

HYDROGENOLYTIC ACTIVITY OF SOLUBLE AND SOLID Fe-BASED CATALYSTS AS RELATED TO COAL LIQUEFACTION EFFICIENCY

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ABSTRACT

A comparative activity study of soluble and solid Fe-containing catalysts for hydrogenolysis of (1) coal-simulating compounds, i.e., 2-isopropyl-naphthalene (IPN) and diphenylmethane (DPM), and (2) a Blind Canyon coal sample (designated as DECS-17), was performed. The soluble catalysts were supported on SiO₂ and included aqua complexes of various Fe salts, i.e., sulfate, acetate and chloride. The solid catalysts consisted of finely dispersed superacids, i.e., Fe₂O₃/SO₄²⁻ and ZrO₂/SO₄²⁻. The soluble catalysts contain the aqua complex ion [Fe(H₂O)₆]³⁺, which is pre-formed or formed *in situ* in the presence of water, and acts as a protonic acid by ligand dissociation especially above 250°C. Kinetic rate constants for hydrodealkylation of IPN and hydrogenolytic cleavage of DPM show that at temperatures of 350-400°C the above solid superacids possess markedly higher activity as compared with that of the SiO₂-supported, soluble Fe salts. In agreement with this finding, the same solid superacids were found to be effective hydrogenolysis catalysts in the depolymerization of the Blind Canyon coal sample. Therefore, small amounts (0.1-0.5 wt %) of Fe-containing solid superacids can be conveniently used in the initial step of a modified version of the previously developed HT-BCD (mild hydro-treatment-base catalyzed depolymerization) coal liquefaction procedure.

INTRODUCTION

An important aspect of direct coal liquefaction research is the development of effective catalysts for the chemical reactions involved in the liquefaction process. A large variety of catalysts have been investigated in fundamental studies, but two groups of catalysts have attracted particular attention, i.e., (1) bifunctional metal sulfides which are believed to act mainly as ring hydrogenation but also as C-O, C-S, C-N, and C-C hydrogenolysis catalysts, and (2) soluble or solid acid catalysts which cause primarily hydrogenolytic bond cleavage⁽¹⁾.

In recent years the concept of applying disposable, highly dispersed iron-based catalysts in coal liquefaction has attracted considerable interest. The advantage of these catalysts is seen in their anticipated high activity, low cost, and environmental acceptance. Iron-based catalysts which can be added to coal in the form of very fine solid dispersions include iron oxide, iron oxyhydroxide, prepared by different methods^(2,3), iron carbides⁽⁴⁾, and others. Alternatively, coal impregnation with soluble iron compounds has been examined using various methods⁽⁵⁻¹²⁾.

Numerous studies have been performed on a sulfated iron oxide catalyst⁽¹³⁻¹⁵⁾. An IR spectroscopic study, performed by Yamaguchi et al. ⁽¹³⁾ indicated the presence of surface

complexes between SO_4^{2-} ions and iron oxide. It was proposed that a chelated iron oxide-sulfate structure, containing two covalent $\text{S}=\text{O}$ double bonds, is responsible for the strong acidity of sulfated iron oxide. Hino and Arata used this catalyst for various acid-catalyzed reactions, e.g., dehydration of ethanol^[14], and skeletal isomerization of butane to isobutane at low temperatures^[15]. They pointed out that $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$ catalyst can be considered as a superacid.

Previous reports have shown that many iron compounds in their original form are not the active catalysts in direct coal liquefaction processes. Rather, it is assumed that such iron compounds are converted under coal liquefaction conditions, viz, in the presence of sulfur^[3,16] or other sulfidation agents^[17] to very active forms of non-stoichiometric pyrrhotites. The introduction of sulfate ions on the surface of iron oxide catalyst apparently enables its transformation into fine particles of pyrrhotite, which is characterized by high acidity and other properties^[18].

Shabtai et al.^[5-7] have recently developed a two-stage, low-temperature coal depolymerization-liquefaction procedure. In the first step of the depolymerization stage, a coal sample is impregnated with a soluble, highly dispersed iron catalyst^[19] and then subjected to mild hydrotreatment (HT) at temperatures $\leq 290^\circ\text{C}$ and a H_2 pressure of 1000-1500 psig. The mild hydrotreatment results in partial depolymerization of the coal by preferential hydrogenolytic cleavage of alkylene, benzyl etheric, cycloalkyl etheric and some activated thioetheric linkages. In the second depolymerization step, the mildly hydrotreated coal sample is subjected to base-catalyzed depolymerization (BCD) at $\leq 290^\circ\text{C}$ with a methanolic solution of KOH or $\text{Ca}(\text{OH})_2$. This completes the coal depolymerization by hydrolysis (alcoholysis) of diaryletheric, aryl cycloalkyl etheric, diaryl thioetheric and other bridging groups. The sequential HT-BCD treatment results in a mixture of low M.W. (about 100-300) products, composed primarily of monocluster compounds.

In the present study the hydrogenolytic activity of soluble vs solid Fe-containing catalysts was compared, using the hydrodealkylation of 2-isopropyl-naphthalene and the hydrogenolysis of diphenylmethane as model reactions. In parallel, the activity of the two types of acid catalysts in the framework of the HT-BCD procedure (as measured by the overall yield of depolymerized coal products) was examined, using a Blind Canyon coal sample (DECS-17) as feed.

EXPERIMENTAL

Materials. 2-isopropyl-naphthalene (purity, 98%) was obtained from Willey Organics. Diphenylmethane (purity, 99%) was obtained from Aldrich Chemical Company, and n-dodecane (purity, 99%) from Phillips Petroleum Company. Coal samples (DECS-17) were supplied by the Penn State Coal Sample Bank.

Preparation of Catalysts. Two series of catalysts were prepared.

The first series consisted of three SiO_2 -supported soluble salts, i.e., $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ and $\text{Fe}(\text{CH}_3\text{COO})_3$. Those were prepared by incipient wetness impregnation of SiO_2 (Aldrich,

grade 62, 60-200 mesh, 150 Å) with aqueous solutions of the respective salts, followed by drying under vacuum for 24 hours at room temperature. An alternative drying procedure, which produced a more active $\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}/\text{SiO}_2$ catalyst involved drying of this catalyst in air at 120°C. The second series of catalysts comprised two solid superacids, i.e., $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$ and $\text{ZrO}_2/\text{SO}_4^{2-}$, which were prepared as follows:

$\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$. A solution of 25 g of $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ and 50 g of urea in 1000 ml of distilled water was heated at 95°C for 2 h. The precipitate formed was filtered, washed with hot water (until no free SO_4^{2-} ions could be detected) and dried at 100°C for 24 h. The dry product was treated with 0.5 M H_2SO_4 (10 ml/g of solid) with continuous stirring, and then filtered, dried at 100°C for 24 h and calcined at 500°C for 3 h.

$\text{ZrO}_2/\text{SO}_4^{2-}$. 25 g of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ was dissolved in 150 ml of water and subjected to hydrolysis at room temperature by slowly adding 28-30 % NH_4OH with vigorous mixing, until a pH=8.5 was reached. The precipitate was filtered, washed with distilled water until no free Cl^- ions could be detected, and then dried at 110°C for 24 h. The dry solid was pulverized to -100 mesh and treated with 0.5 M H_2SO_4 (10 ml/g of solid) for 1 h with continuous stirring, and then filtered, dried at 100°C for 24 h and calcined at 650°C for 3 h.

Procedure of Kinetic Hydrogenolysis Studies. The kinetic studies of model compounds, in particular 2-isopropyl-naphthalene, were carried out in a 50 ml Microclave reactor (Autoclave Engineers) equipped with a special sampling device. Twenty grams of a solution containing 2 wt. % of 2-isopropyl-naphthalene in n-dodecane and the catalyst were introduced in the reactor and the latter was quickly closed, purged with nitrogen and then pressurized with hydrogen to an initial pressure of 800 psig. The reactor was brought to the desired temperature (350-400°C) in 12-15 min., and at this point stirring (800 r.p.m.) was started. After each sampling, at intervals of 5-10 min., some hydrogen addition was necessary to keep a constant hydrogen pressure of 1500 psig. The reaction products were analyzed by gas chromatography using a 4 m x 0.3 cm o.d. stainless steel column packed with 10% OV-17 on Chromosorb W-HP.

The treatment of the kinetic data was made on the basis of pseudo-first-order reaction in reactant concentration, viz.,

$$-\ln(1-x_i) = kWf(t/V)$$

where k is the rate constant; x_i is the conversion at time t_i ; W is the catalyst weight, and $f(t/V)$, (volume-corrected space time) is defined by

$$f(t/V) = \sum_{i=1}^n \frac{t_i^c - t_{i-1}^c}{V_{i-1}}$$

in which, n is the total number of intervals between the samples; V_{i-1} is the liquid volume remaining in the reactor during a given time period, and t' is the corrected time.

RESULTS AND DISCUSSION

Table 1 summarizes the values of the pseudo-first-order kinetic rate constants (k_1) for hydrodealkylation of 2-isopropyl-naphthalene, IPN (to yield naphthalene and propane) as a function of catalyst type. The Table also provides the values of the rate constants (k_2) for the competing ring hydrogenation of IPN to yield 2-isopropyl-1,2,3,4-tetrahydronaphthalene. Kinetic runs were performed at two different temperatures, i.e., 350 and 400°C (for other conditions, and for the experimental procedure, see Experimental). The k_1 values obtained were taken as a measure of the hydrogenolytic activity of the catalysts.

As seen, at 350°C the solid superacid catalysts 4 and 5 show markedly higher hydrogenolytic activity than the supported soluble catalysts 1 and 2. The difference in activity becomes larger with increase in reaction temperature to 400°C. The supported anhydrous $\text{Fe}(\text{CH}_3\text{COO})_3$ catalyst shows the lowest activity among the soluble Fe salt catalysts. Addition of a small amount of water to this catalysts (see footnote d, Table 1) prior to reaction, resulted in some hydrogenolysis activity, which, however is lower than that of catalysts 1 and 2 which contain the pre-formed aqua complex $\text{Fe}(\text{H}_2\text{O})_6^{3+}$. The latter has been previously indicated⁽²⁰⁾ as the precursor of active, protonic acid-generating species, e.g., $\text{H}^+[\text{Fe}(\text{H}_2\text{O})_5\text{OH}]$. The relatively low activity of catalyst 3, even in the presence of water, indicates that it is preferable to use pre-formed aqua complexes of Fe salts. The thermal stability of such catalysts between 250-400°C is presently being investigated in this laboratory. The very low values of the ring hydrogenation rate constants (k_2) with the supported soluble catalysts 1-3 indicates that the latter possess essentially no ring hydrogenation activity, viz., they act as selective, monofunctional hydrogenolysis catalysts. In contrast, the $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$ catalyst 4 shows moderate ring hydrogenation activity, especially at 400°C ($k_2=0.30$). This would indicate that under reaction conditions (H_2 pressure; elevated temperature) the sulfated iron oxide may be converted to a bifunctional catalyst system containing not only a strongly acidic functional group, but also a moderately active ring hydrogenation co-catalytic component. This could explain the overall good efficiency of this catalyst under coal liquefaction conditions.

The observed extraordinarily high hydrogenolytic activity of $\text{ZrO}_2/\text{SO}_4^{2-}$ suggests the desirability of developing active $\text{Fe}_2\text{O}_3\text{-ZrO}_2/\text{SO}_4^{2-}$ co-catalysts. Work on such catalyst systems is presently underway in this laboratory. Parallel hydrogenolytic activity studies with diphenylmethane (DPM) as feed showed similar trends as those in Table 1. However, the rate constants for hydrogenolytic cleavage of DPM (to yield benzene and toluene) were lower, due to the slower protonation rate of the monocyclic aromatic rings in DPM, as compared with that of the bicyclic arene system in IPN.

Table 2 summarizes the total conversions of the Blind Canyon coal sample (DECS-17) into depolymerized, THF-soluble products obtained by HT-BCD treatment, using different acid

TABLE 1. Kinetic Rate Constants for Hydrogenolysis (Hydrodealkylation) and Ring Hydrogenation of 2-Isopropyl-naphthalene (IPN) as a Function of Catalyst Type^{a,c}.

Catalyst	$k_1 \times 10^2$ (ml/g·min), hydrodealkylation		$k_2 \times 10^2$ (ml/g·min), ring hydrogenation	
	350°C	400°C	350°C	400°C
(1) FeCl ₃ ·6H ₂ O/SiO ₂	3.9	31.5	0.2	0.7
(2) Fe ₂ (SO ₄) ₃ ·5H ₂ O/SiO ₂	2.4	10.6	0.4	1.3
(3) Fe(CH ₃ COO) ₃ /SiO ₂ ^d	0.4	6.9	0.2	0.5
(4) Fe ₂ O ₃ /SO ₄ ²⁻	6.2	99.2	4.2	30.0
(5) ZrO ₂ /SO ₄ ²⁻	372.5	565.9	4.1	5.7

^a In each kinetic run was used 20 g (26.7 ml) of a 2.0% by weight solution of IPN in n-dodecane.

^b The amount of SiO₂-supported soluble catalysts 1, 2 and 3 used in each run was 4 g. The rate constants for these catalysts were calculated on a SiO₂-free basis. The amount of superacids 4 and 5 used in each run was 5000 ppm (0.5%).

^c Reaction conditions: H₂ pressure, 1500 psig; temperature, 350 or 400°C; microclave reactor volume, 50 ml; sampling time intervals, 5-10 min.; total reaction time, 75 min.

^d A calculated amount of water, needed for *in situ* formation of the Fe(H₂O)₆³⁺ ion was added to this supported anhydrous salt, prior to reaction.

catalysts in the HT reactor (a flow reactor system was used in this part of the study). As seen, using either the soluble aqua complexes of Fe salts (unsupported; impregnated in the coal) or solid superacids (in the form of fine dispersions; physical mixture with coal) results in a very high level of depolymerization (92.4-94.5 wt. %, calculated on the pre-extracted (THF) DECS-17 sample; MAF basis). However, the impregnated aqua complexes can be applied as acid catalysts at a mild HT temperatures (275-325°C) whereas the use of finely dispersed solid superacids in the HT treatment requires temperatures of $\geq 340^\circ\text{C}$.

TABLE 2. HT-BCD Treatment of Blind Canyon Coal (DECS-17) using different acid catalysts in the HT reactor^a

HT Catalyst	Catalyst/Feed Ratio	HT Temp., °C	HT-BCD Conversion ^b
$\text{Fe}_2(\text{H}_2\text{O})_5(\text{SO}_4)_3$	1:9	325	92.7
$\text{Fe}(\text{H}_2\text{O})_6\text{Cl}_3$	1:9	300	94.1
$\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$	1:200	340	92.4
$\text{ZrO}_2/\text{SO}_4^{2-}$	1:200	340	94.5

^a In each run was used 10.0 g of coal-catalyst mixture. HT reaction conditions: H_2 pressure, 1500 psig; H_2 flow rate, 50 sccm; total reaction time, 2 h. BCD reaction conditions: catalyst-solvent system, 10% KOH solution in MeOH; temperature, 290°C ; total reaction time, 1 h.

^b Total yield of THF solubles (MAF basis), calculated on the pre-extracted Blind Canyon coal feed.

CONCLUSIONS

1. Kinetic studies of acid-catalysed hydrogenolysis of 2-isopropyl-naphthalene and diphenylmethane show that (in the temperature range of $350\text{-}400^\circ\text{C}$) finely dispersed solid superacids, e.g., $\text{Fe}_2\text{O}_3/\text{SO}_4^{2-}$ and $\text{ZrO}_2/\text{SO}_4^{2-}$, possess markedly higher hydrogenolytic activity as compared with that of soluble aqua complexes of Fe salts, e.g., Fe sulfate, chloride and acetate (supported on SiO_2).
2. In agreement with the above, it is found that solid superacids, in very low concentrations (0.1-0.5 wt. %) can be conveniently applied as hydrogenolysis catalysts in the HT step of the HT-BCD coal depolymerization process⁵⁻⁷. The effective application of superacid catalysts in this process, however, requires HT temperatures $\geq 340^\circ\text{C}$, which are considerably higher than those found as optimal in the case of impregnated soluble Fe salts as hydrogenolysis catalysts ($275\text{-}300^\circ\text{C}$).

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