

CATALYSTS FOR AQUEOUS/CO LIQUEFACTION OF SUBBITUMINOUS COAL

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ABSTRACT

Coal liquefaction has been effectively carried out with carbon monoxide reductant in an aqueous solvent (CO steam process). Australian workers demonstrated that sodium aluminate is able to catalyze the conversion of Australian coals in the CO/H₂O system and in water/hydrogen donor solvent mixtures. To demonstrate an economical process for liquefaction of Wyodak subbituminous coal, aqueous sodium aluminate has been utilized as the catalyst. High conversions comparable with those obtained with hydrogen donor solvents and hydrogen sulfide were obtained. The product consists of a large distillate fraction composed of oxygenated compounds and many aromatics. The asphaltene and oil fractions are suitable for second-stage catalytic hydrogenation. Reactions utilizing hydrogen as the reductant gave low conversions with sodium aluminate. The nature of the reductive reactions catalyzed by the sodium aluminate in aqueous/carbon monoxide systems are currently being investigated with various model compounds.

INTRODUCTION

The goal of the UNDEERC coal science group is the development of new homogeneous catalysts for first-stage coal liquefaction. These catalysts are expected to aid in solubilization and preliminary reduction of low-rank coals to a high quality intermediate product that can be easily converted to distillate fuels with low heteroatom content.

Catalysis of the first stage of coal liquefaction involves improving the rates of bond cleavage reactions leading to improved solubility and of preliminary reduction reactions so that oils and asphaltene are produced without extensive retrogressive reactions. These materials should be able to interact effectively with the solid and colloidal coal matter, catalyzing the conversion to soluble oils at moderate temperature, while minimizing problems with low surface areas or mass transfer. Thus various inorganic agents that are soluble in the reaction vehicle or solvent are being investigated. Some of these (e.g., sodium aluminate) are polymeric at the reaction conditions and are precursors for the clays and zeolites that are currently under investigation as second-stage liquefaction catalysts.

EXPERIMENTAL

Catalytic Liquefaction of Coal

A slurry consisting of 5.0 g of coal (as received Wyodak-Clovis Point) and a solution of the desired catalyst in 20 g solvent (water) was placed in a 70-ml

Parr reactor. The reactor was evacuated and charged with a mixture of 1000 psi of desired gas. The reactor was heated to 400°C in a rocking autoclave (initial heatup time = 11 minutes) and left at this temperature for 30 minutes. At the end of the reaction, the reactor was cooled to room temperature, and the gases were removed. The reactor was attached to a set of two traps cooled in ice and liquid nitrogen. The product slurry was distilled to remove water. The distillate was saturated with NaCl and extracted with ether. The extract was mixed with appropriate internal standard and analyzed by GC and GC/FTIR/MS.

The residue was extracted with pentane, toluene, and tetrahydrofuran (THF). The pentane-soluble fraction was mixed with appropriate internal standard and analyzed by GC. The toluene-soluble, THF-soluble, and THF-insoluble fractions were dried in vacuo at 110°C overnight and weighed. The percent conversion was calculated on the basis of the coal (maf) that did not appear in the THF-insoluble fraction. The conversion and yield data are given in Table 1.

Catalytic Hydrotreating of Model Compounds

In a typical run, 0.5 g of model compound, 2 g of solvent (water), and the desired amount of catalyst (if needed) were placed in a tubing bomb (12-mL microreactor). The microreactor was evacuated, pressurized with 1000 psig of carbon monoxide, placed in a rocking autoclave, and heated to 400°C. At the end of the specified reaction period, the microreactor was cooled in a dry ice-acetone slurry, degassed, and opened. The resulting slurry was acidified with dilute HCl. The desired amount of the internal standard was added to the product slurry, and the product slurry was extracted with methylene chloride. The methylene chloride extract was dried over molecular sieves (4Å) and analyzed by GC/FID and GC/FTIR/MS.

Instrumentation

Quantitative GC/FID analyses were performed with a Hewlett Packard 5880A gas chromatograph equipped with a Petrocol capillary column. A mixture of iso-octane and n-octadecane was the internal standard. GC/FTIR/MS was performed on a Finnigan 800 ITD ion trap detector with a HP 5890A gas chromatograph and a J&W 30-m x 0.32-mm (ID), 1.0-micron film of DB-5. A 15-m x 0.25-mm (ID), 0.25-micron DB-5 film capillary column was used for the analysis of high boiling components.

RESULTS AND DISCUSSION

In the first part of our study of homogeneous catalysts for first-stage coal liquefaction, catalysts for improving the conversion and product quality of liquefactions carried out in aqueous systems were investigated. Aqueous reactions that utilize carbon monoxide as the reductant gas have been extensively investigated in this and other laboratories over many years (1-3). Basic catalysts have been employed to achieve higher conversions. The aqueous/CO reduction has been shown to be superior to hydrogen for the first stage of liquefaction.

Little is understood about the mechanism of the aqueous/CO reaction with coal or even with model organic compounds. Jones and others have shown that an aryl ketone (benzophenone) and an aryl carbinol are reduced (4). Bases were required for reduction of the ketone, and higher conversions were obtained for the carbinol reduction in the presence of base. Reduction of anthracene and quinoline were also effected with aqueous CO; however, higher conversions of

anthracene were obtained in the absence of base (5). The reduction of ketones with CO in aqueous sodium carbonate can be explained by sodium ion activation of the CO to give an intermediate such as formate that can donate hydride to the carbonyl. Reduction of anthracene or other hydrocarbons would appear to proceed by a different mechanism.

In screening a number of candidates for improving the conversion in aqueous/CO liquefaction processing, Jackson and others (6,7) found that aqueous sodium aluminate gave good conversions of brown coal to oils at temperatures of 350° to 400°C. Factors such as pH and concentration in aqueous systems of the materials are critical in determining the actual aluminate structures present; however, Jackson did not report the pH of his system. Being amphoteric, the polymeric aluminate form may have Lewis acid sites at moderate pH values of 8-12 that would be effective in cleavage of covalent bonds in coals. Whether the sodium aluminate is able to activate the carbon monoxide so as to produce a hydride- or hydrogen-donating intermediate or some other form of activated hydrogen is still not certain.

The first priority in our work was to verify that sodium aluminate is also effective in improving the aqueous-CO liquefaction of low-rank western U.S. coals and to measure the solubilities and product qualities of the reaction products from these U.S. coals. Since high conversions to THF solubles are easily obtained at 400°C without any promoter or catalyst with the low-rank coals, the conversion to oils, asphaltenes, and distillate needs to be accurately determined. The composition of the distillate, oil, and asphaltene product obtained after first-stage liquefaction in aqueous CO must be determined for comparison with that obtained in organic solvents with CO or with hydrogen. Previous studies have indicated that the volatile first-stage product from aqueous liquefaction should contain large amounts of phenolics rather than hydrocarbons, as for organic solvent liquefaction. If this is the case, the distillate can be removed and used elsewhere, so that hydrogen is not wasted in deoxygenation of phenols.

The conversion of Wyodak subbituminous coal to THF solubles in the aqueous/CO liquefaction with sodium aluminate was 89% (Table 1). This was substantially higher than that obtained with no added sodium aluminate (78%). The high conversion with sodium aluminate is consistent with that observed by Jackson and others for Australian brown coals (6,7). Conversion in an aqueous/CO liquefaction experiment with sodium hydroxide catalyst was actually much lower than expected on the basis of previously reported work. Under the same conditions as the sodium aluminate experiments, only 72% of the Wyodak coal was converted to THF solubles with sodium hydroxide catalyst. After stirring the sodium aluminate and sodium hydroxide solutions with the coal at room temperature, the pH of the reactions was measured, and both reactions were at a pH of 11. At the end of the reactions, the pHs of the aqueous portions of the products were between 6 and 7 as a result of carbon dioxide generation during the liquefaction from decarboxylation and water-gas shift reactions. It is likely that the sodium aluminate is polymeric during the reaction, but further information is needed to understand the nature of the aluminate catalyst under these conditions.

The liquefaction product quality as determined by the distribution of solubility fractions was good for the sodium aluminate-catalyzed reaction. As shown in Table 1, the toluene solubles amounted to 20% of the maf coal, and 42% of the coal was converted pentane solubles, CO₂, and H₂O. The major products in the distillate were oxygenated compounds, such as methanol, 2-propanol (from

acetone), and phenolics. In addition, there were hundreds of hydrocarbon components that are typically found in coal-derived products. A similar distribution was obtained for the NaOH-catalyzed reaction, but the amounts in each of the fractions were much lower.

Reactions were conducted to verify that carbon monoxide was the most effective gas for the liquefaction of Wyodak under the mildly basic conditions. Hydrogen (1000 psi at room temperature) gave only a 43% conversion to THF solubles. Since nitrogen (1000 psi) gave a similar conversion (41%) and a similar product solubility distribution, it is unlikely that hydrogen had any effect at all in the liquefaction and was not activated by the sodium aluminate.

The second priority in our program was to understand something about the nature of the sodium aluminate catalysis. Sodium aluminate could probably activate CO for hydride reduction as well as sodium carbonate, perhaps better. But does it also activate CO so that hydrogenation of hydrocarbons occurs? Can it lower activation energies for cleavage of bonds such as in ether and carboxylate groups? The reactions of several model compounds were investigated in aqueous/CO conditions, and the results were compared with those obtained in the absence of the sodium aluminate.

Anthracene was heated in water at 400°C (2 hr) with 1000 psi of carbon monoxide (measured at room temperature). In the reaction with no promotor, a 79% conversion of the anthracene was observed (Table 2). The main reaction product was 9,10-dihydroanthracene, with 1,2,3,4-tetrahydroanthracene being a minor product. When sodium aluminate (1.25 mmole/g of substrate) was added, the conversion of anthracene increased to 82%. An anthracene reaction carried out with an equivalent amount of sodium hydroxide gave a lower conversion (64%). The lower anthracene conversion with sodium hydroxide is consistent with the lower conversion Stenberg and others reported for reactions of anthracene carried out with added sodium carbonate (5). Stenberg's results were obtained at more severe conditions (425°C, 1500 psi CO at room temperature), and the main product was tetrahydroanthracene, rather than dihydroanthracene. Dihydroanthracene may be an intermediate in the formation of tetrahydroanthracene, and more transformation of the initial dihydroanthracene may occur at the higher temperature. The sodium aluminate can, therefore, promote the reaction of carbon monoxide with polynuclear aromatic hydrocarbons somewhat better than water in a process that is retarded by the presence of other basic compounds and, in addition, can catalyze the reaction of carbon monoxide in the reduction of carbonyl groups in a process that is catalyzed by sodium carbonate or hydroxide.

Substituted naphthalenes were not significantly reduced by CO with the sodium aluminate promotor under the same conditions used for anthracene. Sodium 1-naphthoate was converted to naphthalene with complete decarboxylation and only 2% reduction to tetralin and to 1-methylnaphthalene. Sodium 1-naphtholate and 1-naphthol were recovered mostly unreacted, with 3% reduction to naphthalene and to tetralin. Increasing the amount of sodium aluminate tenfold in the naphthol reduction resulted in only a slight increase in the yield of tetralin.

Further work on the mechanisms and nature of the intermediates involved in these reactions is in progress.

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REFERENCES

1. Appell, H.R.; Wender, I.; Miller, R.D. Prep. Pap.--Am. Chem. Soc., Div. of Fuel Chem. 1969, 13, 39-44.
2. Sondreal, E.A.; Knudson, C.L.; Schiller, J.E.; May, T.H. Proc. 9th Biennial Lignite Symp.: DOE/GFERC/IC-77/1, 1977, 129-158.
3. Ross, D.S.; Green, R.K.; Monsani, R.; Hum, G.P. Energy Fuels 1987, 1, 287.
4. Jones, D.; Baltisberger, R.J.; Klabunde, K.J.; Woolsey, N.F.; Stenberg, V.I. J. Org. Chem. 1978, 43, 175-177.
5. Stenberg, V.I.; Wang, J.; Baltisberger, R.J.; Van Buren, R.; Woolsey, N.F. J. Org. Chem. 1978, 43, 2991-2994.
6. Jackson, W.R.; Lim, S.C.; Stray, G.J.; Larkins, F.P. Proc. 1989 Internat. Conf. on Coal Sci.; Tokyo, Dec. 1989, Vol. II, pp 815-818.
7. Hughes, C.P.; Sridhar, T.; Chuan, L.S.; Redlich, P.J.; Jackson, W.R.; Larkins, F.P. USA/Australia Workshop on Use of Low-Rank Coals; Billings, MT, May 1991.

Table 1 Catalytic Liquefaction of Wyodak Coal

Reaction Temp. = 400°C, Reaction Time = 30 min Coal (as rec.) = 5.0 g, Reductant gas = 1000 psi (at room temp.)					
Catalyst (mmol/g coal)	Reductant	Conv. (%)*	Products (%)		
			Tol.-S	THF-S	Pent.-S#
NaAlO ₂ (0.5)	CO	89	20	27	42
NaOH (0.5)	CO	72	16	22	34
None	CO	78	n	44	34
NaAlO ₂ (0.5)	N ₂	41	n	18	23
NaAlO ₂ (0.5)	H ₂	43	n	17	25

* = Conversions are based upon the amount of initial coal (maf).

= Pentane solubles are by difference, also includes the products extracted by ether from the distillate.

n = Not determined.

Table 2 Reactions of Anthracene

Reaction Temperature = 400°C, Reaction Time = 2 hours Solvent (Water) = 2 g, CO = 1000 psig			
Catalyst (mmol/g substr)	Substr. (mmol)	Conv. (%)	Major Products (mmol)
None	2.77	79	9,10-Dihydroanthracene (2.02) Tetrahydroanthracene (0.11)
NaAlO ₂ (1.25)	2.81	82	9,10-Dihydroanthracene (2.19) Tetrahydroanthracene (0.13)
NaOH (1.25)	2.79	64	9,10-Dihydroanthracene (1.70) Tetrahydroanthracene (0.10)