

SODIUM METALCARBONYLATES AS POTENTIAL CATALYSTS FOR COAL LIQUEFACTION INVOLVING CO/H₂O OR H₂

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INTRODUCTION

Alkalis such as NaAlO₂ and NaOH catalyze CO/H₂O/coal reactions at 350-400 °C [1-5]. Nickel, molybdenum, and cobalt are effective hydrogenation catalysts above 350 °C [6-13]. Previous work has shown that when using 1,2,3,4-tetrahydroquinoline (THQ) [14-15] and molybdenum sulfide catalyst, individually or together, relatively high conversions can be obtained [16]; by synthesizing a catalyst with THQ and molybdenum sulfide, a synergism was noted with a slight increase in conversion for a subbituminous coal [16]. A combination of transition metals and alkali catalysts, added as separate species to the coal, gives higher conversions than metal or alkali catalysts alone for no-solvent CO/H₂O and CO/H₂/H₂O reactions [17-18], particularly for lower-rank Australian coals. We have synthesized catalyst precursors containing sodium and metal carbonylates to determine in the preliminary stages if the combined precursor would increase coal conversion compared to coal reactions without catalyst and other catalyst systems.

EXPERIMENTAL

Elemental analyses of the two coals used are listed in Table 1. The particle size of both coals are -60 mesh (-250 μm). Loy Yang ROM (run of mine) (LYROM) was obtained from the Loy Yang open cut in Australia, and Surat Basin (SSB) was obtained from the Surat Basin deposit in Australia.

Three methods were used to prepare the sodium metal carbonylates. The first method was used to prepare NaHFe(CO)₄ from Fe(CO)₅ and NaOH [19]. The reaction is such that all the Fe(CO)₅ is consumed and NaOH is in excess. For the preparation, 0.48 g of NaOH dissolved in 50 mL of deoxygenated water was added to an evacuated flask containing 0.75 g of Fe(CO)₅. The reactants were stirred for 24 h under argon. The compound of interest (NaHFe(CO)₅) was not isolated and the resulting aqueous mixture was loaded directly onto 10g of coal, stirred under vacuum for 1h, and the water evaporated under vacuum [17-18].

A similar method was used to prepare NaCo(CO)₄ [20] from Co₂(CO)₈ and NaOH (again in excess). For the preparation, 0.53 g of NaOH dissolved in 50 mL of deoxygenated water was added to an evacuated flask containing 0.60 g of Co₂(CO)₈. The reactants were stirred for 24 h under argon. The compound of interest (NaCo(CO)₄) was not isolated and the resulting aqueous mixture was loaded directly onto 10g of coal, stirred under vacuum for 1h, and the water evaporated under vacuum [17-18]. Since the catalyst of interest was not isolated, we refer to these mixtures as "catalyst mixtures."

A third method was used to prepare NaCo(CO)₄ not contaminated with NaOH [21-22]. (Increased coal conversions were noticed with the catalyst mixtures (Table 2), but it was not certain whether the increases were due to the carbonylate or to the excess NaOH in the catalyst mixture.) In this method, dry NaOH (1.8 g, excess) and Co₂(CO)₈ (1.6 g) were added to a flask in the absence of air. Dry tetrahydrofuran (THF) was added very slowly as the reactants can ebullate violently if THF is added quickly. The mixture was stirred for 2 h until a notable color change from deep orange to a pinkish-lavender occurred. The solid was filtered out, and the THF removed by vacuum distillation from the filtered solution. The NaCo(CO)₄ is not air-stable, so it was prepared under vacuum or argon then solubilized in deoxygenated water in a glove bag before being exposed to the air and loaded onto the coal. The coal/catalyst was stirred under vacuum for 1h, and the water evaporated under vacuum.

Several other catalyst precursors were used as comparisons to the precursors synthesized. The following reagent grade chemicals, all added from aqueous solution [17-18], were used as catalyst precursors: the alkalis sodium aluminate and sodium hydroxide (500 mmol Na/kg dry coal); cobalt (II) acetate and iron (II) acetate (300 mmol metal/kg dry coal); and combined ammonium heptamolybdate (100 mmol Mo/kg dry coal)/nickel (II) or cobalt (II) acetate (40 mmol /kg dry coal). The coal/catalyst was stirred under vacuum for 1h, and the water evaporated under vacuum. When combining the alkalis with the metal catalysts, the alkali was added after the metals unless otherwise noted (it was later found the order of addition caused changes in conversion with mixed catalyst systems).

The reaction took place in a 30 mL horizontal microautoclave as described in other publications [23]. One gram of treated coal was loaded into the reactor. For CO/H₂O reactions, 2.5 g of H₂O was added, and the reactor was pressurized to 3.0 MPa of CO (cold). For hydrogenation reactions, the reactor was pressurized to 6 MPa of hydrogen (cold). The reactors were heated in an ebullating sandbath to the required temperature (2 min to heat the reactor and held at temperature for 30 min).

The work-up procedure was as described previously [17-18, 24-25]. The reactors were vented and scraped out using dichloromethane (DCM). The water was removed from the products by Lundin distillation. The products were ultrasonicated for 10 min and filtered. The residues were dried at 105 °C under nitrogen for 2 h. The DCM was vacuum distilled from the DCM-solubles, and then Shell X4 (40-60 °C b.p. petroleum, mainly hexanes) was added for the extraction of the oil fraction. The product was ultrasonicated for at least 2 min, and the DCM-solubles/X4-insolubles (asphaltenes) were filtered out. Total conversion was calculated by (dry coal with catalyst - dry residue with catalyst)/coal (daf). The oil, gas, and water fraction (OGW) was determined by total conversion minus asphaltene fraction.

RESULTS

Table 2 contains the conversion data for Loy Yang run-of-mine (LYROM) coal for two sets of reaction conditions. The CO/H₂O reactions were all at 365 °C for 30 min. The conversion for this reaction condition of LYROM is 30%, mainly to OGW. Addition of the alkali catalysts gives significantly higher conversions, with sodium aluminate increasing conversion to 51% (45% OGW) and sodium hydroxide increasing conversion to 60% (53% OGW). Metal hydrogenation catalysts give much smaller increases in conversion. Iron increases the conversion to 36% (34% OGW) and cobalt to 42% (41% OGW). For the alkali catalyst and the metal catalyst acting together, the conversion (~50-55%) is similar to the conversion for the reaction when using the alkali alone. The sodium metacarbonylate catalyst precursors were first tested by reacting sodium hydroxide with iron pentacarbonyl or dicobalt octacarbonyl and loading the mixture of the carbonylate and excess NaOH on to the coal. Increases in conversion were noted (to 55-63%), but the conversion was similar to that for sodium hydroxide alone (60%). Finally, sodium cobalt tetracarbonyl was used as catalyst, but the conversion is similar to that with cobalt alone (40%). The low conversion with sodium cobalt tetracarbonyl may be due to the non-alkaline form of the sodium.

Some of these catalyst combinations were also used in coal hydrogenation reactions with LYROM at 400 °C for 30 min. The conversion for this reaction condition of LYROM is 32%, mainly to OGW. With cobalt and alkali catalysts, the conversion is 71-77%, with 62-67% OGW. The metal carbonylate catalysts only give 41 to 48% conversion. On-going work in this laboratory has focused on the use of Ni/Mo metal catalysts with sodium aluminate [18]. The work has shown that the order of addition of the alkali and the metals, and the metal "promoter" of Mo, significantly affect the conversion. When the Ni/Mo is added first, conversion is about 75 %, 60% OGW. When sodium aluminate is added first, the conversion increases to 87% with 69% OGW. Co/Mo gives significantly lower conversions than Ni/Mo. It appears that sodium can greatly influence the reaction, but its effect depends on the form and amount of sodium added and the metal used as the hydrogenation catalyst.

Table 3 contains the conversion data for Surat Basin coal (SSB) for two sets of reaction conditions. The CO/H₂O reactions were at 365 °C for 30 min. The conversion for this reaction condition of SSB is 27%, mainly to OGW. Addition of sodium aluminate catalyst gave slightly higher conversions (to 36%, OGW). Cobalt alone did not increase conversion. However, the sodium aluminate and cobalt give a conversion only slightly lower than with the alkali alone (~33%), but with a decrease in asphaltene yield to 4%. Sodium cobalt tetracarbonyl (300 mmols/kg dry coal for each metal) gives a similar conversion to that for cobalt and sodium aluminate (33%). Although sodium aluminate does increase the conversion for the CO/H₂O reactions, the increase in conversion is much smaller for LYROM.

Some of these catalyst combinations were also used in coal hydrogenation reactions with SSB at 400 °C for 30 min. The conversion for this reaction condition using SSB (CS₂ was also in this reaction) is 25%, mainly to OGW. The sodium cobaltcarbonylate catalyst gives a conversion of 62%. For sodium aluminate and Ni/Mo (Ni/Mo loaded first), conversion is 51%, 37% OGW. When sodium aluminate was loaded first, the conversion decreases to 46% with 35% OGW.

DISCUSSION

For LYROM coal, the alkali catalysts containing sodium do significantly increase conversion for CO/H₂O reactions at 365 °C; adding metals to the alkalis for this reaction condition does not increase the conversion. Sodium cobalt tetracarbonyl does increase conversion compared to no catalyst, but the increase in conversion is about the same as only by the same amount as cobalt alone. For SSB coal, alkali catalysts are effective in increasing conversion, but not to the same extent as for LYROM coal. Cobalt/sodium aluminate and to a lesser extent the sodium cobalt carbonylate improve the oil yield compared to sodium aluminate.

However, for hydrogenation reactions at 400 °C, sodium has had varying effects on conversion depending on the coal used, hydrogenation catalyst metals used, the order of addition of catalyst, and the form of sodium added. On-going work in this laboratory has shown Ni/Mo combined with sodium aluminate also produces increased conversions, particularly when adding the sodium aluminate before the metals (conversion under similar reaction conditions is 87% on a DCM-soluble basis, with 69% yield of OGW) [18]. With LYROM, the sodium metacarbonylates under these reaction conditions only increase conversion from the baseline condition about 10-15%,

whereas cobalt/alkali increase conversion by 40%. It is possible the sodium aluminate alters the coal surface of LYROM coal to increase dispersion of the Ni/Mo catalyst [18], and clearly a mixed sodium-metal compound may not affect the metal surface in the same way. However, the catalysts behave differently with SSB coal for hydrogenation at 400 °C for 30 min. Sodium cobalt tetracarbonyl does significantly increase the conversion under hydrogenation reaction conditions, the conversion being 61% with a OGW yield of 39%. Reactions of SSB coal with Ni/Mo and sodium aluminate give conversions around 50%. The order of addition of the alkali and metal catalysts does not alter the conversion significantly with SSB coal as it does with LYROM; yet a higher conversion is obtained when using the sodium cobalt tetracarbonylate than when using Ni/Mo/NaAlO₂ with SSB coal.

CONCLUSIONS

The use of sodium cobalt tetracarbonyl with LYROM coal does increase coal conversion from baseline conditions for both CO/H₂O reactions and hydrogenation reactions; but adding cobalt acetate and alkali as separate precursors gives much higher conversions. For SSB coal, sodium cobalt tetracarbonyl does increase conversion for hydrogenation reactions at 400 °C to a higher level than NaAlO₂/Ni/Mo. The differing effects of these catalysts when using different coals is not yet understood.

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REFERENCES

1. Del Bianco, A. and Girardi, *Fuel Proc. Tech.*, **23**, 205, (1989).
2. Fischer, F. and Schrader, H., *Brennst. Chem.*, **2**, 257, (1921) (*Chem. Abst.*, **15**, 3900, 1921).
3. Ross, D.S., Blessing, J.T., Nguyen, Q.C. and Hum, G.P., *Fuel*, **63**, 1206, (1984).
4. Lim, S.C., Jackson, W.R., and Marshall, M., submitted for publication in *Fuel*.
5. Hughes, C.P., Sridhar, T., Lim, S.C., Redlich, P.J., Jackson, W.R., and Larkins, F.P., *Fuel*, **72**, 205, (1993).
6. Derbyshire, F.J., *Catalysis in Coal Liquefaction*, IEA Coal Research, London, IEA CR/08, (1988).
7. Weller, S., *Energy & Fuels*, **8**, 415, (1994).
8. Derbyshire, F.J., Davis, A., Lin, R., Stansberry, P.G., and Terrer, M-T., *Fuel Proc. Tech.*, **12** (7), 127, (1986).
9. Anderson, R.R. and Bockrath, B.C., *Fuel*, **63**, 329, (1984).
10. Utz, B.R., Cugini, A.V., and Frommel, E.A., *Amer. Chem. Soc. Div. of Fuel Chem. Preprints*, **34** (4), 1423, (1989).
11. Cugini, A.V., Martello, D.V., Krastman, D., Baltrus, J.P., Ciocco, M.V., Frommel, E.F., and Holder, G.D., *Amer. Chem. Soc. Div. of Fuel Chem. Preprints*, **40** (2), 1423, (1995).
12. Cusumano, J.A., Dalla Betta, R.A. and Levy, R.B., *Catalysis in Coal Conversion*, Academic Press: New York, p. 155, (1978).
13. Song, C., Hanaoka, K. and Nomura, *Energy & Fuels*, **6**, 619, (1992).
14. Bockrath, B.C., in *Coal Science*, Gorbaty, M.L., Larsen, J.W., and Wender, I., Editors. Academic Press: New York. p. 65, (1983).
15. Derbyshire, F.J., Odoefer, G.A. and Whitehurst, D.D., *Fuel*, **60**, 201, (1981).
16. Burgess, C.E. and Schobert, H.H., *Fuel*, **70**, 392, (1991).
17. Hulston, C.K.J., Redlich, P.J., Jackson, W.R., Larkins, F.P., and Marshall, M., "Reactions of Coals of Different Ranks With CO/H₂ Mixtures of Varying Composition With and Without Sodium Aluminate", accepted for publication in *Fuel*, 1995.
18. Hulston, C.K.J., Redlich, P.J., Marshall, M., and Jackson, W.R., "Nickel Molybdate Catalysed Hydrogenation of Brown Coal Without Solvent or Added Sulphur," submitted to *Fuel*, 1995.
19. Sternberg, H.W., Markby, R., and Wender, I., *J. Am. Chem. Soc.*, **79**, 6116 (1957).
20. Wender, I., Sternberg, and Orchin, M. *J. Am. Chem. Soc.*, **74**, 1216 (1952).
21. Edgell, W.F. and Lyford IV, J. *Inorg. Chem.*, **9** (8) 1932 (1970).
22. Schroeder, N.C., Richardson Jr., J.W., Wang, S-L, Jacobson, R.A., and Angelici, R.J. *Organometallics*, **4**, 1226 (1985).
23. Hulston, C.K.J., Redlich, P.J., Jackson, W.R., Larkins, F.P., and Marshall, M., "The Effect of Tubular Reactor Orientation on Conversion of Coal to Liquid Products," submitted to *Fuel*, 1995.
24. Cassidy, P.J., Jackson, W.R., Larkins, F.P., Sakurovs, R.J. and Sutton, J.F., *Fuel*, **65**, 374, (1986).
25. Jackson, W.R., Larkins, F.P., Thewlis, P. and Watkins, I., *Fuel*, **62**, 606, (1983).

Table 1: Elemental and Ash Analyses for Coals

Coal	Rank	Elemental Analysis (wt % daf)					Atomic H/C Ratio ^a	Ash (wt% dry)
		C	H	N	S	O (by diff)		
LYROM ^b	lignite	70.7	4.91	0.7	0.51	23.2	0.86	0.5
SSB ^c	hvb ^d	81.0	6.08	1.8	0.56	10.5	0.9	9.8

^a CO₂-free basis^b Loy Yang run-of-mine coal^c Surat Basin coal^d high volatile bituminous

Table 2: Conversion Data for Loy Yang brown coal (LYROM) Using Various Catalysts and Reaction Conditions

Coal	Metal Catalyst ^a	Alkali Catalyst ^b	Temp (°C)	Gas Atm.	Total Conv. ^c	Asph. ^d	OGW ^e
LYROM	none	none	365	CO/H ₂ O	30	0.6	29
	none	NaAlO ₂	365	CO/H ₂ O	51	5.7	45
	none	NaOH	365	CO/H ₂ O	60	6.9	53
	Fe	none	365	CO/H ₂ O	36	1.9	34
	Co	none	365	CO/H ₂ O	42	1.0	41
	Fe	NaAlO ₂	365	CO/H ₂ O	55	9.8	45
	Co	NaAlO ₂	365	CO/H ₂ O	53	7.8	45
	Co	NaOH	365	CO/H ₂ O	54	6.5	48
	NaHFe(CO) ₄ ^f	--	365	CO/H ₂ O	55	6.7	48
	NaCo(CO) ₄ ^f	--	365	CO/H ₂ O	63	11.6	52
	NaCo(CO) ₄ ^g	--	365	CO/H ₂ O	40	0.1	40
	none ^h	none	400	H ₂	32	2	30
	Co	NaAlO ₂	400	H ₂	71	8.5	62
	Co	NaOH	400	H ₂	77	9.8	67
	NaHFe(CO) ₄ ^f	--	400	H ₂	48	6.6	41
	NaCo(CO) ₄ ^g	--	400	H ₂	41	0.1	41
	Ni/Mo ⁱ	NaAlO ₂	400	H ₂	87	18	69
	Ni/Mo ^j	NaAlO ₂	400	H ₂	75	15	60
	Co/Mo ^j	NaAlO ₂	400	H ₂	48	5	43

^a Metal Catalysts - Loaded as aqueous solutions of salts, i.e. cobalt acetate, nickel acetate, ammonium molybdate. Cobalt and nickel salts loaded 300 mmol metal/kg dry coal unless used as mixed catalyst with molybdenum, then cobalt and nickel loaded 40 mmol and molybdenum 100 mmol metal/kg dry coal.^b Alkali Catalysts - Loaded as salts, 500 mmol/kg dry coal^c Total Conversion - based on DCM-insolubles, [(Coal (dry) - Residue (dry))/Coal (daf)]^d Asphaltenes - DCM-solubles/hexane-insolubles^e OGW - Oil, Gas, (Total Conversion - Asphaltenes)^f Sodium metalcarbonylates - loaded as mixture of NaOH and metal carbonyl^g Sodium Carbonyl - loaded as actual salt, 300 mmol metal/kg dry coal^h Reaction contains CS₂, no baseline data available at this timeⁱ Sodium Aluminate loaded before nickel and molybdenum precursors^j Sodium Aluminate loaded after nickel and molybdenum precursors

Table 3: Conversion Data for Surat Basin coal (SSB) Using Various Catalysts and Reaction Conditions

Coal	Metal Catalyst ^a	Alkali Catalyst ^b	Temp (°C)	Gas Atm.	Total Conv. ^c	Asph. ^d	OGW ^e
SSB	none	none	365	CO/H ₂ O	27	4.3	23
	none	NaAlO ₂	365	CO/H ₂ O	36	12	24
	Co	none	365	CO/H ₂ O	27	3.2	23
	Co	NaAlO ₂	365	CO/H ₂ O	33	3.7	29
	NaCo(CO) ₄ ^f	--	365	CO/H ₂ O	33	7.0	26
	none	none	400g	H ₂	25	2	23
	NaCo(CO) ₄ ^f	--	400	H ₂	61	22.3	39
	Ni/Mo ^h	NaAlO ₂	400	H ₂	46	11	35
	Ni/Mo ⁱ	NaAlO ₂	400	H ₂	51	14	37

^a Metal Catalysts - Loaded as aqueous solutions of salts, i.e. cobalt acetate, nickel acetate, ammonium molybdate. Cobalt and nickel salts loaded 300 mmol metal/kg dry coal unless used as mixed catalyst with molybdenum, then cobalt and nickel loaded 40 mmol and molybdenum 100 mmol metal/kg dry coal.

^b Alkali Catalysts - Loaded as salts, 500 mmol/kg dry coal

^c Total Conversion - based on DCM-insolubles, [(Coal (dry) - Residue (dry))/Coal (daf)

^d Asphaltene - DCM-solubles/hexane-insolubles

^e OGW - Oil, Gas, Water, (Total Conversion - Asphaltene)

^f Sodium Cobalt Carbonyl - loaded as actual salt, 300 mmol loading

^g Reaction time 60 minutes

^h Sodium Aluminate loaded before nickel and molybdenum precursors

ⁱ Sodium Aluminate loaded after nickel and molybdenum precursors