al₂O₃ were synthesized following a similar method described elsewhere [15]. ZrCl₄ was dissolved in 1500 ml of distilled water and hydrolyzed at room temperature by slowly adding 28-30% NH₄OH with vigorous agitation until pH = 9 was reached. The mixture was stirred for another 30 min and left to settle overnight. The precipitate [Zr(OH)₄] was filtered and washed with distilled water until no chloride ions were detected. The solid was then dried at 110 °C overnight and ground to below 100 mesh. Sulfation was carried out by treating 10.0 g of the resultant Zr(OH)₄ with 150 ml of 0.5 M H₂SO₄ solution for 30 min with constant stirring. The solid was separated from the liquid by filtration, rinsed with ~150 ml of water and dried at 110 °C overnight. The sample was loaded with 0.5 wt% Pt by incipient wetness impregnation of a H₂PtCl₆ aqueous solution, dried at 110 °C overnight and calcined at 650 °C for 3 hr. Tungsten [WO₃/(ZrO₂ + WO₃) = 8.3 wt%] was loaded on Zr(OH)₄ by incipient wetness impregnation of a (NH₄)₆H₂W₁₂O₄₀ solution. The sample was dried at 110 °C overnight, mixed with γ-Al₂O₃ (ZrO₂:Al₂O₃ = 1:1 by wt), and impregnated with 0.5 wt% Pt (based on total solid) using an H₂PtCl₆ aqueous solution. The sample was dried at 110 °C overnight and calcined at 700 °C for 3 hr.

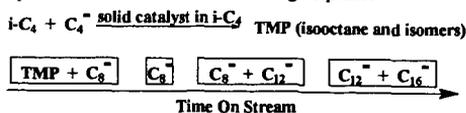
Reactor. A continuous up-flow fixed bed reactor equipped with on-line GC analysis was employed. The isobutane/butene mixture was maintained in liquid phase under He pressure, and fed to the reactor by a piston-type pump. The reactor temperature was controlled by a computer in the range of 30 - 750 °C; pressure was controlled by a back-pressure regulator in the range of ambient to 1000 psig. Various gases, air, He, N₂ and H₂, could be fed into the reactor and the flow rate controlled by a mass flow meter.

Experimental Procedure. Catalysts were formed into pellets and then crushed to 40-60 mesh particles. The catalyst was then mixed with the same weight of 50-70 mesh quartz sand and packed into a 3/8" o.d. stainless steel tubular reactor. Quartz sand was packed before and after the catalyst bed. Before a reaction, the reactor system was purged with He and pressurized. Liquid isobutane was pumped into the reactor and heating started. The feed was switched from an isobutane to isobutane/butene mixture at least 10 min after a stable reaction temperature was reached. Time-on-stream (TOS) was recorded as zero min at the moment of the feed switch. On-line GC analysis (FID detector) was used periodically to analyze product composition. Liquid products condensed by dry ice were kept in a refrigerator (4 °C). After evaporation of isobutane, the remaining liquid products were identified by GC/MS and compared with literature data [18], pure compounds, and boiling points of the species.

Results and Discussion

Alkylation of isobutane and 2-butene. Figure 1 shows liquid product obtained from alkylation of isobutane and 2-butene over a Pt/ZrO₂/SO₄ catalyst at a whsv of 2.0 h⁻¹. The main peak was 2,2,4-TMP, accompanied by 2,3,4- and 2,3,3-TMPs. Dimethylhexanes (DMHs), branched C₈ olefins, C₉ and higher paraffins and olefins as well as C₃-C₇ cracking products were also found. At a lower whsv, 0.25 h⁻¹, under otherwise identical conditions, the catalyst life time was extended and TMP selectivity increased (Table 1). GC analysis revealed that the increase in TMP selectivity at the lower whsv was mainly due to an increase of 2,3,4- and 2,3,3-TMPs (Figure 2). However, fractions higher than C₈ also increased. At prolonged reaction times (1.5 and 5 hr, respectively) TMPs were diminished but selectivities to C₈ olefins and higher hydrocarbons increased in both runs.

Deactivation and regeneration of the catalyst. TMP selectivity was highest at low TOS; C₈ olefins appeared a few minutes later, and gradually replaced TMP as the main peak during alkylation of isobutane and 2-butene over a PtSZ catalyst. At high TOS, C₈, C₁₂ and C₁₆ branched olefins were the main products, as shown in the following sequence:



Conversion of 2-butene remained almost unchanged in the first few hours. The shift in product composition was probably due to adsorption phenomena on the catalyst surface. The catalyst surface was originally covered only by isobutane. When the isobutane/2-butene mixture passed through the catalyst bed, 2-butene first reacted with surface isobutane to yield TMP. The more strongly adsorbed 2-butene then started to replace isobutane from the catalyst surface. After

the concentration of 2-butene reached a certain level, C₈ olefins formed by dimerization of adsorbed 2-butene were the main product. The C₈ olefins reacted further with 2-butene to give C₁₂ and C₁₆ olefins. TMPs as the main product indicated predominant adsorption of isobutane on the catalyst surface, and C₈ olefins as the main product indicated adsorption of 2-butene, and C₁₂ olefins indicated C₈ olefin adsorption. Jong et al. indicated that these side reactions contribute to catalyst deactivation [19]. Low butene concentration is crucial in alkylation to keep good TMP selectivity.

To verify the surface adsorption hypothesis, a series of regeneration experiments on the same catalyst were performed. Since solid alkylation catalysts could be regenerated by air, H₂ stripping [20] and solvent extraction [21], the catalyst deactivation is probably caused by carbonaceous deposits.

Full regeneration was indicated when TMPs appeared as the main product at the beginning of a run. The run was continued until C₁₆ olefins appeared. Without regeneration, only C₈ and higher olefins were observed. As seen in Table 2, the catalyst was successfully regenerated by H₂ accompanied by liquid isobutane flow (400 psig) at 110 °C for 30 min. It can be explained by assuming that the surface was saturated with adsorbed 2-butene and C₈ olefins which were replaced by an excess of isobutane. The catalyst was also successfully regenerated at 71 °C for 2 hr in H₂ and isobutane. However, when the temperature was lowered to 24 °C, the catalyst was only partially regenerated as indicated by both TMP and C₈ olefin peaks at the initial TOS. The catalyst was also regenerated by air at 450 °C and 690 °C. If deactivation of the catalyst were caused by surface lay down of olefins, removal of olefins by desorption would regenerate the catalyst. To test this, He was passed through the reactor which was gradually heated to 450 °C and kept at that temperature for 3 hr, a procedure similar to TPD; the following alkylation reaction showed initial activity to TMPs. Repeated regeneration by He at 450 °C was also successful. The experiments indicated that degradation of the catalyst was caused by strong adsorption of certain species, probably olefins, which covered active sites responsible for alkylation, but the active sites were never destroyed.

Alkylation of isobutane and isobutene. In order to weaken the adsorption of olefins and enhance the adsorption of isobutane on the catalyst surface, the following modifications were made: (1) PtWZ (on a γ -Al₂O₃ support), which has higher hydrogen transfer activity than PtSZ [22,23], was used as catalyst; (2) reaction temperature was increased to 150 °C; and (3) H₂ was used along with the feed. It was found that low H₂ amounts (less than 1 mol% of total feed) was not enough to suppress polymerization reactions while H₂ amounts greater than 100 mol% of isobutene stopped the alkylation reaction by hydrogenation of isobutene. By comparing runs with and without H₂, and other process variables, suitable reaction conditions and product compositions were obtained (Table 3). At 150 °C and 780 psig (supercritical), isobutene conversions reached 100.0% and 2,2,4-TMP selectivity was between 65.1 to 83.2%. On-line GC analysis of this run at 4.0 hr is shown in Figure 3. The run was stopped after 6.8 hr. No deactivation was observed. TMP selectivity had a tendency to increase with TOS; selectivities were 65.1% at 1.7 hr and 83.2% at 6.8 hr. C₈ components other than 2,2,4-TMP were TMP isomers and DMHs. No olefins were observed. All by-products were in trace amounts except C₁₂ branched paraffins, which was about 20 wt%. Total gasoline boiling fractions (C₅-C₁₂) were over to 99% in all TOS. A run with a lower H₂ to isobutene ratio, i.e., H₂ : isobutene = 1 : 5 (mol), was also made for a longer run time, i.e., 8.3 hr (Table 3). Similar results were observed. The H₂ to isobutene molar ratio was varied from 1:5 to 1:3. Larger amounts of H₂ hydrogenated olefins and decreased the TMP yield dramatically. If the amount of H₂ was lower, TMP selectivity could not be maintained, eventually being replaced by C₈ and higher olefins.

Acknowledgment. The research was supported by the U.S. Department of Energy through the Consortium for Fossil Fuel Liquefaction Science (Grant No. DE-FC22-93PC93053).

REFERENCES

- (1) Gonzalez, R. G., editor, *Fuel Reformulation*, January/February, 1995, 37-41.
- (2) Rao, P.; Vatcha, S. R., *Oil & Gas Journal*, September 9, 1996, 56-61.
- (3) Del Rossi, K. J. US Patent 5,220,096 1993.
- (4) Garwood, W. E.; Leaman, W. K.; Myers, C. G.; Plank, C. J. US Patent 3,251,902 1966.
- (5) Yang, C.; Ossining, N. Y. US Patent 3,851,004 1974.
- (6) Chu, Y. F.; Chester, A. W. *Zeolites*, 1986, 6, 195-200.
- (7) Corma, A.; Juan-Rajadell, M. I.; Lopez-Nieto, J. M.; Martinez, A.; Martinez, C. *Applied Catalysis A: General*, 1994, 111, 175-189.
- (8) Taylor, R. J.; Sherwood, D. E. Jr. *Applied Catalysis A: General*, 1997, 155, 195-215.
- (9) Corma, A.; Martinez, A. *Catalysis Reviews-Science & Engineering*, 1993, 35(4), 483-570.
- (10) *Symposium on New Chemistry with Solid-Acid Catalysts in the Alkylation of Isobutane with Olefins, Division of Petroleum Chemistry*, 212th ACS National Meeting, Orlando, FL, August 25-29, 1996, 668-724.

- (11) Song, X.; Sayari, A. *Catalysis Reviews-Science & Engineering*, 1996, 38, 329-412.
- (12) Arata, K. *Applied Catalysis A: General*, 1996, 146, 3-32.
- (13) Misono, M.; Okuhara, T. *CHEMTECH*, November, 1993, 23-29.
- (14) Wen, M. Y.; Wender, I.; Tierney, J. W. *Energy & Fuels*, 1990, 4, 372.
- (15) Venkatesh, K. R.; Hu, J.; Wang, W.; Holder, G. D.; Tierney, J. W.; Wender, I. *Energy & Fuels*, 1996, 10, 1163-1170.
- (16) Shabtai, J.; Xiao, X.; Zmierzczak, W. J. *Energy & Fuels*, 1997, 11, 76-87.
- (17) Guo, C.; Yao, S.; Cao, J.; Qian, Z. *Applied Catalysis A: General*, 1994, 107, 229-238.
- (18) Durrett, L. R.; Taylor, L. M.; Wantland, C. F.; Dvoretzky, I. *Analytical Chemistry*, 1963, 35(6), 637-641.
- (19) de Jong, K. P.; Mesters, C. M. A. M.; Peferoen, D. G. R.; van Brugge, P. T. M.; de Groot, C. *Chemical Engineering Science*, 1996, 51(10), 2053-2060.
- (20) Zhang, S. Y.; Gosling, C. D.; Sechrist, P. A.; Funk, G. A. US Patent 5,489,732 1996.
- (21) Cooper, M. D.; Rao, P.; King, D. L.; Lopez, R. R. US Patent 5,326,923 1994.
- (22) Iglesia, E.; Barton, D. G.; Soled, S. L.; Misco, S.; Baumgartner, J. E.; Gates, W. E.; Fuentes, G. A.; Meitzner, G. D. *11th International Congress on Catalysis - 40th Anniversary Studies in Surface Science and Catalysis*, 1996, 101, 533-542.
- (23) Iglesia, E.; Soled, S. L.; Kramer, G. M. *Journal of Catalysis*, 1993, 144, 238-253.

Table 1. Liquid Product Composition after Evaporation of isobutane

TOS range min	whsv, h ⁻¹	C ₅ -C ₇	C ₈			C ₉ +
			TMPs	other paraffins	olefins	
20 - 70	2.00	4.2	24.6	0.7	17.4	53.1
138 - 285	0.25	2.3	32.7	7.0	7.5	50.5

Catalyst: PtSZ, 40-60 mesh, mixed with the same weight of 50-70 mesh quartz sand.
Reaction temperature, 30 °C; liquid pressure, 400 psig (no H₂); i-C₄:2-C₄* = 20.

Table 2. Various Successful Regeneration Conditions for a PtSZ catalyst for Alkylation of Isobutane with 2-Butene^a

110 °C	30 min	H ₂ /i-C ₄ H ₁₀
71 °C	2 hr	H ₂ /i-C ₄ H ₁₀
690 °C	3 hr	air
450 °C	3 hr	air
450 °C	3 hr	He

* The same catalyst was used.

Table 3. Alkylate Compositions from On-line GC Analysis

TOS, hr	Product Composition				
Run No. 1 (a)	C ₅ -C ₇	2,2,4-TMP	other C ₈	C ₉ -C ₁₂	C ₁₃ +
0.9	2.8	73.7	2.6	20.5	0.4
1.7	1.5	65.1	4.5	28.6	0.3
3.1	0.0	74.4	0.9	24.8	0.0
4.0*	0.3	79.4	2.3	18.0	0.0
4.6	0.0	78.3	1.0	20.6	0.1
6.3	0.0	80.3	1.2	18.1	0.4
6.8	0.0	83.2	0.9	15.9	0.0
Run No. 2 (b)	C ₅ -C ₇	2,2,4-TMP	other C ₈	C ₉ -C ₁₂	C ₁₃ +
5.2	4.7	67.4	7.9	20.0	0.0
5.7	3.4	72.2	7.1	17.3	0.0
6.8	3.1	79.4	6.8	10.7	0.0
8.3	5.1	77.2	11.3	6.4	0.0

Conditions: 150 °C; 780 psig; PtWZ-Al₂O₃ catalyst; (a) whsv, 0.5 h⁻¹; H₂:i-C₄:i-C₄* = 0.3:16.3:1(mol), (b) whsv, 1.5 h⁻¹; H₂:i-C₄:i-C₄* = 0.2:16.3:1 (mol). * See Figure 3.

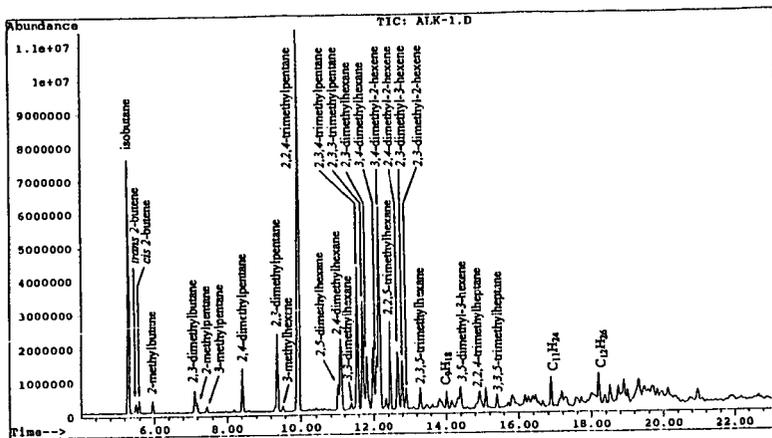


Figure 1. Liquid Products from Alkylation of Isobutane and 2-Butene (fixed bed reactor; isobutane/butene ratio, 20; 30 °C; 400 psig; WHSV, 2.0 h⁻¹; catalyst, PtSZ).

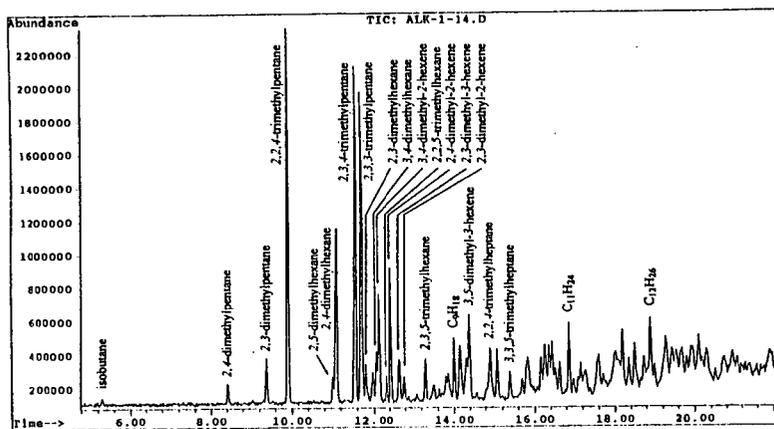


Figure 2. Liquid Products from Alkylation of Isobutane and 2-Butene (fixed bed reactor; isobutane/butene ratio, 20; 30 °C; 400 psig; WHSV, 0.25 h⁻¹; catalyst, PtSZ).

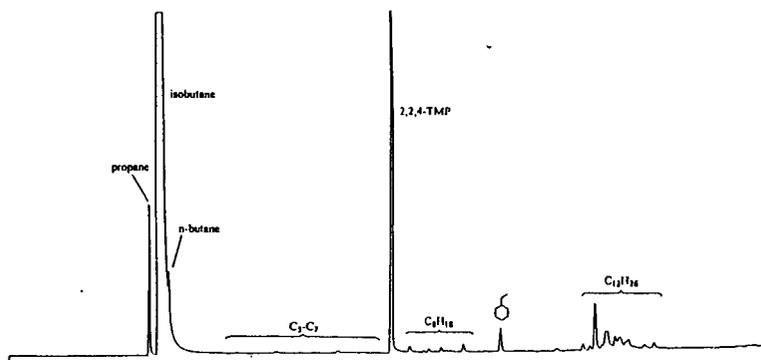


Figure 3. On-line GC Analysis of Alkylate from Isobutane and Isobutene at 242 min TOS (fixed bed reactor; I₂: I-C₁: I-C₂* = 0.3 : 16.3 : 1; 150 °C; 780 psig; WHSV, 0.5 h⁻¹; Pt(WZ-Al₂O₃).

THE OXIDATION STATE OF GALLIUM IN Ga/HZSM-5 LIGHT ALKANE AROMATIZATION CATALYSTS

Z.X. Gao, C.R. Chang and C.Y. Tan

Institute of Coal Chemistry,
Chinese Academy of Sciences,
Taiyuan 030001, P.R. China

Key Words: Ga/HZSM-5, aromatization, gallium state

ABSTRACT:

Gallium modified ZSM-5 catalysts were prepared and the transformations of propane were studied. The influences of catalyst pretreated with H_2 at different temperatures and addition of a small amount of O_2 and H_2 on propane aromatization were investigated. The reduction behavior and physical properties as well as the state and distribution of gallium species of the prepared catalysts were characterized by XPS, H_2 -TPR and NH_3 -TPD techniques. Considering the catalyst evaluation results and the characterization results, it was suggested that the gallium species existed as oxides and did not occupy the exchangeable ion position in the zeolite. Gallium oxides well dispersed on the zeolite and could be easily reduced might be the active species. It was suggested that the probable active oxidation state of gallium was less than +3 but greater than +1.

1. Introduction

Gallium modified HZSM-5 catalysts have been shown to exhibit increased activity and product selectivity for aromatization of light hydrocarbons such as propane and butane^[1]. In recent years, much work has been done on the role of gallium species and the reaction mechanism. It has shown that gallium species is effective not only for dehydrocyclization of oligomers, but also for the direct dehydrogenation of alkanes to corresponding olefins. However the reaction mechanism concerning gallium, especially about the active state of gallium remains unclear^[1]. N.S.Gnep et al proposed Ga^{+3} may be the active state, and the active species may be gallium oxide Ga_2O_3 highly dispersed in the zeolites^[2]. By H_2 -TPR study along with catalytic testing, G.L.Price et al came to the conclusion that the active species was probably Ga^{+1} as a zeolitic cation and was not incorporated in the zeolite lattice^[3]. Yuan et al also suggested that the higher aromatization activities were more likely to be related with the Ga^{+1} species^[4]. Further more, L.Petit et al had shown that at lower conversion level, Ga_2O_3 partially reduced by H_2 produced during propane aromatization had higher dehydrogenation activity than Ga_2O_3 that was further reduced at higher conversion level^[5]. This suggested that the active valence of Ga should be less than +3.

According to our previous study, Ga neither entered into the zeolitic framework nor occupied any exchangeable cation position, it probably existed as highly dispersed Ga_2O_3 on the surface of HZSM-5^[6]. A further study had shown that Ga components can be divided into two parts: active gallium species and free Ga_2O_3 , the former having a strong surface interaction with HZSM-5. The active gallium species could be easily reduced by H_2 at lower temperatures^[7]. So it was difficult to determine the active valence of Ga in the reaction process since H_2 was one of the products.

In this paper, conversion of propane to aromatic hydrocarbons over Ga/HZSM-5 zeolite catalyst was tested as a model reaction. The influence of catalyst pretreatment with H_2 at different temperatures and the influences of H_2 and O_2 on propane conversion were studied. We report here our results about the active valence state of Ga in Ga/HZSM-5 catalysts.

2. Experimental

2.1 Catalyst Preparation: The catalyst Ga/HZSM-5 (I) was prepared by ion-exchange of HZSM-5 (with SiO_2/Al_2O_3 ratio about 56) with gallium nitrate solution. The obtained product then washed with water, dried, and activated for 4hrs at 540 °C in air. The Ga/HZSM-5(M) was obtained by mixing HZSM-5 with gallium oxide, and then calcinated at 570 °C in air.

2.2 Catalytic test: propane aromatization reactions were carried out at atmospheric pressure in a microflow reactor using 1.2g catalyst. In all case, the concentration of propane in Ar was 20%

by volume, and in some other cases a small amount of oxygen or hydrogen was added in the feeding gas. Reaction temperatures were varied among 520-550 °C. After 1h time on stream, the reaction products were analyzed by gas chromatography.

2.3 Catalyst Characterization: NH_3 -TPD Method was used to measure the surface acidity of catalyst samples pretreated at different conditions^[8]. XPS spectra were recorded with a PHI 5300 ESCA SYSTEM as in ref. 7. TG technique was applied for the catalyst reduction process.

3. Results and discussion

3.1 Catalytic activity

As we had noticed before, the catalytic activity of propane conversion over Ga/HZSM-5 varied with catalyst pretreatment conditions. After the regeneration process, the conversion level changed compared to that of freshly activated catalyst. The activity leveled off upon several reaction regeneration performances. So in this paper, the catalyst had been subjected to several reaction-regeneration performances before the following data were obtained.

The catalytic reactions for propane aromatization were studied. Results shown that catalyst Ga/HZSM-5(I) had higher catalytic activity than Ga/HZSM-5(M) catalyst. Ga/HZSM-5 pretreated with various conditions were tested for propane conversion and the results are listed in table 1. Compared to the catalytic activity of the oxidized catalyst, the activity changed little with catalysts treated by 5% H_2 at 540 °C for 1h. Much activity decrease was obtained when the catalyst was reduced in 5% H_2 at 600 °C for 1h. The catalytic activity was largely restored after the catalyst was re-oxidized.

In order to obtain more information about the active state of gallium species, the effects of O_2 and H_2 addition to the feed on propane aromatization were also tested. The results are listed in table 2. As one can see in this table, a small amount of O_2 addition in the propane feed caused a surprising decrease of propane conversion and BTX selectivity. On the other hand, the influence of H_2 was small, the conversion of propane and the BTX selectivity changed slightly despite a higher yield of methane.

3.2 Characterization of the catalyst

Using IR technique, we had found that there was a little change of acidity before and after the introduction of gallium^[9]. Here conventional NH_3 -TPD method was applied to study the acidic properties of Ga/HZSM-5. Upon pretreatment by 5% H_2 at 540 °C for 1h, the total acidity did not change. Even pretreated at 600 °C the total acidity decreased only 3.2%, and most of acidic centers and their distribution remained unchanged. This further convinced that there was no exchange of Gallium with Bronsted acid site in the zeolite upon reduction at higher temperatures, and thus gallium existed as oxides dispersed into the zeolites.

Using TG technique, we calculated the Oxidation states of gallium, in the presence of H_2 , up to 540 °C the oxidation state of Ga appeared to about +2, up to 600 °C less than +1. The results were inconsistent with that of G.L.Price^[10]. The oxidation states of Ga before and after H_2 reduction were also studied by XPS technique. As one can see in fig. 1, after pretreatment in H_2 at 540 °C, an additional peak appeared on the lower binding energy side of Ga 2p, which indicated that gallium species existed in several oxidation states. Because the reduced sample was stored for several days before XPS measurement, it was likely that the above result did not reflect the true oxidation state in the sample. Unfortunately we were not able to perform reduction experiment directly in the preparation chamber of the XPS device. However the XPS revealed that at least Ga/HZSM-5 can be reduced in 5% H_2 . Since H_2 is one of the products in propane aromatization process, we propose that Ga species can be reduced during propane aromatization as was proposed by L.Petit^[1].

3.3 The active state of gallium species

In the present investigation, our main aim is to determine the active state of gallium species that is still disputed in the literature. Considering the above results, we come to the following conclusions. As is known in the literature, acidic property of Ga/HZSM-5 catalysts is of great importance for propane aromatization. After the catalyst was pretreated at 600 °C in the presence of H_2 , the acidity did not change much but the Ga oxidation state change to lower oxidation state less than +1. So in table 1 the activity decrease can be attributed to the gallium state change. This is to say that lower oxidation state of Ga can not be the active state. If we assume the higher oxidation state be the active state, thus after the catalyst was pretreated in H_2 , the

Table1. Aromatization of propane over Ga/HZSM-5 pretreated at different condition ^a

No	Catalyst pretreatment ^b condition ^b	C ₃ ⁰ conv. (%)	BTX yield (%)	Product selectivity(%)				
				C ₁	C ₂	C ₃	C ₄₋₇	BTX
1	Oxidized at 540 °C	43.3	31.4	7.8	9.7	7.1	2.7	72.6
2	Reduced at 540 °C	42.3	30.3	7.8	10.4	7.1	3.0	71.6
3	Reduced at 600 °C	32.8	22.0	7.6	12.5	8.8	3.9	67.1
4	Re-Oxidized at 540	40.6	29.5	8.4	9.7	6.4	2.9	72.6

a. Reaction temperature 535 °C, WHSV of propane 1.84.

b. The catalyst was regenerated by air in Ar in all cases.

Table2. Effects of O₂ and H₂ on propane aromatization over Ga/HZSM-5^a

Composition of feed				C ₃ conv. (%)	BTX yield (%)	Product selectivity(%)					
C ₃ ⁰	Ar	O ₂	H ₂			C ₁	C ₂	C ₃	C ₄₋₇	BTX	COx
20	80	--	--	60.3	43.2	9.8	9.9	5.3	3.4	71.6	--
20	75.8	4.2	--	48.0	27.8	9.4	11.1	6.6	2.2	57.9	12.9
20	72.5	--	7.5	59.1	41.7	11.6	10.8	5.4	1.7	70.6	--

a. Reaction temperature 545 °C, WHSV of propane 2.0

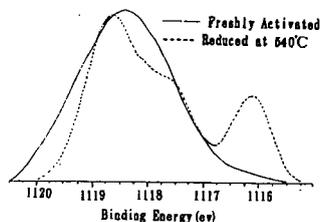


Fig.1 XPS spectra of Ga/HZSM-5 catalyst

catalytic activity would decrease due to the fact that the gallium was reduced to lower oxidation state. However this was not the case, after the catalyst was pretreated by 5% H_2 at 540 °C for 1h, the state of Ga changed, but the activity did not change much. Further more, the addition of a small amount of O_2 in the feeding gas caused a decrease of propane conversion level and the BTX selectivity also decreased. In theory, O_2 reacts with H_2 and thus accelerates the propane aromatization as in the case of using HZSM-5 as catalysts^[11]; the negative effects on Ga modified HZSM-5 may due to the fact that presence of O_2 maintained Ga in its higher oxidation state. These results suggested that the higher oxidation state of Ga not be the active state.

With mild reduction at 540 °C for 1h, the activity did not change much compared to that of oxidized catalyst. Since in this case, Ga exists as +1 \rightarrow +2, we presume that this should be the active valence state. This is further convinced by introducing a small amount of H_2 into the reaction system. The effect of H_2 on propane aromatization could be divided into two parts: on chemical equilibrium H_2 did not favor the propane conversion, but on the other hand, the presence of additional H_2 caused gallium in its active state; the first effect was balanced by the second one. So in this case, the activity did not change much.

Recently, P. Meriaudeau et al^[12] has studied the adsorption properties of Ga_2O_3 by FIIR technique, and found that with H_2 as adsorbate, the number of $Ga^{3+}-H$ function group was higher when Ga was in -1 \sim +2 oxidation state. Our suggestion of gallium active state is strongly supported by Meriaudeau's findings.

References

- [1] M. Guisnet, N.S. Gnep and F. Alario, *Appl. Catal. A: General*, 89(1992)1.
- [2] N.S. Gnep, J.Y. Doyemet, et al, *Appl. Catal.*, 43(1988)155-166.
- [3] G.L. Price and V. KanaziRev, *J. Catal.* 126(1990)267-278
- [4] S. B. Yuan, L. Q. She, X. Y. Liu, X. W. Li, P. Li, H. Z. Huang and Y. Zhou, *Chinese J. Catal.* 9(1988)25
- [5] L. Petit, J.P. Burnonville and F. Raatz, in P.A. Jacobs and R. Van Santen (eds.) *Stud. Surf. Sci. Catal.* Vol. 44, Part B, Elsevier, Amsterdam, 1989, P1163.
- [6] C. Y. Tan, C.R. Cheng, L.X. Zhou and S.Y. Peng, C1-C3 Hydrocarbons Workshop Meeting, 1991.9, Krasnoyarsk, USSR
- [7] Z.X. Gao, C.Y. Tan, C.R. Cheng, *J. Fuel Chem. and Tech.* (Chinese), 1995, 23(3)300
- [8] C.Y. Tan, C.R. Cheng, L.X. Zhou and S.Y. Peng, in "Proceedings 9th international Congress on Catalysis (editors: M.J. Phillips and M. Ternan)", Calgary, 1988, The Chem. Institute of Canada, Ottawa, 1988, P. 445.
- [9] Z.X. Gao, MS Thesis of ICC, 1992.
- [10] G.L. Price and V. KanaziRev, *J. Mol. Catal.* 66(1991)115-120
- [11] G. Centi, G. Golinelli, *J. Catal.*, 115(1989)452
- [12] P. Meriaudeau, and M. Primet, *J. Mol. Catal.* 61(1990)227-234