

ACTIVITY AND SELECTIVITY OF DISPERSED IRON CATALYST IN COAL LIQUEFACTION AND MODEL COMPOUND REACTIONS

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INTRODUCTION

Owing to the difficulties of recovering more expensive catalysts such as Ni, Mo after use, iron has continued to be of interest as the basis of an economical and disposable catalyst for coal liquefaction. Most of the investigations on iron catalysts have focused on non-supported highly dispersed catalysts, introduced via impregnation techniques and as finely divided powder. It is believed that dispersed phase catalysts in coal liquefaction can offer several advantages over conventional ones^[2,3,6]. A suitably dispersed catalyst helps to establish a highly reducing environment with the coal matrix in the presence of hydrogen, thus reducing the need for a good hydrogen donating solvent. Effective contact of coal-solvent slurries with the catalyst surface can be achieved even at low catalyst concentration. Diffusion limitations are minimized because of the small catalyst particles. In addition, certain bond cleavage reactions can be promoted during the early liquefaction step which minimize the detrimental regressive reactions. The objective of our research is to examine the catalytic activity of dispersed iron oxide catalyst in the coal liquefaction process. To lay a good foundation for this work we have also examined the selectivity and activity of several forms of iron including Fe_2O_3 , FeS_x and reduced Fe in both a continuous and a tubing bomb microreactor (TBMR) using naphthalene and biphenyl as model compounds. Coal liquefaction experiments were also performed with a small particle iron catalyst.

EXPERIMENTAL

Coal Liquefaction Reaction Procedures: Coal liquefaction experiments were carried out in 45 cc tubing bomb microreactors (TBMR's) at the reaction conditions outlined in Table 1. The ratio of reaction solvent (tetralin, 1-methylnaphthalene, or mineral oil) to coal (Blind Canyon DECS-17 and Illinois #6) was 3:1. Elemental sulfur was added as a sulfur source with the DECS-17 coal. The iron catalyst employed was Fe-3 (Nanocat superfine iron oxide, Mach-1 Inc.). According to the product specification, it is α - Fe_2O_3 with a surface area of 282 m^2/g , and particle size of 30 Å and approximately one-half of the atoms reside on the particle surface. For each run, two horizontal TBMR's were agitated in a fluidized sand bath that was maintained at 400°C. After 60 minutes reaction time, the two TBMR's were removed and quenched in water. The pentane and THF solubles formed by coal liquefaction were measured and used as an indication of catalyst activity and liquefaction reactivity for coal samples. The equation used to calculate the pentane and THF solubles is as follows:

$$\%SOLUBLES = \frac{W_o(1-M) - (I.S. - W_c \cdot \frac{2MW_{FeS}}{MW_{Fe_2O_3}})}{W_o(1-A-M)} \cdot 100$$

W_o : initial weight of coal charged to bomb

A: fraction of ash in the coal

M: fraction of moisture in the coal

I.S.: weight of insolubles

W_c : weight of catalyst

MW: molecular weight of specified species

Model Compound Reaction Procedures: The hydrogenation activities of iron catalysts with model compounds were investigated in both tubing bomb microreactor (TBMR) and continuous reactor. Table 1 shows the TBMR experimental conditions. The two model compound systems employed were 2 wt% naphthalene (NAPH) in mineral oil (M.O.) and 2 wt% biphenyl in hexadecane. The iron catalysts were Fe-2 (Strem Chemical Inc., unsupported Fe_2O_3 powder) and Fe-3 as described earlier. CS_2 was utilized as sulfur source at 2 wt% in the liquid solution for the Fe-2 catalyst and 0.2 wt% for the Fe-3 catalyst. The catalyst loading of Fe-2 was ten times of that of Fe-3 to keep the surface area of these two catalysts about the same. The H_2 charged to the reactor was generally 1000 psig at ambient temperature. For Fe-2 catalyst, when CS_2 was added to the reactants, the initial H_2 pressure charged was increased to 1250 psig to compensate for H_2 used in converting CS_2 to H_2S . The in-situ reduction of catalysts was performed in a H_2 atmosphere for 24 hrs.

The model compound system of NAPH/M.O. and Fe-2 catalyst were tested in a CDS 900 trickle bed reactor shown schematically in Figure 1, and which has been described in detail elsewhere^[7]. The reactor was operated at 250°C and 1000 psi at a hydrogen flow rate of 100 ml/min (STP) and liquid feedstock flow rate of 0.2 ml/min. Nitrogen was used to purge and pressurize the reactor before starting the reaction.

The product samples collected from both the continuous reactor and the TBMR were analyzed with a Varian 3300 gas chromatograph. Temperature programming was used to improve peak resolution and decane used as an internal standard.

RESULTS AND DISCUSSION

Coal Liquefaction Studies

When moisture free Illinois #6 coal was used with tetralin as the reaction solvent in the tubing bomb runs, the percentage of pentane solubles (%PS) increased from 33% without catalyst to 36% with Fe-3 catalyst. For Blind Canyon coal, the %PS increased from 36% without catalyst to 44% with 2 wt.% catalyst. When sulfur was added to the coal in addition to the catalyst, the %PS increased further to 46%. This is the highest value of the pentane solubles obtained so far for any coal studied in our research.

Various other reaction solvents (e.g. mineral oil and 1-methylnaphthalene) were also used in place of tetralin; but their use did not show a significant advantage over tetralin. Figure 2 shows an overall comparison of the various reaction solvents studied. When mineral oil (a non-hydrogen donor) was used in place of tetralin, little difference was obtained between the values for pentane and THF solubles of the coals with or without catalyst. Although the use of 1-methylnaphthalene showed a similar trend as tetralin in the %PS for the coals with or without catalyst, the actual values of the %PS were somewhat lower. The percentage of THF solubles, however, increased from 74% without catalyst to 97% with catalyst. Although dispersed catalyst might be expected to reduce the influence of the reaction solvent, our study indicates that the properties of the solvent remain very significant with a dispersed catalyst.

Blind Canyon coal was used to study the effect of sintering the catalyst by preheating the catalyst alone at 400°C, 200°C, and 100°C before use. Sulfur was added to the catalyst in all liquefaction runs. The results, shown in Figure 3, show that preheating the catalyst lowers its activity presumably by lowering its surface area.

Blind Canyon coal was also used in a catalyst loading study with Fe-3 catalyst. The results, shown in Figure 4, are consistent in showing that coal conversion is increased when the number of catalytic active sites is increased; however, the effect is not great.

Model Compound Studies in TBMR In these experiments, a hydrogenation activity A_H was defined as follows to characterize the extent of hydrogenation reaction:

$$A_H = \frac{2M_T + 5M_D}{5(M_N + M_T + M_D)} \quad \text{or} \quad A_H = \frac{3M_{CHB} + 6M_{DCH}}{6(M_{BPH} + M_{CHB} + M_{DCH})}$$

Where, M_N : moles of naphthalene/gram of liquid product
 M_T : moles of tetralin/gram of liquid product
 M_D : moles of decalin/gram of liquid product
 M_{BPH} : moles of biphenyl/gram of liquid product
 M_{CHB} : moles of cyclohexylbenzene/gram of liquid product
 M_{DCH} : moles of dicyclohexyl/gram of liquid product

Fe-2 catalyst was reduced in hydrogen at 400°C, and Fe-3 catalyst was reduced at different temperatures in advance to examine the activity with naphthalene as reactant. Figure 5 showed that 200-250°C would be a suitable reduction temperature. It is likely that a higher temperature would cause the 30 Å catalyst to be sintered and thus lower the activity. Therefore, a reduction temperature of 200°C for Fe-3 was chosen for the later runs. Figure 6 indicated that, for the naphthalene hydrogenation, both the pre-reduced iron catalysts gave higher activities than their oxide forms, and sulfur almost completely poisoned both catalysts, whether in the oxide or metallic form. Similar results were obtained for the hydrogenation of biphenyl as shown in Figure 7. A notable phenomenon observed was that, in both reaction systems, secondary reactions, e.g., the conversion from tetralin to decalin, took place only when the catalysts had been reduced, even at the highest catalyst loadings. This suggests that the metallic iron is more active for

hydrogenation than iron oxide owing to active sites of greater activity rather than an increase in number of sites.

Model Compound Studies in Continuous Reactor The test results of three trickle bed reaction runs with sulfur in the feed in different periods are shown in Figure 8. It can be seen that when iron oxide was used as catalyst, without sulfur in the feed, the hydrogenation activity of NAPH increased gradually to a relatively stable level. However, once the sulfur was introduced, the A_H dropped continuously to about zero after 32 hrs during this process indicating that the hydrogenation reactions have been inhibited by the presence of CS_2 . The other two runs were performed by adding CS_2 to the feed first and then switching to the CS_2 free feed. The results (Figure 8) showed no reaction at 250°C once there was CS_2 in the feed, and A_H could not be restored. This indicates that H_2S has poisoned the iron catalyst permanently for the hydrogenation reactions and/or that the sulfide form of the iron is much less active than the hydrogen reduced form. After removal of the CS_2 in the feed at 48 and 92 hours, both runs showed very small, but stable A_H as the residual H_2S concentration in the reactor became smaller. This indicates that the FeS_x form of the catalyst has finite, although significantly lower hydrogenation activity than the H_2 reduced form of iron. The inhibition effect of H_2S is consistent with the earlier works by Rhee^[4] with NAPH hydrogenation in batch reactor using Ni-Mo/ Al_2O_3 catalyst and Sapre^[5] with biphenyl hydrogenation in the continuous reactor using Co-Mo/ Al_2O_3 catalyst.

Considering the hydrogenation behavior of NAPH over iron catalysts in both continuous reactor and TBMR, we think there probably exists a corresponding reduction process before the reaction occurs when iron oxide is employed. We suggest that the active phase of iron catalyst in the hydrogenation processes investigated in the absence of sulfur may be metallic iron. We have also reported^[1] that hydrogen reduced iron generally yields higher hydrogenation activity than the iron sulfide which is a much less active hydrogenation catalyst. However, the iron sulfide form may possess a higher cracking activity which may be more beneficial to coal liquefaction.

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Table 1. TBMR Reaction Conditions

Reactant wt. (g)	Coal 3	NAPH 0.24		BPH 0.24
Catalyst wt. (g)	Fe-3 0.66	Fe-2 0.6	Fe-3 0.06	Fe-3 0.06
Solvent wt. (g)	Tetralin etc. 10	Mineral Oil 12	Mineral Oil 12	Hexadecane 12
Sulfur Source wt. (g)	Elementary Sulfur 0.1	CS ₂ 0.24	CS ₂ 0.024	CS ₂ 0.024
Temp. (°C)	400	350	350	300
H₂ Pressure (psi)	1250	1000 (1250)	1000	1000
Time (h)	1	1	1	1

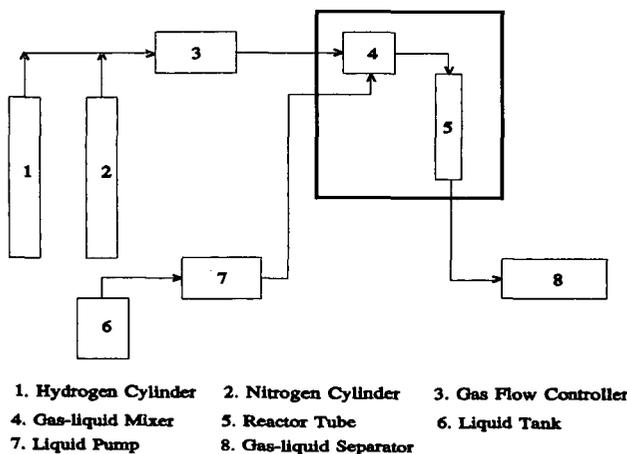


Figure 1. CDS 900 Reactor System

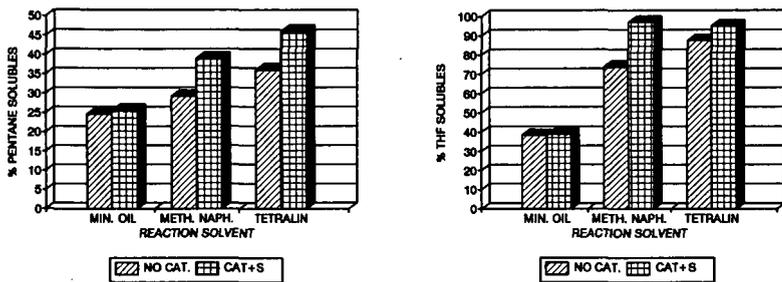


Figure 2. Comparison of Reaction Solvents using Blind Canyon Coal

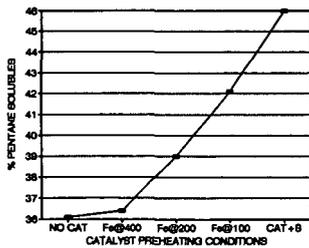


Figure 3. Effect of Preheating the Catalyst at Different Temperatures

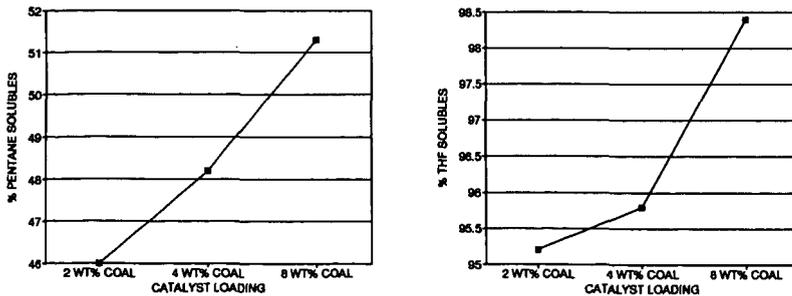


Figure 4. Comparison of Different Loadings of Catalyst

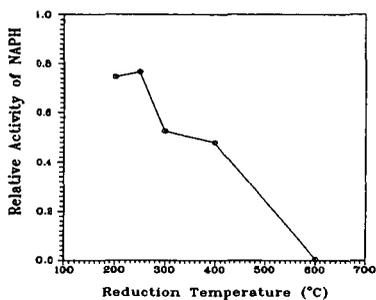


Figure 5. Effect of Reduction of Fe-3 Catalyst at Different Temperatures on NAPH Activity in TBMR

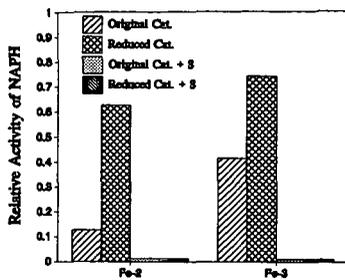


Figure 6. NAPH Hydrogenation Activity at 350 °C in TBMR

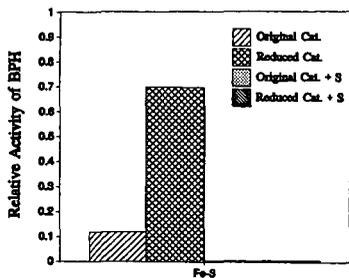


Figure 7. BPH Hydrogenation Activity at 300°C in TBMR

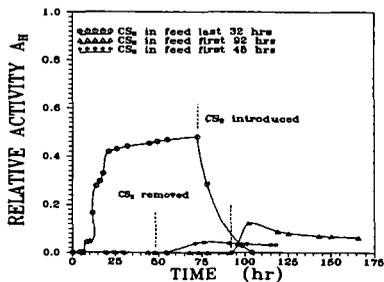


Figure 8. NAPH Hydrogenation Activity at 250°C in Continuous Reactor