

CATALYTIC DEHYDROGENATION OF PHENOLICS AND POLYCYCLIC OLEFINS IN THE PRESENCE OF HYDROAROMATIC COMPOUNDS

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Introduction

The dehydrogenation of coal is a reaction that likely plays an important role in direct coal liquefaction and in various stages of coalification. Reggel, Wender and Raymond,¹ in what has been termed a classic study,² dehydrogenated coals using a 1%Pd on calcium carbonate catalyst in refluxing phenanthridine. For 24 vitrains, all obtained from coals ranging in rank from high volatile C bituminous to low-volatile bituminous, the data scatter about a reasonably smooth curve, in which the hydrogen evolution decreases gradually as the carbon content increases from 75.7% m.a.f. to 91.0% m.a.f. Three other points for semi-anthracite and anthracite show that hydrogen evolution decreases rapidly for ranks above low-volatile bituminous. The authors suggested that these findings were an indication of hydroaromatic structures in coal. It is important to note that the catalyst support, CaCO₃, and most of the phenanthridine could be removed by treatment with HCl, allowing examination of the dehydrogenation residues.

This paper looks into the possible effects of two structures in coal that could play a role in influencing the results obtained by Reggel et al.: the part played by phenolic structures and the effect of polynuclear olefinic entities.

Experimental

The original dehydrogenation apparatus¹ was modified so that the pressure difference between the reaction flask and the ambient pressure was controlled by a computer linked to the apparatus. Reaction products were removed from the flask and ground to a fine powder to achieve uniformity. A sample of this ground mixture, dissolved in CDCl₃, was analyzed in a 300 MHz Bruker spectrometer interfaced with a Silicon Graphics workstation. Gases were analyzed using an HP-5890 GC. Illinois #6 coal was from the Argonne Premium Coal Sample Bank. Oils from the dehydrogenation of coals were analyzed using simulated distillation

Results and Discussion

It is known that about half of the oxygen in bituminous coals occurs in phenolic structures^{3,4}. Skowronski et al.⁵ have suggested that secondary reactions involving oxygenated structures could have a significant impact on the catalytic dehydrogenation results using the Pd/phenanthridine system. Reggel et al. raised the question in their original papers in regard to the effect of phenolic groups on their catalytic dehydrogenation of coals. They found that certain phenolic compounds (not designated) yielded hydrogen on catalytic dehydrogenation "probably by reactions of the type"

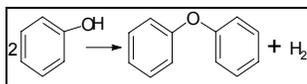


Figure 1. Postulated dehydrogenation of phenol¹.

Phenol as such does not exist in coal. We chose to investigate the catalytic dehydrogenation of 9-phenanthrol which has a phenolic group on a phenanthrene structure, in the absence and in the presence of coal. 9-Phenanthrol is a type of structure likely to exist in bituminous coal. Similar catalytic dehydrogenations, all in the

Pd/CaCO₃-phenanthridine system, were carried out with "- and \$-naphthols.

Analysis by GCMS of the residue from 9-phenanthrol dehydrogenation showed that evolution of hydrogen was due to reaction between two phenanthrol molecules to form aromatic ethers, by the reaction of a phenolic OH group with the aromatic ring in another phenanthrol molecule. The structure of this ether was confirmed by NMR spectroscopy and the overall reaction is given in Figure 2.

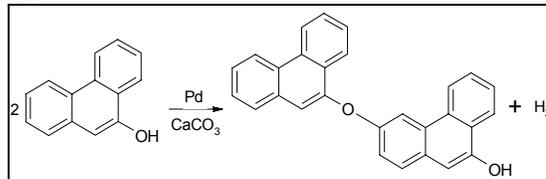


Figure 2. Dehydrogenation of 9-phenanthrol with Pd/CaCO₃ to form aromatic ethers.

The bond dissociation energy of a hydrogen atom attached to a benzene ring is about 103 kcal/mole; that of a benzylic hydrogen is about 85 kcal/mole. Hydrogens attached to the 9,10 position of 9,10-dihydroanthracene (9,10-DHA) or the 9,10 position in 9,10-dihydrophenanthrene (9,10-DHP) have much lower bond dissociation energies.

We therefore dehydrogenated mixtures of 9-phenanthrol with 9,10-DHA and also with 9,10-DHP. The amounts of hydrogen evolved were consistently lower than those which would be obtained by simple addition of the amount of hydrogen from the phenol plus that from the hydroaromatic compound.

The interaction has a negative influence on the rate of H₂ evolution and the final H₂ yield so that the actual yield is always less than theoretical. Proton NMR of the residue from the dehydrogenation of 9,10-DHA and 9-phenanthrol showed that there is a peak in the region of 4.9-5 ppm which is attributed to the formation of an aliphatic aromatic ether.

To determine if there was any interaction between 9-phenanthrol and coal during the catalytic dehydrogenation process, a mixture of 0.2 g of Illinois #6 coal was dehydrogenated, along with 0.2 g of 9-phenanthrol, using 0.3 g of Pd/CaCO₃ in phenanthridine. The results are shown in Figure 3. The final volume of hydrogen evolved for the mixture is less than that which would be obtained by adding the two individual volumes obtained from coal and 9-phenanthrol. This is an indication of the influence of phenolic structures likely to be present in coal on the evolution of hydrogen from what may be hydroaromatic substrates in coal.

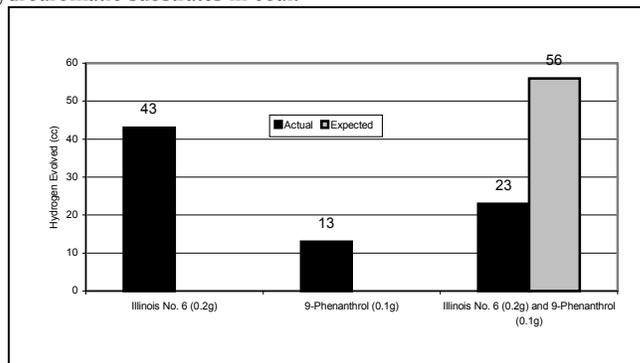


Figure 3. Final hydrogen yields from Illinois #6 coal, 9-phenanthrol and a mixture of the two.

Effect of Polycyclic Olefinic Structures. It is known that all petroleum contains optically active structures. Zahn et al. found that oils from the hydrogenation of coal at 450-525°C and 8000 psig still

contained distillates that were indeed still optically active. They postulated that part of these structures were probably derived from various steroids and terpenes.⁶

Many of the cyclic triterpenoid substances occur in organisms and their fate is of considerable interest as coal precursors. These include the tetracyclic steroids such as cholesterol in animals and sitosterol in plants; these compounds differ in structure only near the end of the aliphatic side chain.⁷ All sterols are unsaturated alcohols, generally with an olefinic bond in one ring

We chose to investigate the dehydrogenation of the readily available cholesterol (Figure 4) in the same catalytic dehydrogenation system. No hydrogen was evolved from cholestane, a fully saturated naphthene. Cholesterol, with a single double bond evolved seven moles of hydrogen plus some methane per mole of cholesterol. When the hydroxyl group in cholesterol was blocked by formation of its silyl ether, only six moles of hydrogen were evolved. The one mole difference in the amount of hydrogen evolution indicated that two naphthenic hydrogens in ring A cannot be removed if the hydroxyl group is blocked.

It was not surprising to find that cholesterol is a very good vehicle for the dehydrogenation of coal; a better dehydrogenation solvent than even 9,10-DHA.

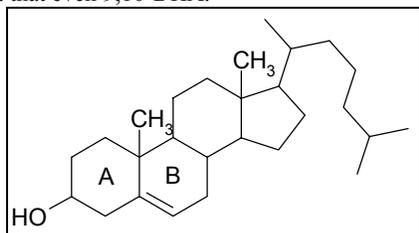


Figure 4. Structure of cholesterol.

It appeared possible that structures resembling cholesterol could be good hydrogen donors in direct coal liquefaction. We liquefied Illinois No. 6 coal using cholesterol as a donor solvent (400°C, 1000 psig of He). As shown in Table 1, the use of cholesterol in coal liquefaction resulted in both a high conversion and a higher oil yield as compared to the use of 9,10-DHA. Even partially dehydrogenated cholesterol gave higher conversions (THF solubles) and oil yields (pentane solubles) than did 9,10-DHA. The oils were characterized by simulated distillation. Lighter oils were obtained from the reaction of coal with cholesterol as solvent than with 9,10-DHA, indicating that naphthenic structures containing a single double bond in a ring can be superior hydrogen donors.

Acknowledgement. Support from the United States Department of Energy is gratefully acknowledged.

Table 1. Comparison of Hydrogen Donor Ability of Cholesterol with 9,10-DHA in Liquefaction of Illinois #6 Coal at 400°C.

Donor Solvent	Conversion (%)	Oil Yield (%)
9,10-DHA	66.7	18.8
Cholesterol	78.2	22.1
Partially Dehydrogenated Cholesterol	75.4	20.3

¹ Reggel, L.; Wender, I.; Raymond, R. *Science* **1962**, *137*, 681. *Fuel*, **1964**, *47*, 373; **1970**, *49*, 287; **1971**, *50*, 152; **1973**, *52*, 162.

² Larsen, J.W.; Ozik, M.; Lapucha, A.; Li, S. *Energy & Fuels*, **2001**, *15*, 801.

³ Blom, L.; Edelhause, L.; van Krevelen, D.W. *Fuel* **1959**, *38*, 537.

⁴ Friedman, S.; Kaufman, M.L.; Steiner, W.A.; and Wender, I. *Fuel*, **1961**, *40*, 33.

⁵ Skowronski, R.P.; Heredy, L.A.; Ratto, J.J.; Neuworth, M.B. *Am. Chem. Soc., Fuel Chem. Div. Reprints*, **1985**, 30(4), 333.

⁶ Zahn, C.; Langer, S.H.; Blaustein, B.D.; Wender, I. *Nature*, **1963**, *200*, 53.

⁷ Given, P.H. in *Coal Science*, Vol. 3, edited by Gorbaty, M.L., Larsen, J.W., and Wender I., "An Essay on the Organic Geochemistry of Coal", **1984**, 63.

FISCHER-TROPSCH SYNTHESIS MECHANISM – STORCH WAS CORRECT?

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Storch experienced during a brief period the best of times and the worst of times. The U.S. had just experienced WW II and a demonstration of the impact of a plentiful fuel supply. To overcome the lack of a supply of petroleum, Germany developed a synfuels industry based on direct and indirect coal liquefaction during the 1930's. The German synfuels industry developed to the extent that it made a significant contribution to the overall supply of transportation fuel until production was severely hampered by Allied bombing. The U.S. petroleum production was not significantly hampered by the war effort and the industry expanded to provide about four of the five billion barrels of fuel needed for the Allied effort in Europe. Research efforts were rapidly utilized in various efforts, including the Manhattan Project and the petroleum industry. At the end of WW II, the research directors were very positive in their attitude toward the benefit of research (1,2). There was a general consensus that the world was facing a severe shortage of petroleum crude. For example, Dobie Keith founded Hydrocarbon Research, Inc. to develop a commercial Fischer-Tropsch plant at Brownville, Texas. Because of the anticipated shortage, the U.S. Bureau of Mines was able to develop a major research effort in both direct and indirect coal liquefaction. This effort, headed by Henry H. Storch, led to the development of major pilot plants for direct and indirect coal liquefaction. In 1944, the 78th Congress passed an act authorizing the construction and operation of demonstration plants to produce synthetic liquid fuels from coal, oil shales, agricultural and forestry products, and other substances, in order to aid the prosecution of the war, to conserve and increase the oil resources of the Nation, and for other purposes (3). The funding authorization was \$30 million, and this was increased to \$87 million, with \$85 million actually appropriated. Approximately \$10 million was expended to construct direct and indirect coal liquefaction pilot plants at Louisiana, Missouri; this was a major project at that time. In addition to the major funding devoted to both basic and development research, the Bureau worked to compile the literature and to provide major reviews, including translations of the materials obtained in Germany and Japan following WW II. In 1945 Storch headed a group of more than 300.

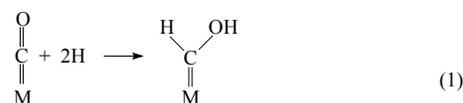
Storch, together with Norma Golumbic and Robert B. Anderson, wrote the definitive book on Fischer-Tropsch in 1951 (4). In subsequent years, Pichler is reported to have indicated that this book was flawed since the Germans, following WW II, did not provide accurate data to the U.S. scientists (5). However, considering the extensive reviews of German work prior to, and the primary documents obtained following, WW II, this assertion does not appear to be valid. Thus, in 1950 Storch was in an enviable position, heading an exceptionally well-funded research and development activity.

With the recognition of the vast reserves of petroleum available in the Middle Eastern countries in the early 1950s, governments of developed countries lost interest in a synfuels industry. In the U.S., there was a dramatic reduction in funding of research by the government for synfuels research and Storch faced

the unpleasant task of having his research activities dramatically reduced.

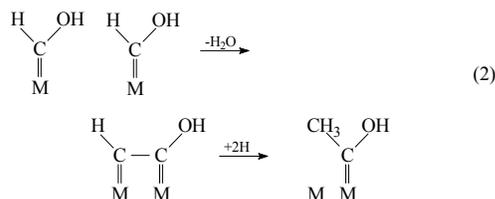
The mechanisms predating 1950 were reviewed in Storch's book and then the mechanism supported by the Bureau's work, and reinforced by the ¹⁴C tracer studies, was presented. In this mechanism it was assumed that (a) hydrogen is chemisorbed as atoms; (b) carbon monoxide is chemisorbed on surface metal atoms in a manner similar to that postulated for bonds in metal carbonyls; and (c) the adsorbed carbon monoxide is partially hydrogenated according to equation 1. Chain-building reactions occur in two ways: (a) by addition to end carbon atoms (equations 2 and 3) and (b) by addition to adjacent-to-end carbons (equations 4 and 5). It was postulated that double bonds between carbon and metal atoms were more resistant to hydrogenation if the carbon atom is also attached to a hydroxyl group. Intermediate β may grow by reaction 5 to produce a product with a methyl side chain while intermediate α will grow to produce normal products. Equations 6 and 7 illustrate ways of terminating the growth of chains. According to equation 6, aldehydes and alcohols result from desorption and hydrogenation of the alcohol-like groups at the surface. Equation 7 leads to olefin and paraffin products.

Chain Initiation

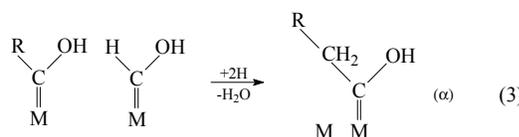


Chain Growth

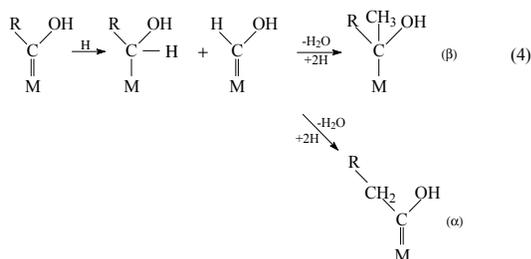
a. At end carbon

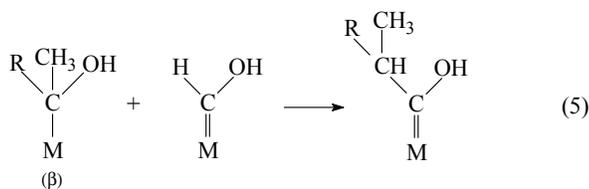


and for the general case



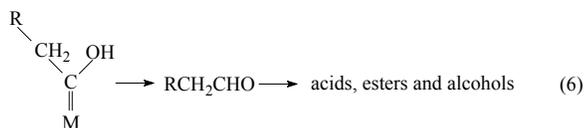
b. At adjacent-to-end carbon



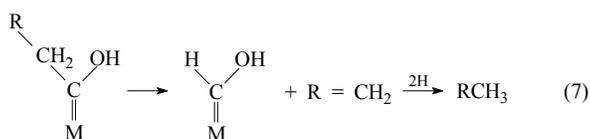


Chain Ending

a.



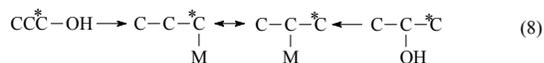
b.



The popularity of this mechanism outlived Storch but the widespread utilization of surface science instruments in the 1970's produced results that led to abandonment of the oxygenate mechanism in favor of a surface carbide mechanism. For example, measurements of the surface concentrations following adsorption of the reactants, always at low pressure, showed a surface rich in carbon but very low, or undetectable, levels of oxygen. These results were interpreted to indicate that adsorbed CO rapidly dissociated to form adsorbed carbon and oxygen. Hydrogenation of adsorbed oxygen was considered to be very rapid, as was the desorption of the water that formed, in order to account for the low levels of oxygen. The hydrogenation of adsorbed carbon to form adsorbed CH_x species was slow compared to the hydrogenation of O. In fact, this was used to explain the inverse kinetic isotope effect obtained with deuterium. We have also obtained an inverse kinetic isotope effect with an iron catalyst but when all products are considered rather than just the disappearance of CO, the situation is very complex. Today the surface carbide mechanism is the one that is almost universally accepted.

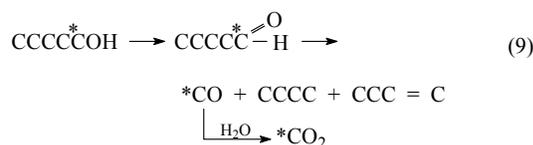
We have obtained data, using ^{14}C tracers, that agree with the Storch mechanism better than with the surface carbide mechanism. Some of these results are outlined below.

We have determined the ^{14}C distribution in the products obtained when ^{14}C -1-propanol or ^{14}C -2-propanol is fed together with the syngas. The surprising conclusion is that 1-propanol produces predominantly n-products. 2-Propanol contributes to the products to a lesser degree than 1-propanol and produces predominantly iso-products (branched chain products). The loss of the oxygenate group from either alcohol would lead to the same intermediate if the half-hydrogenated intermediate is able to isomerize:

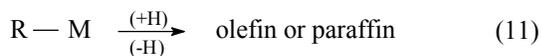
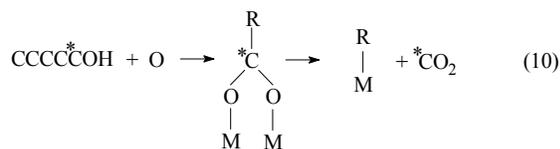


Since obtaining data with these ^{14}C -labeled alcohols, we have obtained conclusive evidence to show that the isomerization shown above for the half-hydrogenated state does occur at a rate that is rapid compared to FTS (6). The simplest explanation for these observations is that the oxygenate species is retained until the irreversible reaction leading to the final product occurs.

Another observation was the conversion of 1- ^{14}C -1-pentanol. Here, the CO_2 produced had a significantly higher concentration of ^{14}C than CO. If the reverse hydrocarbonylation reaction had occurred, as shown in equation 9, this could not have happened.



For the CO_2 to have been formed from CO, the radioactivity/mole of the CO_2 could only be equal to that of CO but could never exceed that of CO. Experimentally, it was found that the ^{14}C in CO was very much lower than in the CO_2 . Furthermore, the activity in CO and CO_2 that was formed from 2- ^{14}C -1-hexanol was very low, indicating that the carbonyl carbon was lost predominantly as CO_2 . It is proposed that the adsorbed n-alcohol reacts with surface oxygen to form a species that is similar to, or the same as, an adsorbed carboxylic acid which then undergoes conversion by eliminating CO_2 as shown below:



Another experiment that provided data to support an oxygenate mechanism was obtained during the conversion of $^{14}\text{CO}_2$, added to the syngas at about 2% of the CO. The results are shown in Figure 1. If the hydrocarbon products are formed only from CO, the methane could never have a greater ^{14}C content than the CO. As shown, this is not the case. Furthermore, the C_2 products can only have a ^{14}C content that is two times that of the CO; again, this is not the case. All hydrocarbon products have a much higher ^{14}C content than the CO. It therefore appears that the CO_2 that is converted to hydrocarbons does so not by first being converted to CO and then hydrocarbons but by being initiated by a species that is formed from CO_2 . Based on the data shown in figure 1, it appears that about half of the CO_2 that is converted goes to produce hydrocarbons and the other

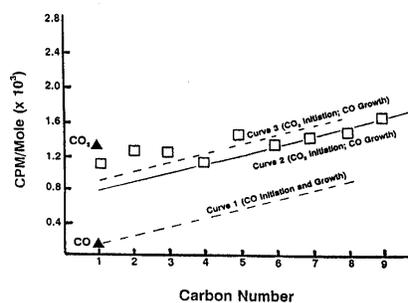


Figure 1. Radioactivity in products when $^{14}\text{CO}_2$ is added to the synthesis gas.

half to produce CO by the reverse water-gas-shift reaction. To account for this observation, it is proposed that the intermediate responsible for the water-gas-shift reaction also initiates FTS. A likely intermediate resembles an adsorbed formate.

In summary, we have gone through at least three cycles of intense interest followed by neglect for indirect liquefaction since Storch's best period. The interest in FTS now appears to be one of optimism. It also appears that at least for an iron catalyst the FTS mechanism involves an oxygenate species and not a surface carbide intermediate. In this respect, we believe that the Storch mechanism is more appropriate for an iron catalyst than the carbide mechanism.

Acknowledgment. This work was supported by U.S. DOE contract number DE-FC26-98FT40308 and the Commonwealth of Kentucky. The author is especially appreciative of the effort expended by several members of the Fuel Chemistry Division to keep the Storch Award alive - this has not been an easy task even though Storch certainly merits the continued recognition the award provides.

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GAS-TO-LIQUIDS TECHNOLOGY - FT CATALYSIS IN EXXONMOBIL'S AGC-21 PROCESS -

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Abstract. Conversion of natural gas to liquids (GTL) utilizing Fischer-Tropsch (FT) hydrocarbon synthesis technology is an attractive option to bring static gas resources to market. ExxonMobil's Advanced Gas Conversion for the 21st Century (AGC-21)¹ is state-of-the-art GTL technology that provides an important commercial option for utilization of stranded natural gas around the world. Continuing research at ExxonMobil is leading to additional catalyst and technology improvements that will further reduce the cost of producing liquids from natural gas. This article discusses advances in ExxonMobil's AGC-21 technology achieved over the years as a result of an ongoing, comprehensive research, development and engineering program.

INTRODUCTION

Over the last decade, there has been renewed interest in the production of synthetic fuels via Fischer-Tropsch synthesis, using synthesis gas produced from remote natural gas.² Emphasis is being placed on use of cobalt catalysts in fixed bed and slurry reactors to achieve high yields of paraffinic wax that can be further converted to other products.

ExxonMobil's three step AGC-21 process is shown in Figure 1.⁴⁻⁹

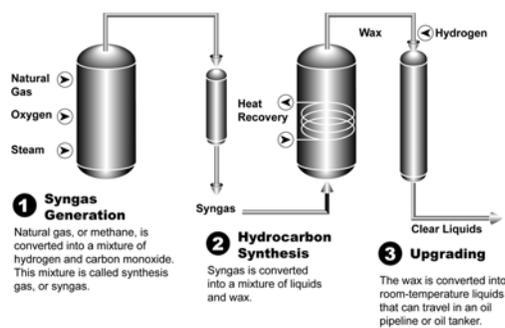


Figure 1 – AGC-21 Flow Scheme

HYDROCARBON SYNTHESIS

ExxonMobil's Fischer-Tropsch HCS technology operates in a novel slurry reactor, using new, high-activity thin layer cobalt catalysts under controlled hydrodynamic operating conditions. The combination of the slurry reactor design with advanced catalyst tailored for slurry reactor operation has resulted in higher hydrocarbon productivity levels and selectivity to 650°F+ boiling material than previously thought possible.

Over the past two decades ExxonMobil has pioneered the development of cobalt catalysts and advanced slurry reactors for high productivity wax synthesis.

The high performance HCS process is characterized by the achievement of high catalyst activity, high selectivity to C10+ hydrocarbon yield and low rate of catalyst deactivation, resulting in sustained operations at high productivity and high yield. While improvements in either activity, selectivity or activity maintenance have been reported in the literature, AGC-21 technology is unique in having achieved all three of these attributes simultaneously.

ExxonMobil has patented cobalt catalyst systems consisting of cobalt on inorganic oxide supports, including titania, alumina, silica and silica-alumina. The preferred formulation consists of cobalt on modified titania, specifically tailored for slurry Fischer-Tropsch operation, to achieve high C10+ productivity.⁷⁻⁸ The catalyst is designed to avoid diffusion limitations associated with intraparticle mass transfer, which is particularly important when operating at high productivities. Performance tests have shown that by maintaining cobalt in a dispersed RIM or thin layer on the outer surface of the catalyst, it is possible to achieve very high productivity with minimum gas make. The thin cobalt layer minimizes relative H₂ and CO diffusion rates and also avoids particle overheating.

The catalyst composition and activation procedures provide high activity and the manner in which it is fabricated results in high selectivity to desired high molecular weight products under moderate slurry reactor operating pressures. The catalyst is also highly resistant to attrition, which is particularly important for efficient separation of the catalyst from the HCS reactor product.

As shown in Figure 3 Current HCS reactor productivity is more than double previously reported ExxonMobil performance, and more than four times recently reported iron slurry results. Progress in increasing reactor productivity, which translates into fewer reactors required to achieve desired plant capacity, is continuing, with the ongoing research advancing new catalysts that show promise of further substantial increases in productivity.

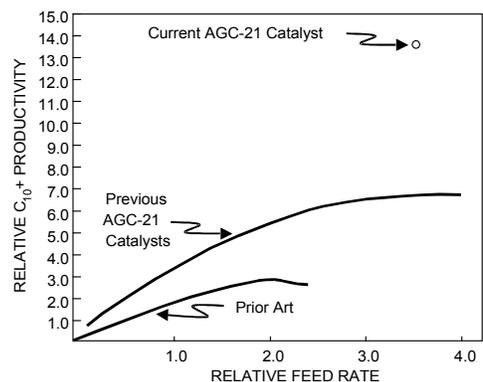


Figure 3 – Relative Productivity vs. Relative Feed Rate

A plot of HCS reactor performance during a large scale pilot plant run is shown in Figure 4. High levels of productivity with low methane yield were demonstrated in extended operations. This was achieved through use of a proprietary catalyst rejuvenation system that maintains a high level of catalyst activity by stripping reaction inhibitors from the catalyst surface, coupled with good catalyst fluidization.

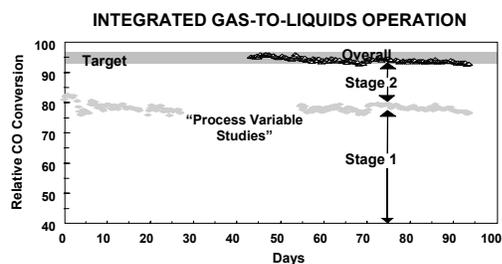


Figure 4 – Days of Operation vs. CO Conversion

This high level of performance is consistent with the fundamental understanding developed over years of research in the areas of reaction kinetics, hydrodynamics and catalytic surface chemistry relationships that impact activity maintenance. This understanding is used to set conditions and operating procedures that have extended previously accepted performance limitations and identified additional process improvement opportunities.

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Promoted Pt catalysts for the dry reforming of methane in the presence of oxygen

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Introduction

The production of synthesis gas via CO₂ reforming of CH₄ received significant attention over the past decade as the push for environmentally friendly processes and the elimination of greenhouse gases became a major focus in industry. Even though it has been shown that the reduction of CO₂ is not a valid argument for dry reforming, interest in the reaction and finding stable catalytic materials has remained high. Reasons for this interest include the simultaneous presence of both reactants in natural gas reservoirs [1] and the ability to combine the dry reforming reaction with partial oxidation and steam reforming to obtain any ratio of H₂:CO in the synthesis gas [2].

Catalyst deactivation continues to be an obstacle at high temperatures and the majority of the research has focused on finding materials capable of withstanding the reaction conditions. Previous studies have shown that Pt metal supported on ZrO₂ promoted with La³⁺ and Ce⁴⁺ can be stable for the reforming reaction at 800°C and a 2:1 ratio of CH₄:CO₂ [3]. These results demonstrated that the reaction proceeded through a bifunctional mechanism in which methane decomposes on the metal resulting in the formation of hydrogen and carbon adsorbed on the metal. This carbon can react with oxygen from the support to produce carbon monoxide and create an oxygen vacancy in the support near the perimeter of the particle. Carbon dioxide adsorbs at the vacancy site and dissociates to form CO and replenish the support oxygen. The balance between the rate of decomposition and dissociation determines the overall activity of the catalyst. The addition of the promoters resulted in a support that facilitated the reaction mechanism and substantially improved the stability and overall catalytic performance. The Ce-promoted catalysts were found to be more readily reducible which aided in the removal of the carbon species from the metal. The La-promoted catalysts helped to retard particle growth and had increased CO₂ adsorption and dissociation capability.

More recent studies have shown that the loading of Ce in the support impacts the catalytic performance, and the activity can be correlated to the reducibility of the oxide [4]. XPS studies have shown that catalysts with 50% Ce and 50% Zr exhibited the highest degree of Ce reduction and the highest activity. Previous studies have shown that the addition of Ce and La to ZrO₂ does not result in a significant increase in catalytic performance [5] however; no investigations to explain the observed activity have been performed.

In this contribution we are focusing on the promotion of ZrO₂ with both Ce and La and the effect of the components on the Pt metal. We have prepared 0.5 wt% Pt supported on Ce-, La-, and CeLa-doped ZrO₂ and characterized the materials using TPR, BET surface area measurements, H₂ chemisorption, and pulse studies. The activity and stability of these materials has been compared to a 0.5 wt% and 1.5 wt% Pt/ZrO₂ catalyst for the dry reforming reaction in the presence and absence of oxygen.

Experimental

The ZrO₂, lanthanum (5 wt%)-doped ZrO₂, cerium (18 wt%)-doped ZrO₂, and lanthanum (5 wt%)-cerium (18 wt%)-doped ZrO₂ were all obtained from Magnesium Elektron Inc. Prior to the addition of the metal the supports were calcined at 800°C in stagnant air for 4 hours. Pt was added to the supports using incipient wetness

impregnation of an aqueous solution of H₂PtCl₆·6H₂O. The metal loading on the promoted catalysts was 0.5 wt%. Two un-promoted samples were made, with metal loadings of 0.5 wt% and 1.5 wt%. The nomenclature for the unpromoted catalysts will be 0.5PZ and 1.5PZ, respectively. All of the catalysts were dried overnight at 110°C, and then reduced *in-situ* in H₂ (30 cm³/min) at 500°C for 1.5 h, prior to reaction.

Dry reforming activity measurements were performed in a quartz flow reactor at 800°C using a CH₄:CO₂ ratio of 1:1 and a GSHV of 180,000 h⁻¹. For the experiments in the presence of oxygen, the composition of the feedstock was 61.5 % CH₄, 10.5 % CO₂, and 28 % O₂. The GSHV for these reactions was 85,000 h⁻¹. Temperature-programmed reduction (TPR) experiments were performed on each sample. The samples were heated to 800°C at a rate of 6.5 °C/min in a stream of 5% H₂/Ar (30 cm³/min).

Pulse studies were performed on each sample at 800°C following the pretreatment described for the activity experiments. The catalysts were exposed to 100 μL pulses of CH₄ followed by pulses of CO₂ and then CH₄. Information about the H₂ and CO production during each pulse was obtained using a mass spectrometer (Pfeiffer Vacuum).

Results and Discussion

Table 1 shows the BET surface area and the H₂ chemisorption measurements for the various catalysts. Chemisorption values were taken after reduction at 500°C and heating to 800°C in He, to simulate the particle size at the beginning of the reaction. The surface area for the promoted catalysts was much higher than the observed surface area of the unpromoted ZrO₂. The support containing both Ce and La had a surface area greater than 200 m²/g. These results are in agreement with previous studies [4], in which x-ray diffraction was used to demonstrate that the promoters stabilize the tetragonal form of the ZrO₂ leading to increased surface areas after high temperature calcination.

Table 1. BET Surface Area and Chemisorption Measurements of the Catalysts Investigated

Catalyst	BET surface Area (m ² /g)	Dispersion (%)
0.5PZ	24.862	35.012
1.5PZ	24.862	17.669
PCZ	49.257	23.96
PLC	53.997	9.19
PLCZ	224.92	14.98

Pulse studies performed on the various catalysts allow for the probing of the degree of support reduction and the ability of the support to facilitate CO₂ dissociation. The degree of reducibility of the support can be observed by monitoring CO production during pulses of pure CH₄, while the CO₂ dissociation can be monitored by the CO produced during pulses of CO₂. The ability of the catalyst to remove carbon deposited during the reaction can be observed by comparing the amount of H₂ produced in the first pulse of each series of CH₄ pulses. Pulse studies performed on the PCZ, PLZ, and PLCZ, showed that the presence of Ce results in more CO produced during CH₄ pulses, and thus a more readily reducible oxide. The catalysts containing La showed more CO₂ dissociation capability which agrees with TPD results reported elsewhere [6]. Finally, unlike the 0.5PZ catalyst, the promoted catalysts all show the ability to effectively remove carbon from the metal by exhibiting similar hydrogen production during the first pulse of each set of CH₄ pulses.

Based on the BET surface area, the measured dispersion, and the knowledge of the role of the promoters we anticipated that the

addition of both promoters would utilize the increased reducibility of ceria and the enhanced CO₂ dissociation of La to improve the catalytic performance. Contrary to what we anticipated, Figure 1 shows that the PLCZ catalysts did not exhibit improved performance for the dry reforming reaction. The methane conversion on the dual promoted material was less than the La- or Ce-doped material as well as the unpromoted catalysts. Figure 1 also shows that the PCZ and PLZ catalysts were more active than the 1.5PZ catalyst even with three times less Pt. Finally, the 0.5PZ catalyst, although having the highest initial activity, experienced significant deactivation during the 15 hour reaction. The conversion of methane observed after 15 hours was less than the 1.5PZ catalyst and was still decreasing.

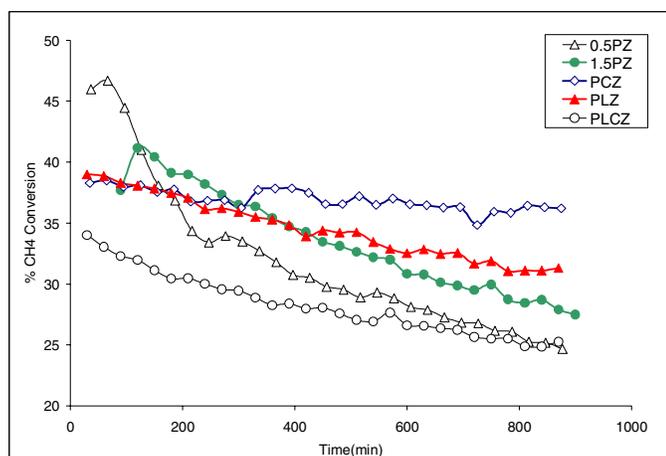


Figure 1. CH₄ conversion during dry reforming reaction at 800°C with 1:1 feed ratio of CH₄:CO₂ (GHSV=180,000 h⁻¹).

The high initial activity of the 0.5PZ catalyst is not surprising based on the dispersion values measured by chemisorption. Using the chemisorption information and assuming that all particles on the catalyst were uniform in size and shape, an average particle size was determined for each catalyst. Using the particle size, an estimate was made of the perimeter of the particle and ultimately the total contact area of the metal and support. If the catalyst with the higher loading of Pt had more total interfacial area this might explain the observed higher stability. However, our results show that based on the pre-reaction chemisorption, the 0.5% Pt catalyst had the most interfacial area, and therefore should exhibit the highest stability. X-ray absorption studies have suggested that sintering of the Pt particles at 800°C may be responsible for the deactivation of the Pt/ZrO₂ catalyst due to the loss of the metal-support interfacial area [6]. Our chemisorption results suggest that if particle size is the primary factor in determining long-term activity, then sintering of the metal particle not during the pretreatment, but during the reaction, resulting in a dramatic decrease in activity. In addition, the 1.5 wt% Pt/ZrO₂ catalyst appears to be more resistant to sintering resulting in a more stable catalyst with higher long-term activity. Further investigations are being performed to determine the optimal Pt metal loading for the dry reforming reaction.

TPR experiments performed on the 0.5PZ and 1.5PZ catalysts show that the reduction of PtO to metallic Pt occurs in the temperature range of 180-200°C. Similar results were obtained on the PCZ catalyst. A shift in the reduction temperature was observed on the catalysts containing La. On the PLZ catalyst the reduction of PtO appears at 220°C, while on the PLCZ catalyst the shift is even greater with complete reduction not occurring until 300°C. The shift in

reduction temperature indicates a modification of the Pt by the support. XPS studies are currently being performed to determine if the Pt is being altered due to the presence of the La and Ce.

Figure 2 shows the results of the reaction of CH₄ and CO₂ in the presence of O₂. The promoted catalysts still perform better than the unpromoted catalyst with the same loading of metal. The performance of the promoted catalysts in the presence of O₂ is very similar, with a final conversion of CH₄ after 15 hours within 2%. It is interesting to note that unlike the dry reforming reaction, the CH₄ conversion observed on the 1.5PZ catalyst in the presence of O₂ was higher than the promoted materials. These results suggest that the beneficial effect of the promoters in facilitating the two path mechanism may not be as significant when oxygen is present to assist in carbon removal from the metal.

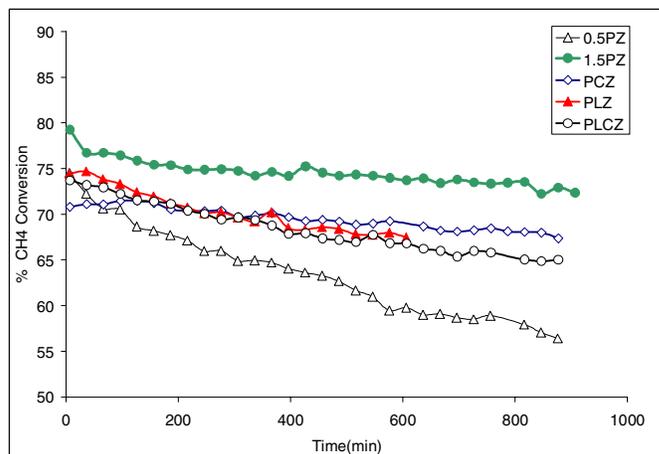


Figure 2. CH₄ conversion during dry reforming reaction in the presence of oxygen at 800°C with a feed composition of 61.5% CH₄, 28% O₂, and 10.5% CO₂ (GHSV=85,000 h⁻¹).

Conclusions

The results of this work have shown that the addition of both La and Ce to Pt/ZrO₂ catalysts does not result in improved performance for the dry reforming reaction. Although the material does show high surface area, good metal dispersion, increased reducibility, and increased CO₂ dissociation capabilities, the methane conversion observed is significantly lower than that observed on the LaZrO₂ and CeZrO₂ supports. The decreased activity could be due to modification of the Pt by the support as observed through TPR studies. XPS characterization is being performed to further explain the source of the modification. In the presence of O₂, the beneficial effects of the promoters may not be as significant due to the ability of the O₂ to aid in carbon removal from the metal.

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Shape-Selective Catalysis for Specialty Chemicals from Coal-Derived Polycyclic Hydrocarbons

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Introduction

Coal-derived liquids, such as distillates from coal liquefaction, pyrolysis, and carbonization, are rich in polycyclic aromatic hydrocarbons. These PAHs are not desirable components of conventional liquid fuels such as gasoline or diesel fuels. However, they can be converted into value-added chemicals and advanced polymer materials.

There are some exciting developments in advanced polymer materials and specialty chemicals which present new opportunities for catalytic research on selective conversion of polycyclic compounds that can be obtained from coal-derived liquids and some refinery streams [1-4].

PAH Conversion

This presentation is a review of our recent studies on synthesis of value-added organic chemicals from 2-ring and 3-ring polycyclic hydrocarbons by selective conversion over certain 12-MR or 10-MR zeolite catalysts or zeolite-supported metal catalysts [4-7].

Early studies and publications on chemicals from coal till 1980s seem to be dominated by the approaches to obtain chemical feedstocks or commodity chemicals or alternate chemicals from coal in connection with alternate fuels from coal (as an alternative to petroleum-based fuels and chemicals). Such chemicals typically include olefins, BTX and phenol, which are currently produced in petrochemical industry.

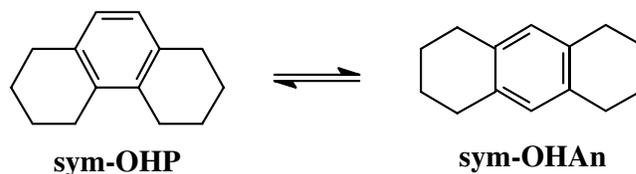
However, our attention has been focused on how to make use of the unique structural features of the aromatic compounds, particularly polycyclic compounds, in coal-derived liquids for producing value-added organic chemicals.

Specifically, this review will discuss the new developments in the following catalytic reactions over large-pore zeolite catalysts:

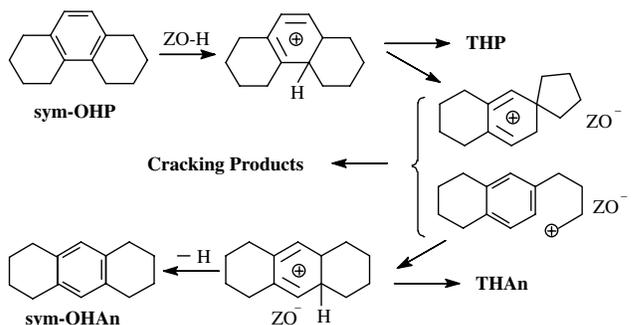
- (1) ring-shift isomerization of phenanthrene derivatives to anthracene derivatives;
- (2) shape-selective alkylation of naphthalene for synthesizing 2,6-dialkyl naphthalene;
- (3) shape-selective alkylation of biphenyl for synthesizing 4,4'-dialkyl biphenyl;
- (4) conformational isomerization of cis-decahydronaphthalene into trans-decahydronaphthalene;
- (5) shape-selective hydrogenation of naphthalene into either cis- or trans-decalin, and
- (6) regio-selective hydrogenation of 1-naphthol and quinoline for synthesizing specialty fuel additives.

Schemes 1 to 8 illustrate these reactions. In most case, the selectivity strongly depends on the type and nature of catalysts, as well as reaction conditions.

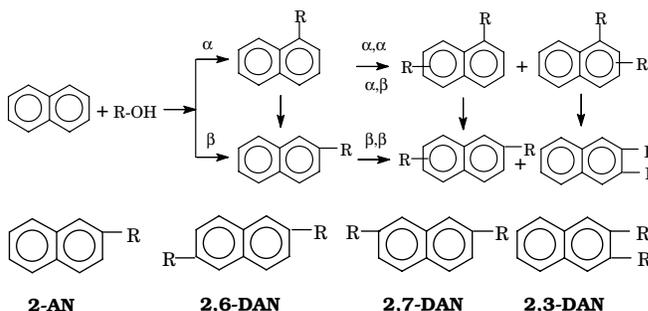
Scheme 1. Ring-Shift Isomerization



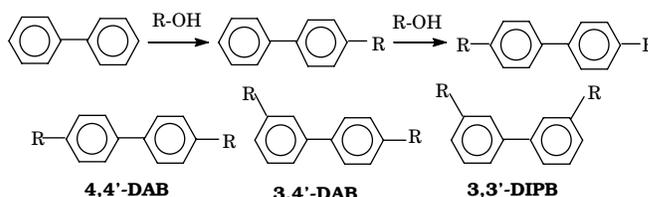
Scheme 2. Reaction Pathways for Ring-Shift of sym-OHP



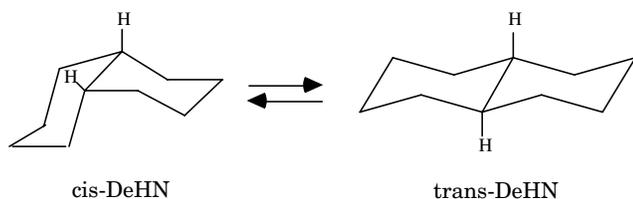
Scheme 3. Alkylation of Naphthalene



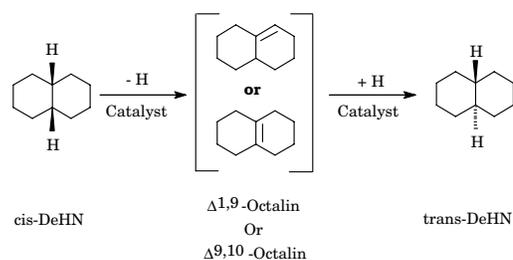
Scheme 4. Alkylation of Biphenyl



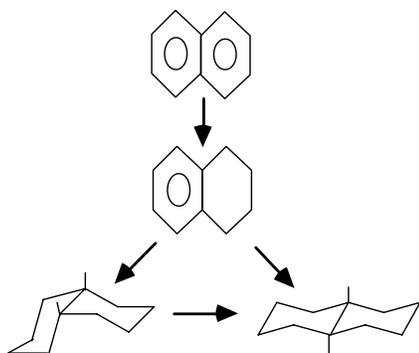
Scheme 5. Conformational Isomerization of cis-DeHN



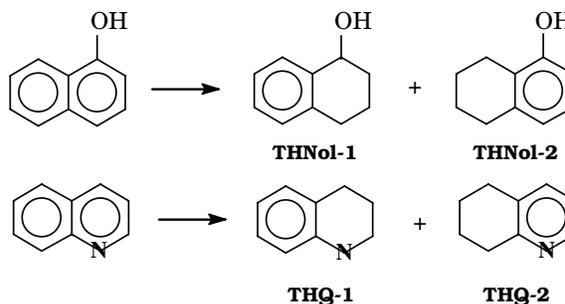
Scheme 6. Proposed reaction pathway for isomerization of cis-DeHN into trans-DeHN.



Scheme 7. Selective Hydrogenation of Naphthalene.



Scheme 8. Regio-selective Hydrogenation



The products of the selective catalytic reactions discussed above are intermediates for making specialty chemicals, monomers of advanced polymer materials such as high-performance polyesters including polyethylene naphthalate, polybutylene naphthalate, and liquid crystalline polymers, and components of advanced thermally stable aviation jet fuels for high-Mach aircraft. The possible reaction mechanisms, pathways and factors affecting the selectivity have also been discussed [5-7].

Concluding Remarks

This presentation is a selective review based on recent studies in our laboratory. Selective catalytic conversion of PAHs can be very useful for making polycyclic specialty chemicals that have potential industrial applications.

Because of the presence of two or more isomers of polycyclic compounds, a major challenge is to direct the reaction along a very specific pathway to the desired isomer.

Substantial progress has been made in the applied fundamental research in the past several years. In many cases, further improvement in catalyst selectivity and stability is needed, and many fundamental questions concerning mechanistic aspects remain to be answered by future study.

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