

Cobalt Stearate-Aluminum Alkyl Catalyzed Hydrogenation of Illinois  
no. 6 High Volatile Bituminous Coal and Model Compounds

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INTRODUCTION

In a previous study, some preliminary results (1) showed that a particular cobalt stearate-aluminum alkyl ( $\text{Co}(\text{stearate})_2\text{Et}_3\text{Al}$ ), [I], homogeneous transition metal complex related to Ziegler catalysts was a very effective hydrogenation promoter under mild temperature conditions ( $50\text{-}100^\circ\text{C}$ ) and hydrogen pressures of from 500-1000 psi. Initial results indicated significant yields of gasoline-light oil products from solvent refined coal at  $90^\circ\text{C}$  and hydrogen pressures of 700 psi. Ziegler catalysts are not often used for hydrogenation and are rarely employed for coal hydrocracking. However since they have been shown to hydrogenate olefins (2) and aromatic compounds and are Lewis acids, it seems possible to use them in some instances as hydrocracking catalysts. Besides our earlier findings for [I], Dinh et al. (3) have also described selective hydrogenation of naphthalene by Ziegler type catalysts consisting of metal stearates, acetylacetonates and aluminum alkyls. For example hydrogenation of naphthalene using a nickel stearate -  $\text{AlEt}_3$  catalyst (5:20 mole equivalent ratio of  $\text{Ni}/\text{Et}_3\text{Al}$ ) yielded 93% tetralin at 150°C and 44 psi, while the use of cobalt acetylacetonate -  $\text{AlEt}_3$  (5:25) yielded 99% tetralin at 150°C and 145 psi in an eight hour reaction period. Other Ziegler hydrogenation catalysts have been reported to promote the hydrogenation of aromatic compounds but under more drastic conditions. The complexes of triethylaluminum with  $\text{Co}(2\text{-ethylhexanoate})_2$  and  $\text{Ni}(2\text{-ethylhexanoate})_2$  have been used to produce 100% conversion (2) of naphthalene [II] to decalin and tetralin at  $210^\circ\text{C}$  and 1000 psi. Both catalysts have also been used with benzene, a particularly difficult compound to hydrogenate (2, 4).

Studies (2, 4-5) have shown that the reactivity of the catalyst varies with the transition metal and anionic ligand in the order  $\text{Ni} > \text{Co} > \text{Fe} > \text{Cr} > \text{Cu}$  and  $2\text{-ethylhexanoate} > \text{benzoate} > \text{acetoacetate} > \text{acetate} > \text{chloride}$  respectively. This roughly follows the order of solubility of the transition metal salts in the hydrocarbon solvents used in the reactions.

Since most of the aromatic structures studied consisted of one, two and three ring units, the Ziegler catalysts used as hydrogenation catalysts should successfully add hydrogen to the aromatic rings in coal. Significantly, aromatic compounds such as naphthalene [II] and polynuclear nitrogen heteroaromatic compounds such as quinoline [III] are found to occur in coal and oil shale. The selective hydrogenation of these materials to form additional useful compounds i.e., naphthalene [II] to form 1,2,3,4-tetrahydronaphthalene [IV] would provide an alternate use of a rather abundant natural resource. Recently, it has been reported (6) that quinolines and isoquinoline can be selectively hydrogenated in the nitrogen-containing ring to form 1,2,3,4-tetrahydroquinoline [V] and N-formyl-1,2,3,4-tetrahydro-

isoquinoline by means of a carbon monoxide and water mixture in the presence of a catalytic amount of rhodium carbonyl cluster at 150°C, 800 psi hydrogen and with stirring for 24 hr. We wish to report that similar hydrogenation of naphthalene [II], quinoline [III], 2-methylquinoline, and isoquinoline can be carried out using catalyst [I] under somewhat milder conditions but no hydrogenation occurs for nitro- or chloro substituted quinolines. We will also discuss the results of using catalyst [I] to hydrogenate Illinois no. 6 coal from the premium coal sample program.

#### EXPERIMENTAL

The catalyst system [I] for the hydrogenation of the model compounds, was prepared by the addition of 2.2 mmol of triethylaluminum in a dry N<sub>2</sub> atmosphere to a suspension of 1.9 mmole cobalt stearate in hexane. The black catalyst mixture was transferred under dry N<sub>2</sub> to a bomb reactor and 31 mmol of substrate was added. The reactor was pressurized to the desired pressure and heated to the value given in Tables I and II. The products were

Table I. Hydrogenation of naphthalene (II) with the Co(stearate)<sub>2</sub>-Et<sub>3</sub>Al Catalyst

Time/h	Conditions		Tetrahydro-naphthalene (IV)	% Yield*	
	Temp °C	Pressure Psi		Cis-Decalin	Trans-Decalin
16	90	700	95	-	-
7	90	700	95	3	1
16	90	300	5	-	-
16	22	700	94	3	1
16	45	700	90	6	2

\*based on GC analysis.

Table II. Hydrogenation of nitrogen heteroaromatic by Co(stearate)<sub>2</sub>-Et<sub>3</sub>Al Catalyst.

Substrate	Conditions*		% Yield		
	Temp	A	B	C	
quinoline (III)	90	66	21	0	
	RT	73	--	27	
isoquinoline	90	70	--	--	
	RT	--	--	100	
2-methylquinoline	90	76	--	--	
	RT	44	--	52	
8-nitro-2-methylquinoline	90	--	--	100	
4-chloro-2-methylquinoline	90	--	--	100	
5-nitroquinoline	90	--	--	100	

A) 1,2,3,4-tetrahydro product.  
 B) 5,6,7,8-tetrahydro product.  
 C) remaining starting material.

\*all reactions were carried out at 700 psi pressure for 16 hrs.

purified by either distillation under reduced pressure or by running the crude products through a silica gel column (chloroform). NMR spectra of the products were recorded on a 60 MHz Varian EM 360L spectrometer. Gas chromatography analyses of products were performed on a Hewlett-Packard 5790 A Series chromatograph using ultra cross-linked methyl Silicon gum column (25 m x 0.2 mm x 0.33  $\mu$ m film thickness).

The hexane solvent was stored and distilled from Na/benzophenone. Naphthalene was used as purchased, however quinolines were dried over  $MgSO_4$ , filtered, and vacuum distilled. All reactions were carried out in a 150 cm<sup>3</sup> capacity stainless steel high pressure bomb reactor that could be varied in temperature. The preparation of the catalyst, the assembly of the bomb reactor, and the preparation of the reactants were all carried out under nitrogen in a dry box. The yield of hydrogenated product from naphthalene and quinolines is given in Table I and II for some typical runs.

Hydrogenation of Illinois no. 6 premium coal was also carried out using catalyst [I]. In a typical experiment, 5 g. of coal was added to the catalyst, prepared as described before, in hexane (35 cm<sup>3</sup>) in a bomb reactor. The bomb reactor was heated at 90°C under hydrogen pressure of 800 psi and shaken for 24 hrs. The bomb reactor was cooled to room temperature and gas samples collected for analysis. Mass spectrometer-GC analysis of the gaseous products was carried out on a Hewlett Packard 5890 GC/MS system using a J&W DBS thick film column (5  $\mu$ m) (12 m x 0.32 mm I.D.). The bomb reactor was then depressurized and a sample of the crude product was filtered through cotton wool or Celite. NMR analysis of the filtrate was carried out in hexane or after removal of hexane.

## RESULTS AND DISCUSSION

### A. Model Compounds

The NMR spectrum for the hydrogenation of II was in agreement with the spectrum previously recorded for IV. GC analysis of the crude products in Table I shows that naphthalene was hydrogenated selectively at room temperature and at 90°C with only negligible amount of decalin produced. It is important to note that if the hydrogen pressure is dropped to 300 psi from 700 psi, only a 5% yield of IV occurs, with the other 95% being the starting material. Reducing the temperature from 90°C to room temperature (22°C) does not significantly change the 95% yield of IV. Thus the value of the hydrogen pressure is critical to the hydrogenation of II. Lowering the temperature and changing the length of the reaction has almost no effect on the hydrogenation yield. From Table II, it is seen that III is hydrogenated selectively at room temperature to give 73% yield of V and 27% of III remained intact. However, when the temperature is raised to 90°C, MS/GC analysis revealed 66% yield of V along with 21% yield of 5,6,7,8-tetrahydronaphthalene with no sign of the starting material. 2-Methylquinoline was also hydrogenated to 2-methyl-1,2,3,4-tetrahydroquinoline at room temperature and 90°C with 45 and 76% yield respectively. Isoquinoline on the other hand, can only be hydrogenated at 90°C to 1,2,3,4-tetrahydroisoquinoline (70%); at room temperature no hydrogenation took place and the starting material was recovered completely. Hydrogenation of isoquinoline under water-gas

shift condition (6) produced N-formyl-1,2,3,4-tetrahydroisoquinoline whereas under our catalytic conditions, 1,2,3,4-tetrahydroisoquinoline can be prepared in good yield.

Catalyst [I] failed to hydrogenate compounds such as 5-nitroquinoline, 8-nitro-2-methylquinoline, and 4-chloro-2-methylquinoline. In each case the starting material was recovered. It is thought that functional groups such as nitro and chlorine interact with the aluminum alkyl, a Lewis base, and deactivate the catalyst. It has been reported that nitrobenzene and p-nitrophenol could not be hydrogenated in the presence of a catalyst system made of  $\text{Ni}(\text{2-ethylhexanoate})_2\text{-AlEt}_3$  whereas benzene was successfully hydrogenated to cyclohexane at 150-190°C (2).

#### B. Hydrogenation of Illinois no.6 premium coal

The successful results obtained from hydrogenation of the model compounds suggested the possibility of hydrogenating coal under almost similar conditions. Comparison of the NMR spectrum of the coal hydrogenation product with that of a control experiment (heating the same sample of coal in hexane under similar conditions but in the absence of the catalyst), revealed that more signals appeared in the aliphatic region (3.5-1 ppm) when hydrogenation was carried out in the presence of the catalyst, indicating that some aromatic material was converted to saturated products. However, due to the small quantity of the coal sample, it has been difficult to identify the liquefied mixture. Mass spectrum-GC analysis of the gaseous products on the other hand, showed that methane, ethane, propane, cyclohexane, methylpentane and butane, and a few fragments assigned to unsaturated material had been produced. We regard this attempt at this stage, as a primary study and are planning further investigations under different conditions and more suitable media for coal liquefaction.

#### SUMMARY

Naphthalene (II), quinoline (III), isoquinoline and 2-methylquinoline can be hydrogenated selectively to form 1,2,3,4-tetrahydronaphthalene (IV) (94% yield) at room temperature, 1,2,3,4-tetrahydroquinoline (V) (73% yield at 22°C), 1,2,3,4-tetrahydroisoquinoline (70% yield at 90°C), and 2-methyl-1,2,3,4-tetrahydroquinoline (76% at 90°C) by use of the Ziegler catalyst  $\text{Co}(\text{stearate})_2\text{-AlEt}_3$  in a hexane solvent at a hydrogen pressure of 700 psi. Hydrogenation of Illinois no. 6 coal using catalyst [I] has produced a liquefied product and identifiable gaseous components.

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