

ERL 91-078(OP+J)

HYDROCRACKING GAS OILS FROM SYNTHETIC CRUDE WITH MIXED PILLARED CLAY-ALUMINA SUPPORTED CATALYSTS

J. Monnier, J.-P. Charland, J. R. Brown and M. F. Wilson

Energy Research Laboratories, CANMET, Energy, Mines and Resources Canada, 555 Booth
Street, Ottawa, K1A 0G1 Ontario, Canada



Abstract

Nickel-molybdenum catalysts supported on mixed pillared clay-alumina extrudates were prepared and tested for hydrocracking denitrogenated Canadian synthetic crude gas oil using an automated microreactor system. Compared with Ni-Mo on Y-zeolite-alumina, the catalysts were found to be superior as they utilized H₂ more efficiently and produced more liquids in the combined middle distillate and naphtha ranges. Very little hydrocarbon gases were formed over pillared clay-alumina supported catalysts. X-ray photoelectron spectroscopy provided information on the nickel and molybdenum active sites in the catalysts. Basal spacings of pillared clays were determined using X-ray diffraction.

1. INTRODUCTION

Synthetic crude gas oils derived from Canadian oil sands are difficult to hydrocrack due to the presence of nitrogen compounds which poison acidic sites and cause rapid deactivation of the catalyst [1]. To overcome this problem, a two-stage process has been developed whereby synthetic crude gas oil is first hydrotreated to eliminate most of the nitrogen compounds and then hydrocracked to middle distillates and naphtha [2-5]. The performance of nickel-molybdenum catalysts supported on mixed pillared clay-alumina (PILC-Al₂O₃) as second-stage hydrocracking catalysts is discussed in terms of product distribution, quality, and catalyst characteristics.

2. EXPERIMENTAL

Two montmorillonite clays were obtained from American Colloid Company. The starting materials were either Polargel NF (PGL) or Microfine Panther Creek (MPC) and were pillared by ion-exchanging aluminum polynuclear cations [Al₁₃O₄(OH)₂₄(H₂O)₁₂]⁷⁺ between the clay lamellas, followed by drying and calcining. This led to increases in the basal spacings as monitored by X-ray diffraction: from 9.92 to 19.33 Å for PGL and from 12.05 to 18.85 Å for MPC. Nickel-molybdenum catalysts (16 wt % MoO₃ and 4 wt % NiO) were then prepared by the incipient wetness method from extruded supports

ERL 91-078 (OP+J)

01-0010973

containing 50 or 70% Al_2O_3 mixed with PILC or Y-zeolite (Linde LZY-72). The catalysts were then characterized by proton-induced X-ray emission spectrometry (PIXE) and X-ray photoelectron spectroscopy (XPS).

Synthetic crude gas oil (SGO) from northern Alberta was hydrotreated with a commercial Ni-Mo/ $\gamma\text{-Al}_2\text{O}_3$ catalyst at 10.3 MPa and 375°C to reduce the nitrogen content from 1100 to 92 ppm. The performance of Ni-Mo on PILC- Al_2O_3 catalysts was then compared with Ni-Mo on Y-zeolite- Al_2O_3 for hydrocracking denitrogenated synthetic gas oil (DSGO) using an automated 10-mL microreactor system at 360°C, 380°C, 400°C and 420°C, 15.2 MPa pressure, 0.5 and 1.0 h^{-1} LHSV and 1000 L H_2 /L DSGO feed ratio. Catalyst presulphiding was performed in situ with a gas mixture of 10% H_2S in H_2 flowed through the microreactor at 400°C, 0.3 MPa and 1000 h^{-1} GHSV for 2.5 h. The liquid products obtained after a minimum of 50 h at steady state conditions were characterized to give information on gas oil conversion, product yields, N and S contents and ^{13}C -NMR aromaticity.

3. RESULTS AND DISCUSSION

The calcined Ni-Mo catalysts on PILC- Al_2O_3 and Y-zeolite- Al_2O_3 supports were examined by XPS. The Mo 3d spectra indicated that molybdenum was in the Mo^{6+} oxidation state ($\text{Mo } 3d_{5/2} = 232.6 \text{ eV}$) for both catalysts, indicating the presence of MoO_3

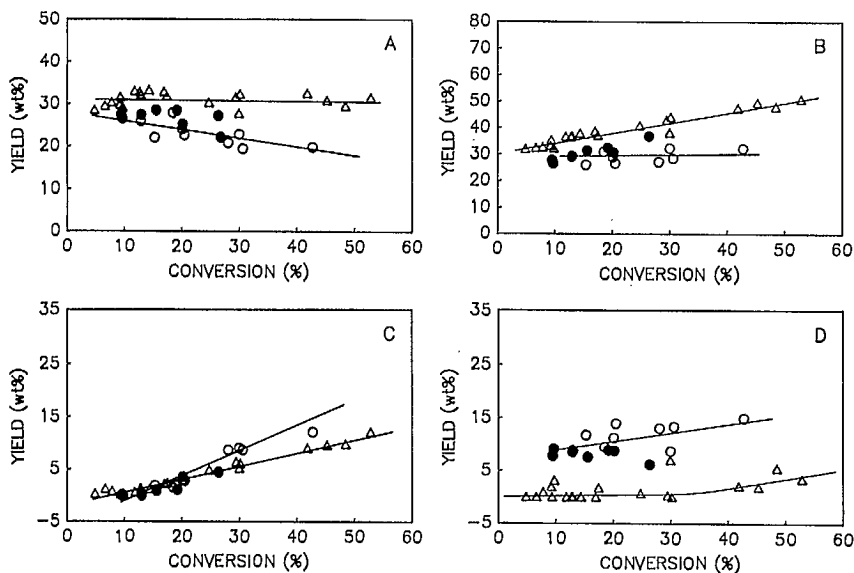


Figure 1. Yields of heavy middle distillates (A), middle distillates (B), naphtha (C) and gases (D) as functions of DSGO conversion using catalysts supported on mixed PILC- Al_2O_3 (Δ) or zeolite- Al_2O_3 [experimental (\circ) or commercial (\bullet)].

and/or $\text{Al}_2(\text{MoO}_4)_3$ phases. However, the catalysts differ with regard to the Ni $2p_{3/2}$ photoline peak energy. The curve-fitted XPS Ni $2p_{3/2}$ envelopes suggest that the state of nickel was more electronegative on PILC- Al_2O_3 (Ni $2p_{3/2}$ = 857.2 eV) than on Y-zeolite- Al_2O_3 (Ni $2p_{3/2}$ = 856.8 eV). In both cases, nickel was likely present as Ni-silicate and Ni-aluminate phases; a small amount of Ni-hydroxide was detected in PILC- Al_2O_3 .

Figure 1 presents the yields of (A) heavy middle distillate (290-360°C), (B) middle distillate (195-360°C), (C) naphtha (IBP-195°C) and (D) gases as functions of DSGO conversion. Table 1 compares characteristics of products obtained at similar conversions over the two different catalyst supports. It was found that below 30% DSGO conversion, slightly more naphtha was produced over PILC- Al_2O_3 supports whereas at higher conversions, the use of Y-zeolite- Al_2O_3 support favoured high production of naphtha. For middle distillates, the yields obtained over Y-zeolite- Al_2O_3 support remained constant at about 28-30 wt % up to 50% conversion and then dropped. For mixed PILC- Al_2O_3 supports, the middle distillate yields steadily increased from 30 to 50 wt % with DSGO conversion. As expected, the Y-zeolite's high cracking activity caused excessive gas production (Fig. 1, D) which did not fall below 5 wt % and actually increased at higher conversions. In contrast, PILC- Al_2O_3 supported catalysts were more selective towards liquid products and their production of gases remained close to zero. No major difference in catalyst selectivity was observed in using PGL or MPC PILC or in varying concentration from 30 to 50%. In summary, Ni-Mo catalysts on mixed PILC- Al_2O_3 supports showed superior selectivity compared with Y-zeolite- Al_2O_3 supported catalysts as indicated by substantially lower gas yield, higher liquid production and better utilization of H_2 feedstock.

Table 1

Performance of Ni-Mo on experimental mixed PILC- or Y-zeolite- Al_2O_3 support as second-stage hydrocracking catalyst used at 420°C, 0.5 h⁻¹ LHSV and 15.2 MPa

	Gas oil feedstock (DSGO)	Supported Ni-Mo catalysts containing	
		30% Polargel NF	30% Y-zeolite
Gas oil conversion (%)		52.9	56.6
Liquid yield (wt %)		96.6	84.7
IBP-195°C	0.0	12.1	22.2
195-290°C	0.0	19.4	14.2
290-360°C	28.7	31.5	17.4
≥360°C	71.3	33.6	30.9
Gas yield (wt %), by diff.		3.4	15.3
Liquid products			
H/C (atomic)	1.72	1.83	1.83
N (ppm)	92	≤0.5	0.6
S (ppm)	80	1.7	2.1
¹³ C-NMR f _a	0.114	0.078	0.093

PILC- Al_2O_3 supported catalysts produced liquid fuels containing less aromatic hydrocarbons as indicated by the ^{13}C -NMR aromaticity f_a which varied between 0.04 and 0.08. The f_a values followed an ascending trend with temperature which is consistent with a shift of thermodynamic equilibrium which favoured the dehydrogenation of naphthenes to form aromatics above 380°C [6]. Conversely, the f_a values for the hydrocracked products from Y-zeolite- Al_2O_3 supported catalysts remained high between 0.09 and 0.12.

The superior selectivity of mixed PILC- Al_2O_3 supported catalysts in terms of product distribution and quality may be attributed to a reduction in the molecular diffusion limitations which are usually encountered in Y-zeolites. Compared with the smaller diameter size of Y-zeolite pore openings (7.4 \AA) which limits diffusion of small hydrocarbon molecules [7], mass transfer appears to be less impeded inside the porous structure of the PILC- Al_2O_3 support. It is also possible that the improved selectivity is due to the formation of macropores within the support. The macropores may be formed from edge-to-face aggregation of clay platelets creating a "house-of-cards" type structure [8]. Thus polynuclear aromatics which are present in gas oil and middle distillate fractions might penetrate the porous structure of the PILC- Al_2O_3 more easily. Increased diffusion rates implied shorter residence times for hydrocracked products which had a direct impact on gas formation and hydrogen utilization.

4. CONCLUSIONS

Nickel-molybdenum catalysts supported on mixed PILC- Al_2O_3 were found to be very effective for hydrocracking synthetic crude gas oil having reduced nitrogen content. Their liquid yields and product quality were significantly better than those obtained using Y-zeolite-alumina supports. The results obtained using pillared clays were attributed to the larger pore diameter of the molecular sieve structure and the possible formation of macropores from aggregation of clay lamellas, which are both expected to enhance the diffusion of multi-ring compounds.

© Minister of Supply and Services Canada, 1991.

5. REFERENCES

- 1 M.F. Wilson, R.A. Simmons and H. Notzl, Am. Chem. Soc. Div. Petr. Chem., Prepr., 32 (1987) 383.
- 2 J. Monnier, Y. Yoshimura and J.F. Kriz, 11th North American Meeting of the Catalysis Society, Dearborn, Michigan (1989), Paper PD14.
- 3 J. Monnier, J. Christensen, J.-P. Charland and M.F. Wilson, 12th North American Meeting of the Catalysis Society, Lexington, Kentucky (1991), Paper D36.
- 4 J. Monnier, G.T. Smiley and M.F. Wilson, 12th North American Meeting of the Catalysis Society, Lexington, Kentucky (1991), Paper C22.
- 5 A. Mahay, J. Chmielowiec, I.P. Fisher and J. Monnier, Fuel Proc. Technol., (1992) in press.
- 6 M.F. Wilson, I.P. Fisher and J.F. Kriz, J. Catal. 95 (1985) 155.
- 7 R.M. Moore and J.R. Katzer, AIChE J. 18 (1972) 816.
- 8 M.L. Occelli, S.D. Landau, and T.J. Pinnavaia, J. Catal. 104 (1987) 331.