

Catalytic hydrogenation of anthracene oil with red mud

Juan J. Llano, Roberto Rosal, Herminio Sastre and Fernando V. Díez

Department of Chemical Engineering, University of Oviedo, 33071 Oviedo, Spain

(Received 18 March 1993; revised 28 May 1993)

Red mud, and red mud activated by dissolution in hydrochloric acid and reprecipitation with ammonia, were tested as catalysts for the hydrogenation of an anthracene oil in a trickle-bed reactor. Conversion data were determined for the different polyaromatic compounds in the anthracene oil. Red mud shows appreciable catalytic activity, which is enhanced by the activation. Although both red mud and activated red mud are less active than a commercial Ni-Mo/ γ -alumina hydrotreating catalyst, the difference in activity is smaller when conversion to hydroaromatics instead of total conversion of reactants is considered.

(Keywords: hydrogenation; anthracene oil; red mud)

Red mud (RM) is a by-product in the production of alumina by the Bayer process, and contains a high proportion of iron oxides. RM has been proposed as catalyst for the liquefaction of coal¹⁻³ and biomass⁴ and has also shown activity as a hydrogenation catalyst. Pratt and Christoverson⁵ tested RM as a catalyst for the hydrogenation of naphthalene, and more recently³ the work was extended to the hydrogenation of phenanthrene and pyrene. These experiments were carried out using pure compounds in stirred or rocking autoclaves, and conversion results were reported only for a given reaction time.

The catalytic activity of iron ores can be enhanced by several methods. Morita *et al.*⁶ proposed two: refluxing the ore particles in water, and calcination at temperatures between 573 and 1073 K followed by immersion in water. They reported significant changes in specific surface and pore volume distribution of the ores, and an increase in the oil yield from the liquefaction of a subbituminous Japanese coal^{6,7}. Pratt and Christoverson⁵ proposed a dissolution-precipitation method which decreased the Ca and Na contents and increased the specific surface of the RM. Activation increased the catalytic activity of RM for the hydrogenation of naphthalene, phenanthrene and pyrene, and the oil yield in the hydroliquefaction of a low-rank coal in the presence of a poor hydrogen donor solvent³. Although RM has been shown to be an active hydrogenation catalyst for pure compounds, no data have been reported for the hydrogenation of complex industrial fractions. In this paper, RM is tested as a catalyst for the hydrogenation of an anthracene oil.

Anthracene oil is a fraction obtained by distillation of coal tar. It contains considerable amounts of condensed aromatic hydrocarbons with molecular weights between those of naphthalene and chrysene. Anthracene oil can be hydrogenated with conventional Ni or Ni-Mo hydrogenation and hydroprocessing catalysts⁸, yielding a hydrogenated oil containing appreciable concentrations of hydrogen donor substances, mainly hydroaromatic compounds. Hydrogenated anthracene oil can be used

as hydrogen-transfer agent for processes (under development) in which transferable hydrogen plays an important role, such as coal liquefaction⁹, coprocessing¹⁰ and coke production by carbonization of low-rank coals with pitch-like materials¹¹. Under the conditions used for the extraction of coal, the complex organic structures in the coal undergo thermolysis which results in free radicals¹². It has been shown that the transfer of hydrogen from a donor solvent stabilizes the radicals thus generated. In addition, direct interaction between hydrogenated molecules in the solvent and coal or coal-derived fragments may take place^{13,14}.

In this work, RM and red mud activated by the method of Pratt and Christoverson⁵ (ARM) were tested as catalysts for the hydrogenation of anthracene oil. Experiments were carried out in a continuous trickle-bed reactor permitting decoupling of the effects of space time and catalyst deactivation upon conversion. Anthracene oil was also hydrogenated using a commercial Ni-Mo/ γ -alumina catalyst (CC) as a reference.

EXPERIMENTAL

Materials

The catalysts tested were Shell S-214, a commercial Ni-Mo/ γ -alumina hydroprocessing catalyst (denoted CC), and a RM from the San Ciprián (La Coruña, Spain) plant of the Spanish aluminium company INESPAL. RM was activated by the method proposed by Pratt and Christoverson⁵ (ARM). Activation consisted essentially in dissolving the RM in aqueous HCl, boiling the resulting solution for 20 min, and adding aqueous ammonia to pH \approx 8. The resulting precipitate was filtered, washed with distilled water, dried at 383 K, and calcined at 773 K for 2 h. The compositions of CC, RM and ARM are given in Table 1. CC is available as extrudates, which were crushed to a particle size of 0.5–0.36 mm. RM average particle size was 8.5 μ m.

A light fraction of anthracene oil, supplied by NalonChem (Asturias, Spain) was used for the hydrogen-

Table 1 Composition of catalysts (wt%)

S-214		Red mud		Activated red mud
NiO	2.8	Fe ₂ O ₃	28	36
MoO ₃	13.5	Al ₂ O ₃	15	17
Na ₂ O	0.04	TiO ₂	22	27
Al ₂ O ₃	(base)	SiO ₂	10	11
		CaO	7	1.3
		Na ₂ O	5	0.1

Table 2 Composition of anthracene oil (wt%)

Naphthalene	3.2
Acenaphthene	5.5
Dibenzofuran	3.1
Fluorene	6.2
9,10-Dihydroanthracene	0.9
Phenanthrene	17.7
Anthracene	6.0
Carbazole	5.5
Fluoroanthene	11.2
Pyrene	9.0

ation runs. Concentrations of the major components identified in this material are given in Table 2.

Reaction studies

The hydrogenation experiments were performed in a high-pressure trickle-bed reactor. The reactor was a stainless steel cylinder of 9 mm i.d. and 45 cm length, placed inside a tubular electric furnace. Five thermocouples monitored the temperature at different reactor heights. Catalyst (2.4 g) was placed in the middle section of the reactor. The lower and upper parts were packed with low-area inert alumina (diameter 0.25–0.08 mm), the upper alumina bed being used as preheating zone.

The liquid feed consisted of 20 wt% anthracene oil dissolved in toluene (99.5% pure) for easier handling. The liquid feed flowed down the reactor, pumped by a liquid chromatography pump. Hydrogen was fed concurrently at a controlled flow rate. The reaction products were collected in a cylindrical receiver connected to a back-pressure regulator which maintained the operating pressure by venting the excess gas. Liquid samples were taken by emptying the receiver at selected time intervals. The apparatus was equipped with safety features such as temperature and pressure controls and rupture disc. A schematic diagram of the reactor is shown in Figure 1.

Catalysts were sulfided *in situ* before use by passing 3 l h⁻¹ of a mixture of 10 vol.% H₂S in H₂ at atmospheric pressure, heated to 673 K, through the reactor for 4 h. CS₂ (1 wt%) was added to the liquid feed to maintain the catalyst in the sulfided form.

Hydrogenations were carried out at 623 K and 10 MPa. A constant hydrogen flow of 4 ml s⁻¹ (at s.t.p.) was maintained in all experiments. The liquid feed flow rate ranged between 0.3 and 1.5 ml min⁻¹; low and high flow rates were interspersed randomly. The reaction was run for an initial period without taking samples, to allow the catalyst to reach constant activity. To avoid transient effects, the samples taken after a change in the liquid flow rate were discarded.

Analysis and catalyst characterization

Anthracene oil fractions were analysed by gas chromatography with f.i.d. and *n*-nonane as internal standard, using a 30 m capillary fused silica column with apolar stationary phase SE-30. The oven was heated from 353 to 533 K at 4 K min⁻¹. Peak assignment was performed by g.c.-m.s. Response factors of the hydrogenation derivatives for which no pure standards were available were taken as unity. Catalyst pore structure was characterized by nitrogen adsorption.

RESULTS AND DISCUSSION

Pore volume distributions for RM, ARM and CC, calculated by the BJH method¹⁵, are given in Figure 2. It can be seen that the commercial catalyst has a pore volume much greater than that of RM and ARM, and that activation increases the pore volume as well as (slightly) the pore diameter of the RM. The specific surface (pores 1.7–300 nm) follows the same trend: 243 m² g⁻¹ for CC, 29.4 m² g⁻¹ for RM and 60.7 m² g⁻¹ for ARM.

The aromatic compounds in the anthracene oil

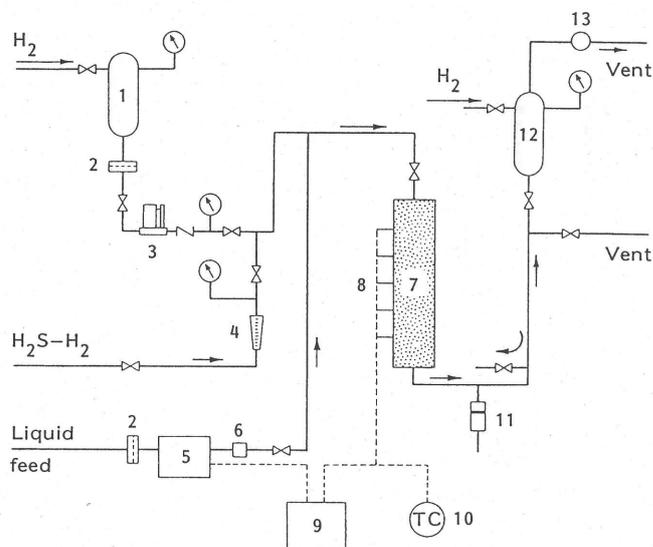


Figure 1 Scheme of hydrogenation trickle-bed reactor: 1, hydrogen cylinder; 2, filter; 3, mass flow regulator; 4, rotameter; 5, liquid pump; 6, pulse damper; 7, reactor; 8, thermocouples; 9, recorder; 10, temperature controller; 11, rupture disc; 12, receiver; 13, back-pressure regulator

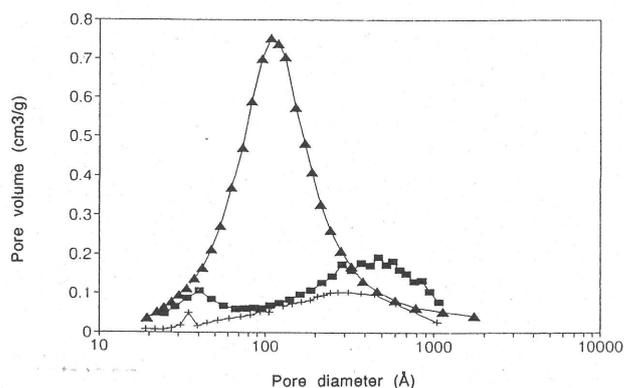


Figure 2 Pore volume distributions of the catalysts: ▲, CC; +, RM; ■, ARM

that were hydrogenated to a measurable degree were naphthalene, acenaphthene, anthracene, phenanthrene, fluoranthene and pyrene. A decrease in the concentration of other compounds such as chrysene and dibenzofuran was observed, but no reaction products were identified, because of their complexity. *Figure 3* shows examples of gas chromatograms of raw and hydrogenated anthracene oil, and *Table 3* the identifications of the peaks. The hydrogenation products detected and quantified were tetralin, 2a,3,4,5-tetrahydroacenaphthene, 9,10-dihydroanthracene, 1,2,3,4-tetrahydroanthracene, 1,2,3,4,5,6,7,8-octahydroanthracene, 9,10-dihydrophenanthrene, 1,2,3,4-tetrahydrophenanthrene, 1,2,3,4,5,6,7,8-octahydrophenanthrene, 1,2,3,10b-tetrahydrofluoranthene, and 4,5-dihdropyrene. Decalin and 1,2,3,4,9,10,11,12-octahydrophenanthrene were also detected in low amounts. However, they were not taken into account in quantifying the mass of hydroaromatics produced in the reaction, because they are poor hydrogen donors. 1,2,3,4,9,10,11,12-Octahydroanthracene was not identified. Mass balances, performed on the assumption that no compounds other than those listed above were produced, fitted for all reaction conditions for naphthalene and acenaphthene. In the case of anthracene, the mass balances fitted for the low-activity catalysts (RM and ARM). Phenanthrene and pyrene mass balances fitted only for RM, whereas that of fluoranthene did not fit for any of the catalysts tested. The lack of fit in the mass balances was caused by hydrogenolysis reactions of hydroaromatics, which produced unidentified cracked products (*Figure 4*)¹⁶⁻²⁰.

Figure 5 shows the total conversion of the different polyaromatics present in anthracene oil as a function of space time. Total conversion is defined as $100([PA]_0 - [PA])/[PA]_0$, where $[PA]_0$ is the initial concentration of the polyaromatic considered, and $[PA]$ is the polyaromatic concentration in the reaction product.

The polyaromatic compound most readily hydrogenated by CC is anthracene, as reported previously for a similar Ni-Mo/ γ -alumina commercial catalyst⁸. CC is more active than RM and ARM for the hydrogenation of all the compounds. The difference in activity between CC and the others is particularly great for naphthalene and acenaphthene. Activation enhances the hydrogenation activity of RM for all compounds except naphthalene, for which both RM and ARM show very low activity.

If it is considered that the hydrogenation is carried out to produce a hydrogen donor solvent, it is interesting to compare the catalysts in terms of selective production of hydroaromatics instead of total conversion. Selective conversions to hydroaromatics for anthracene, phenanthrene, fluoranthene and pyrene are plotted in *Figure 6*. Selective conversion of a compound to hydroaromatics is defined as $100(\sum[HA] - \sum[HA]_0)/[PA]_0$, where $\sum[HA]$ is the sum of the concentrations of all the hydroaromatics derived from the polyaromatic considered. Data for naphthalene and acenaphthene are not given, since these compounds did not produce cracking products, and conversion to hydroaromatics coincided with total conversion except for a very small amount of decalin (*Figure 5a* and *d*). The more active the catalyst, the greater is the tendency to form cracked products from hydroaromatics, decreasing the conversion to hydroaromatics compared with total conversion. As a consequence, conversions to hydroaromatics for CC, the most active catalyst tested, were lower than total conversions, the decrease being very marked for anthracene, fluoranthene and pyrene at high space times. For these compounds and high space times, ARM produced higher hydroaromatic concentrations than did CC.

The hydrogen-donor quality of a solvent depends not only on its total hydroaromatic concentration but also

Table 3 Identification of numbered peaks in *Figure 3*

1. Indane	27. Methylphenanthrene
2. Naphthalene	28. Cyclopenta[def]phenanthrene
3. Quinoline	29. 2-Phenylnaphthalene
4. 2-Methylnaphthalene	30. Fluoranthene
5. 1-Methylnaphthalene	31. Pyrene
6. Biphenyl	32. Methylpyrene
7. 2-Ethylnaphthalene	33. Benzo[b]fluorene
8. 1-Ethylnaphthalene	34. Chrysene
9. Dimethylnaphthalene	35. Triphenylene
10. Acenaphthene	36. Decalin
11. Dibenzofuran	37. Tetralin
12. Fluorene	38 and 39. Methyltetrahydronaphthalene
13 and 14. Methylbiphenyl	40. 5-Methyltetrahydronaphthalene
15. 4-Methyldibenzofuran	41. Ethyltetrahydronaphthalene
16. Xanthene	42. Bicyclohexyl
17. 9,10-Dihydroanthracene	43. 2a,3,4,5-Tetrahydroacenaphthene
18. 9,10-Dihydrophenanthrene	44. 1,2,3,4,9,10,11,12-Octahydrophenanthrene
19 and 20. Methylfluorene	45. 1,2,3,4,5,6,7,8-Octahydroanthracene
21. Dibenzothiophene	46. 1,2,3,4,5,6,7,8-Octahydrophenanthrene
22. Phenanthrene	47. 1,2,3,4-Tetrahydroanthracene
23. Anthracene	48. 1,2,3,4-Tetrahydrophenanthrene
24. Carbazole	49. Tetrahydromethylphenanthrene
25. Benzoquinoline	50. 1,2,3,10b-Tetrahydrofluoranthene
26. Methylanthracene	51. 4,5-Dihdropyrene

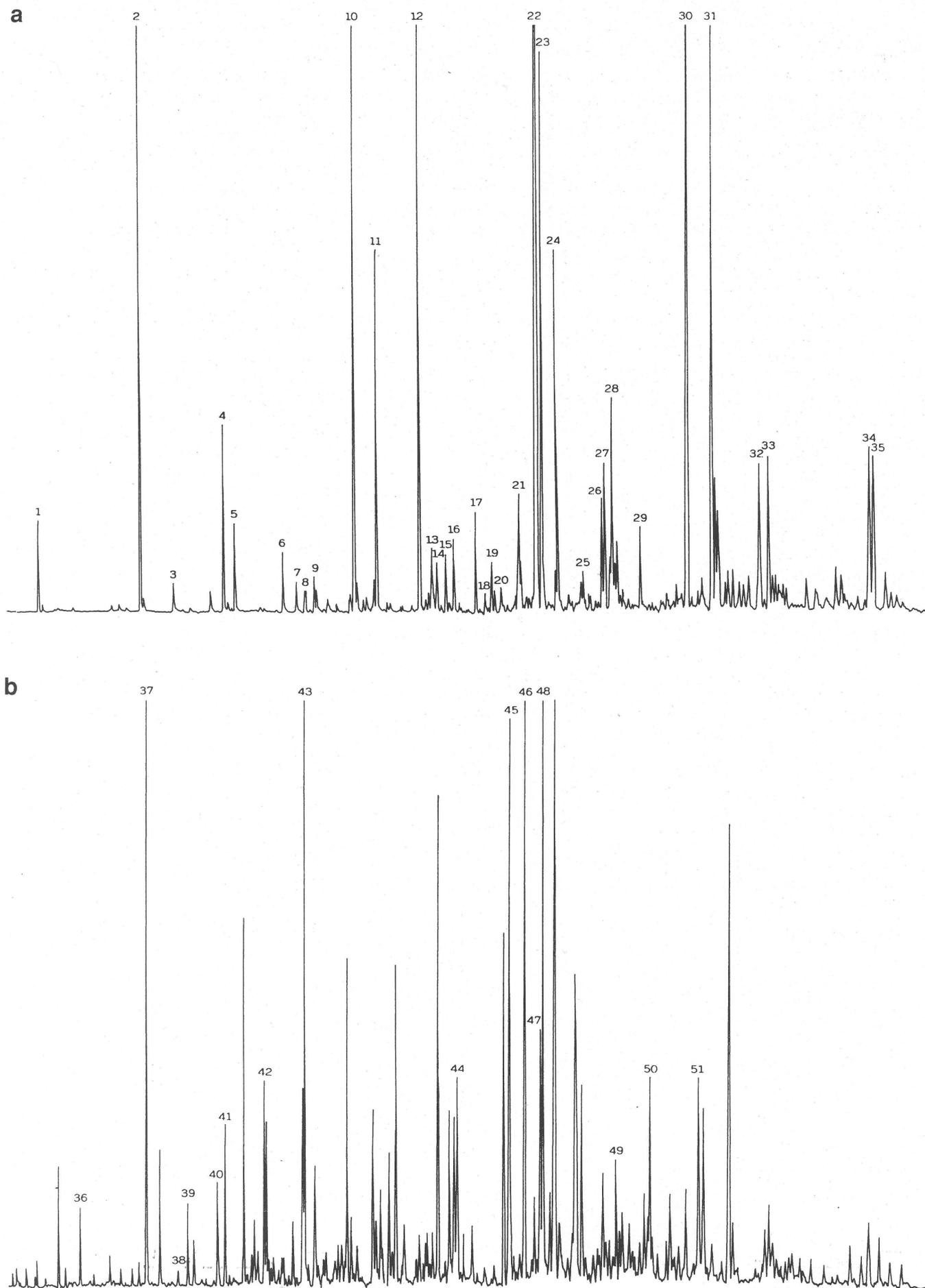


Figure 3 Gas chromatograms of (a) fresh and (b) hydrogenated anthracene oil (see Table 3 for key)

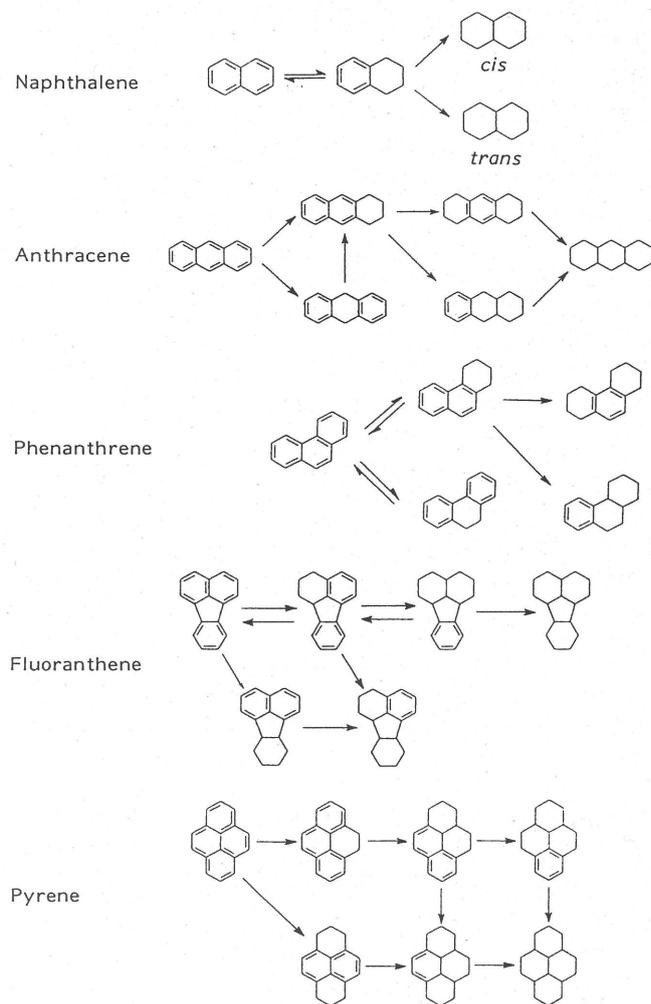


Figure 4 Proposed reaction networks for naphthalene, anthracene, phenanthrene, fluoranthene and pyrene (refs 16, 17, 18, 19 and 20 respectively)

on the individual hydroaromatics it contains. It has been reported¹⁴ that tetrahydrofluoranthene is a significant compound in hydrogen transfer processes, and that dihydroanthracene and dihydrophenanthrene are more active as hydrogen donors than the corresponding tetrahydro compounds. Conversions to dihydroanthracene and dihydrophenanthrene are represented in Figure 7. Conversions to tetrahydrofluoranthene corresponded to conversions of fluoranthene to hydroaromatics (Figure 6b), since tetrahydrofluoranthene was the only fluoranthene hydroderivative detected. CC produced higher amounts of tetrahydrofluoranthene and dihydrophenanthrene, but lower amounts of dihydroanthracene. With CC, the dihydroanthracene initially present in anthracene oil was partly converted to tetrahydroanthracene, yielding negative conversions. Because of the complex nature of the hydrogenated solvents produced, it is difficult to predict their quality as hydrogen donors, and an experimental study is needed. According to the concentration of the different hydroaromatics obtained with the catalysts tested, it is likely that the best hydrogen donor solvent is produced with CC, especially for short space times, but the difference in quality from the solvent obtained with ARM is not as great as could be expected if only total conversion of polyaromatics is taken into account.

The selectivities of the catalysts can be compared by plotting the conversion to hydroaromatics vs. total conversion for each polyaromatic present in anthracene oil (Figure 8). Data for naphthalene and acenaphthene are not given because the conversion to hydroaromatics equalled total conversion for these compounds. Figure 8 shows that activation did not appreciably change the selectivity of RM. Direct comparison of the selectivity of RM and ARM with that of CC is possible only for pyrene, since conversions with CC were in a different range from those with RM and ARM for the other compounds. The

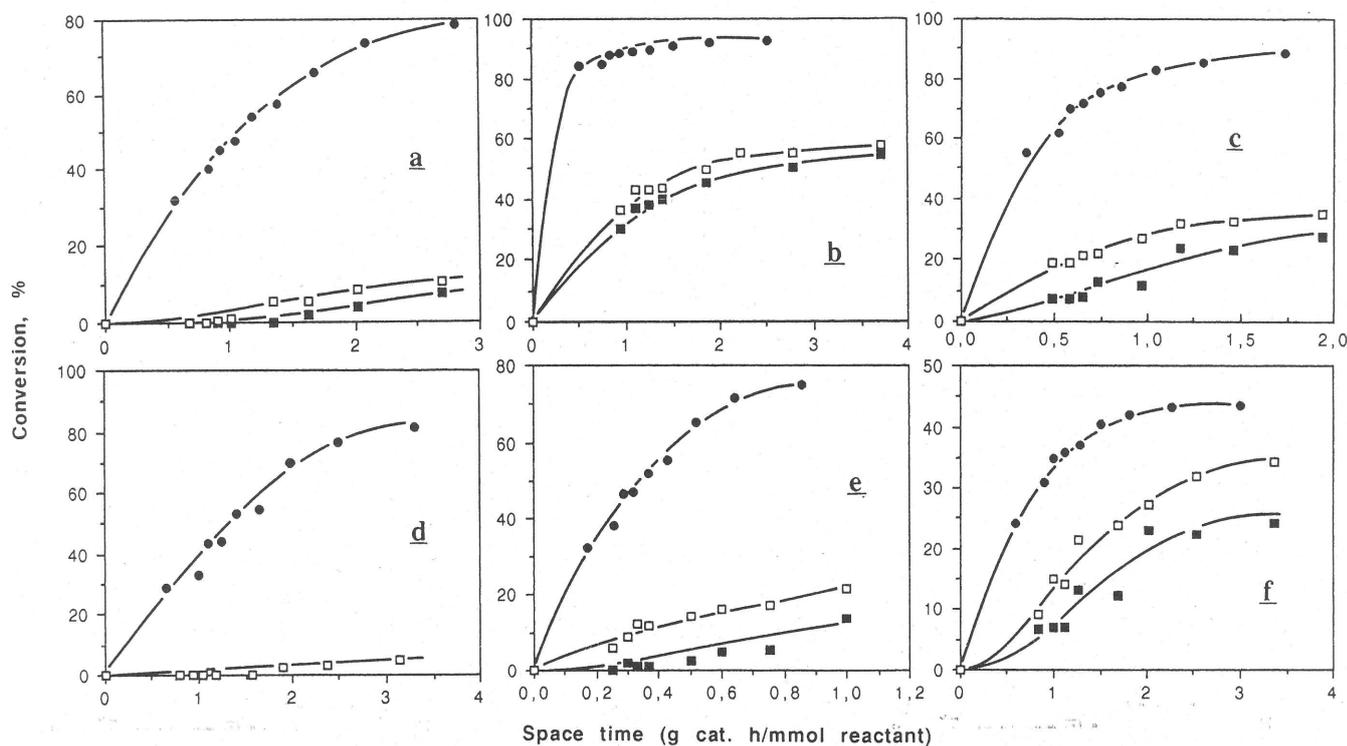


Figure 5 Conversion vs. space time: a, naphthalene; b, anthracene; c, fluoranthene; d, acenaphthene; e, phenanthrene; f, pyrene. Catalyst: ●, CC; ■, RM; □, ARM

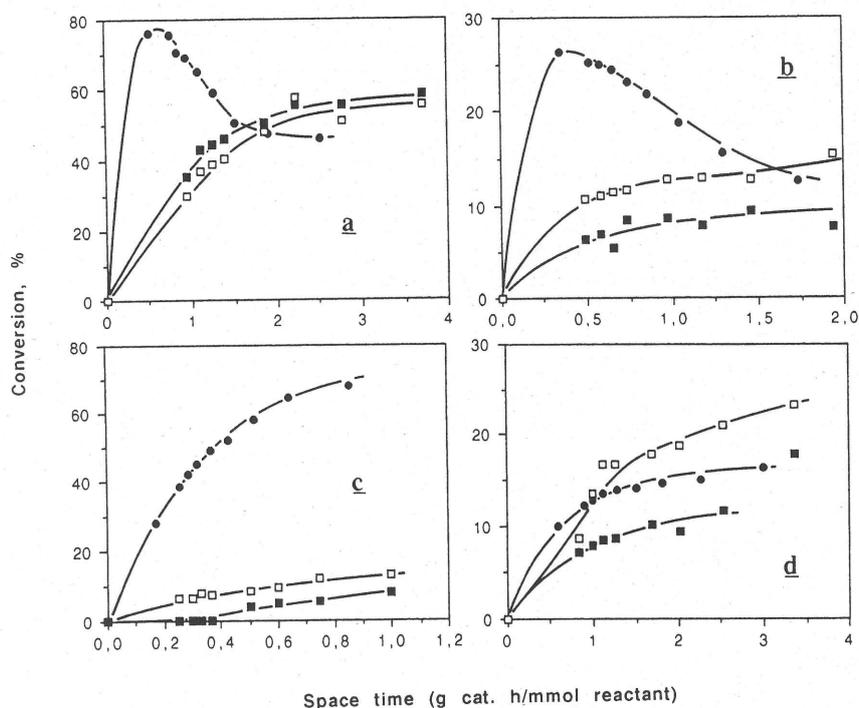


Figure 6 Conversion to hydroaromatics vs. space time: a, anthracene; b, fluoranthene; c, phenanthrene; d, pyrene. Catalyst symbols as in Figure 5

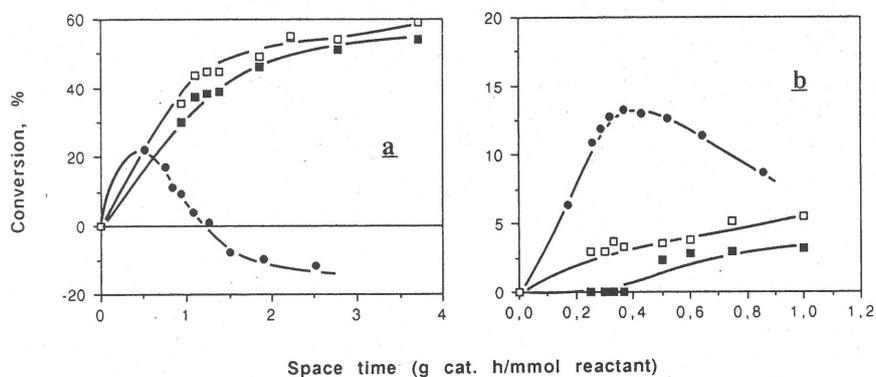


Figure 7 Conversion to (a) dihydroanthracene and (b) dihydrophenanthrene vs. space time. Catalyst symbols as in Figure 5

data for pyrene show a slightly higher selectivity for hydroaromatics with ARM, but more results are necessary if clear conclusions are to be drawn.

CONCLUSIONS

Red mud, although less active than a commercial Ni-Mo hydroprocessing catalyst, is active for the hydrogenation of anthracene oil. Its pore volume and catalytic activity can be increased by the pretreatment method proposed by Pratt and Christoverson⁵. The difference in activity between red mud, activated red mud and the commercial catalyst is smaller if conversion to hydroaromatics is considered instead of total conversion. Space time is an important factor in comparing catalyst activity. There is no clear evidence of difference in selectivity among red mud, activated red mud and the commercial catalyst.

ACKNOWLEDGEMENTS

This work was supported by FICYT (Foundation for the Support of Research in Applied Science and Technology, Asturias, Spain) and Industrial Química del Nalón (NalonChem), Asturias, Spain.

REFERENCES

- Garg, D. and Givens, E. N. *Ind. Eng. Chem. Process Des. Dev.* 1985, **24**, 66
- Sato, S., Morita, M., Hashimoto, T., Mitunori, I., Chiba, K. and Tagaya, H. *Fuel* 1989, **68**, 622
- Eamsiri, A., Jackson, R., Pratt, K. C., Christov, V. and Marshall, M. *Fuel* 1992, **71**, 449
- Klopries, B., Hodek, W. and Bandermann, F. *Fuel* 1990, **69**, 448
- Pratt, K. C. and Christoverson, V. *Fuel* 1982, **61**, 460
- Morita, M., Ikezoe, M., Hashimoto, T., Sato, S., Imaizumi, T. and Nihei, H. *Energy Dev. Japan* 1983, **6**, 187
- Morita, M., Sato, S. and Hashimoto, T. in Proceedings,

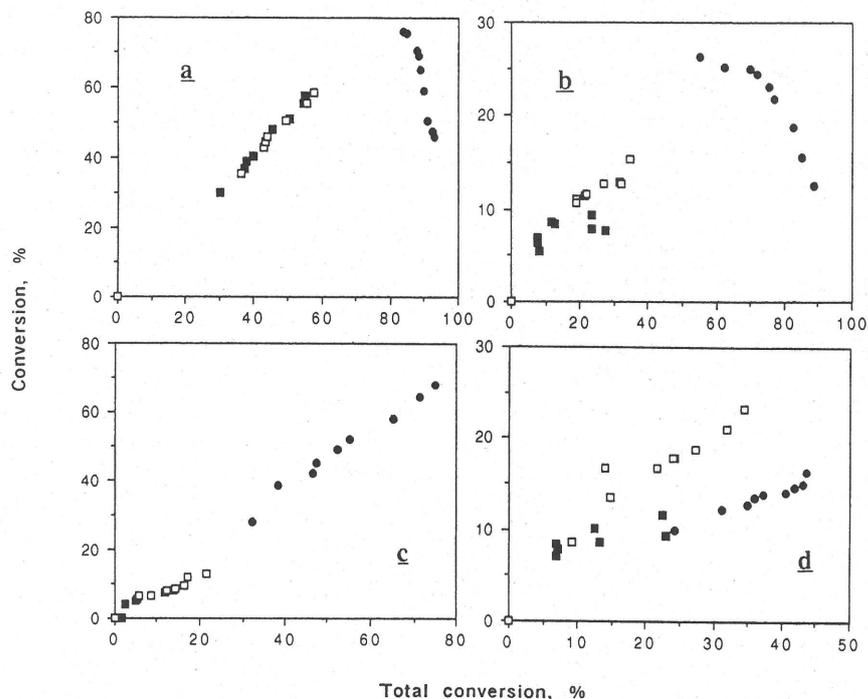


Figure 8 Conversion to hydroaromatics vs. total conversion: a, anthracene; b, fluoranthene; c, phenanthrene; d, pyrene. Catalyst symbols as in Figure 5

- | | |
|---|---|
| <p>International Conference on Coal Science, Butterworth-Heinemann, London, 1991, pp. 679-682</p> <p>8 Rosal, R., Diez, F. V. and Sastre, H. <i>Ind. Eng. Chem. Res.</i> 1992, 31, 2407</p> <p>9 Whitehurst, D. D., Mitchell, T. O. and Farcasiu, M. 'Coal Liquefaction', Academic Press, New York, 1980</p> <p>10 Moschopedis, S. E., Hawkins, J. G., Fryer, J. F. and Speight, J. G. <i>Fuel</i> 1980, 59, 647</p> <p>11 Yokono, T. and Marsh, H. in 'Coal Liquefaction Products: NMR Spectroscopic Characterization and Production Processes' (Ed. H. D. Schultz), Wiley, New York, 1983, pp. 125-138</p> <p>12 Curran, G. P., Struck, R. T. and Gorin, E. <i>Ind. Eng. Chem. Process Des. Dev.</i> 1967, 6, 166</p> <p>13 Mochida, I., Kishino, M., Sakanishi, K., Korai, Y. and</p> | <p>Takahashi, R. <i>Energy Fuels</i> 1987, 1, 343</p> <p>14 Mochida, I., Kazumasa, O. and Korai, Y. <i>Fuel</i> 1985, 64, 906</p> <p>15 Barrett, E. P., Joyner, L. J. and Halenda, P. P. <i>J. Am. Chem. Soc.</i> 1951, 73, 373</p> <p>16 Shabtai, J., Veloswamy, L. and Oblad, A. G. <i>Am. Chem. Soc. Div. Fuel Chem. Preprints</i> 1978, 23 (4), 107</p> <p>17 Sapre, A. V. and Gates, B. C. <i>Ind. Eng. Chem. Process Des. Dev.</i> 1981, 20, 68</p> <p>18 Wiser, W. H. Quarterly Progress Report DOE/ET/14700-9, US Department of Energy, 1982</p> <p>19 Lapinas, A. T., Klein, M. T., Gates, B. C., Macris, A. and Lyons, J. E. <i>Ind. Eng. Chem. Res.</i> 1987, 26, 1026</p> <p>20 Girgis, M. J., PhD Dissertation, University of Delaware, 1988</p> |
|---|---|