

Catalytic Activity of Coal Hydrogenation Catalysts

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INTRODUCTION

Catalytic hydrogenation of coal has been the subject of extensive investigation for many years. Mills has reviewed recent developments in catalyst systems. Molten halide salts have been shown to be effective catalysts for hydrocracking coal and coal extracts². Zinc chloride and stannous chloride have been found to be effective catalysts for the hydrogenation of coal in a short-residence-time reactor³. This study is part of an investigation of the catalytic processes in coal hydrogenation. A previous paper was concerned with the thermal behavior of coal-catalyst systems⁴. The acidity of hydrogenation catalysts and their catalytic activity for simple reactions are discussed.

EXPERIMENTAL

The acid strength of the catalysts was determined with amine bases. A 0.2 g sample was placed in a test tube with 4.0 ml of a solution containing 0.1 mg of indicator in benzene. The mixture was agitated briefly and color changes were noted. The benzene was distilled over metallic sodium to remove water and the solid catalysts were heated to 150°C for 5 to 6 hours prior to the experiments. Experiments were performed at room temperature.

Surface acidities were determined by back titration of n-butyl amine with hydrochloric acid⁵. About 5 g of sample was added to 25 ml of 0.0963 M solution of n-butylamine in benzene. The suspension was stirred vigorously for 3 hours and filtered to remove the solid catalyst. The amine solution was titrated with aqueous hydrochloric acid using phenolphthalein indicator. The acidity of the sample was calculated from the decrease in the n-butylamine concentration. All samples except $\text{SmCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were heated at 150°C for 6 hours prior to the experiment.

The polymerization of propylene was studied in a 90 ml reaction vessel. About 1.5 - 2.0 g of catalyst was evacuated to 10^{-6} torr in the vessel and heated to 200°C for 3 hours. Propylene was introduced at 400 torr and the temperature was held at 150°C. Changes in pressure were noted. The propylene was purified by alternate condensation and vaporization, with evacuation following condensation.

The isomerization of n-butenes was studied in the system shown in Figure 1. A large vessel was used to eliminate diffusion effects. About 1.5 g of catalyst was evacuated at 150°C for 3 hours. A sample of n-butene or trans-2-butene was introduced to the vessel at a pressure of 300 torr. The reaction was carried out at 100-150°C with periodic sampling of the gas. Gas samples were analyzed by chromatography at room temperature using a 15 ft. column of propylene carbonate on activated alumina and a thermal conductivity detector.

The hydrogenation of ethylene was studied in the apparatus shown in Figure 1. The catalyst was introduced into the vessel and evacuated and heated. A known mixture of hydrogen and ethylene was introduced and the reaction was followed at 130-140°C by periodic sampling and analysis by gas chromatography in the system previously described. A typical composition would be an initial hydrogen pressure of 40 torr and an ethylene pressure of 19 torr.

Reagent grade chemicals were used as catalysis. In some cases, the catalysts were impregnated on Hiawatha, Utah coal (4% V.M., daf basis) from aqueous solution.

RESULTS AND DISCUSSION

The acid strength of various halide catalysts are shown in Table I along with a silica-alumina catalysts (Houdry, 13% Al₂O₃). Zinc chloride shows a slightly higher acid strength with a maximum pKa of 1.5. The other halide catalysts show a maximum pKa of 3.3. The acid strength of the halide catalysts is much less than that of the silica-alumina catalyst. The surface acidities are shown in Table II. The acidities of the halide catalysts are greater than the silica-alumina catalyst. Impregnation of the catalyst on coal decreases the acidity significantly.

Table I
Acid Strength of Catalysts

PKa	Phenylazo Naphthylamine 4.0	Dimethyl Yellow 3.3	Benzeneazo Diphenylamine 1.5	Dicinnamal Acetone -3.0	Anthraqui- none -8.2
Wt. % H ₂ SO ₄ of corresponding acid strength	5X10 ⁻⁵	3X10 ⁻⁴	0.02	48	90
Color Change					
ZnCl ₂	Yes	Yes	Yes	No	No
ZnBr ₂	Yes	Yes	No	No	No
ZnI ₂	Yes	Yes	No	No	No
SnCl ₂ ·2H ₂ O	Yes	Yes	No	No	No
FeCl ₃ ·6H ₂ O	Yes	Yes	No	No	No
SiO ₂ ·Al ₂ O ₃	Yes	Yes	Yes	Yes	Yes

Table II
Surface Acidity of Catalysts
Decrease in n-butylamine
concentration, M moles/l

Catalyst	Acidity, M moles/g
ZnCl ₂	0.0907
ZnBr ₂	0.0739
ZnI ₂	0.0590
SnCl ₂ ·2H ₂ O	0.0844
FeCl ₃ ·6H ₂ O	0.0847
SiO ₂ ·Al ₂ O ₃	0.0216
ZnCl ₂ /coal (12.3%)	0.0545
ZnI ₂ /coal (12.4%)	0.0398
SnCl ₂ /coal (12.2%)	0.0313

The catalytic activity of ZnCl₂, ZnBr₂, and ZnI₂ was determined for the polymerization of propylene. This reaction is catalyzed by Bronsted acids. The catalysts show no activity for this reaction. It is concluded that the halides whose Bronsted acidity is very weak, if present at all, are not responsible for carbonium ion reactions. Bronsted and Lewis acids may catalyze the isomerization of butenes. Zinc chloride and bromide show very little activity for the isomerization of 1-butene or trans-2-butene under the conditions of these experiments. The activity was much less than that of other solid acids such as silica-alumina and BF₃ treated alumina⁷. Zinc chloride and bromide also show no activity for the hydrogenation of ethylene although other solid acids show considerable activity at lower temperatures than those employed in these studies⁸⁻¹⁰.

The metal halide catalysts used in these studies, with the exception of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, show strong catalytic activity for the hydrogenation of coal at short reaction times^{3c}. They all show high acidity, but much lower acid strength than silica-alumina cracking catalysts. They show little activity for the acid-catalyzed reactions of this study. Temperature would be expected to be an important factor. In these experiments, the catalysts were in the solid form. In coal hydrogenation reactions, the temperature is about 500°C and the catalysts are molten.

REFERENCES

1. Mills, G. A., *Ind. Eng. Chem.*, 61, No. 7, 6 (1969).
2. Zielke, C. W., Struck, R. T., Evans, J.M., Constanza, C.P., and Gorin, E., *Ind. Eng. Chem., Process Des. Develop.*, 5, 151, 158 (1966).
3. Wood, R. E., and Hill, G. R., *Preprints Division Fuel Chem., Am. Chem. Soc.*, 17, No. 1, 28 (1972).
4. Bodily, D. M., Lee, H., and Hill, G. R., *Preprints Division Fuel Chem., Am. Chem. Soc.*, 16, No. 2, 124 (1972).
5. Shibata, K., Kiyoura, T., and Tanabe, K., *J. Res. Inst. Catalysis, Hokkaido Univ.*, 18, 189 (1970).
6. Mitsutani, A., "Catalytic Engineering," Vol. 10, *Catalysis Society of Japan*, Ed., Chijinshokan and Co., Tokyo, 1967, p. 108.
7. Matsuura, K., Suzuki, A., and Itoh, M., *J. Catal.*, 23, 395 (1971).
8. Dent, A. L., and Kokes, R. J., *J. Phys. Chem.*, 73, 3772, 3781 (1969).
9. Tanaka, K., and Blyholder, G., *J. Phys. Chem.*, 1393 (1972).
10. Harrison, D. L., Nichollas, D., and Steiner, H., *J. Catal.*, 7, 359 (1967).

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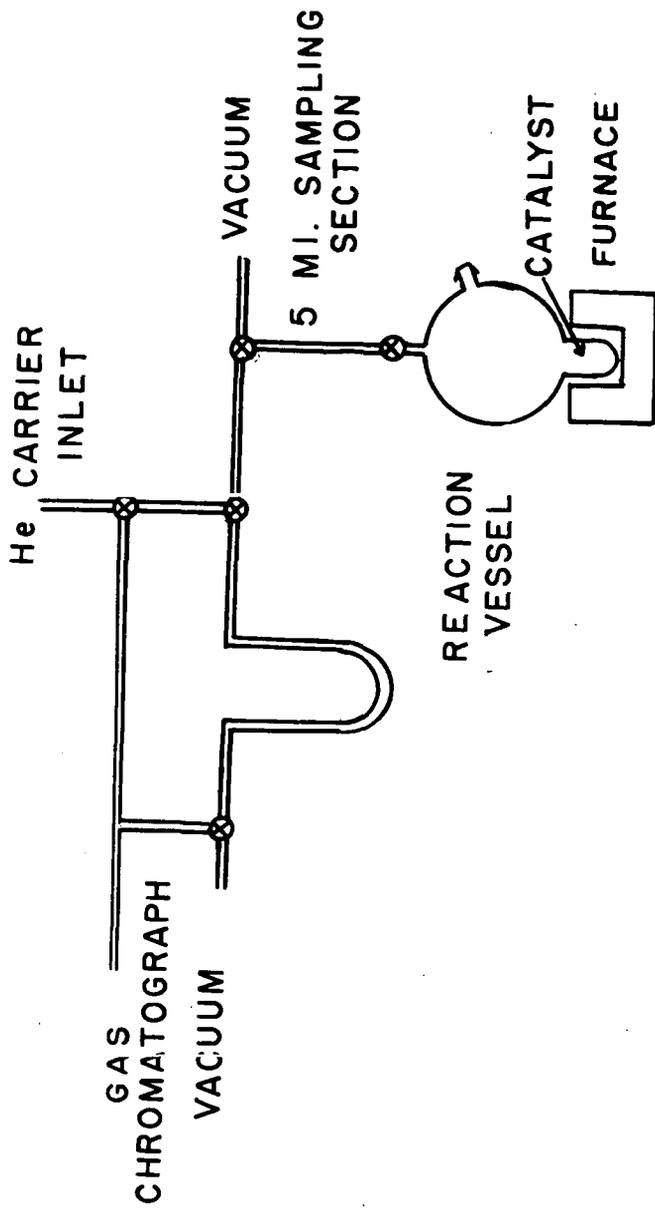


FIGURE 1
REACTION SYSTEM