Competitive reactions catalyzed by NiMo-containing zeolites

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The rates of benzene hydrogenation and of n-heptane hydroconversion were measured simultaneously over a series of bifunctional catalysts. The catalysts were Y zeolites containing a Ni or Mo sulfide. At 280 °C, and for the more acidic catalysts, both rates appeared linearly correlated, suggesting that the hydrogenation function was limiting.

Keywords: Zeolites; dealuminated zeolites; sulfide catalysts: nickel-molybdenum sulfide; benzene hydrogenation; hydrocracking

Introduction

HY zeolites containing a NiMo or NiW sulfide behave as bifunctional catalysts and accordingly, they have found use in hydrocracking processes [1–3]. But the "metallic" function associated with the NiMo sulfide is considerably weaker than the one found for example in Pt/HY hydroisomerization catalysts [4,5]; hence, reactions have to be carried out under a high pressure of hydrogen. In these conditions, the rate of benzene hydrogenation can be used as a measure of the hydrogenation function. Preliminary studies have shown that this reaction followed a zero order down to rather low benzene pressures. Primary products were methylcyclopentane (MCP) and cyclohexane (CHX), but secondary products were also noted, mainly open-chain hexanes and propane [6,7].

The present paper reports the competitive reactions of benzene and n-heptane with hydrogen over a series of zeolite-supported sulfides. The objective is to compare the rates of hydrogenation and hydrocracking, over catalysts containing various metal sulfides (Ni, Mo or NiMo), or differing in acidity. The acidity depends on the Si/Al ratio, which was changed from 3 to 17 through steam-treatment of a NH_4Y zeolite, eventually followed by washing with HCl [8]. The compositions and textural properties of the solids are given in table 1. Further

Table 1
Characteristics of the catalysts: composition, surface area and micropore volume (oxide state); sulfur content (sulfide state)

Catalyst/support		NiO (wt%)	MoO_3 (wt%)	S_{BET} ($m^2\ g^{-1}$)	V_{mic} ($cm^3\ g^{-1}$)	Sulfur (wt%)
	HY-3	0	0	541	0.233	0
Ni	HY-3	4.25	0	637	0.273	0.87
Mo	HY-3	0	12.1	502	0.211	1.42
NiMo (a)	HY-3	3.5	13.6	449	0.196	3.30
NiMo (b)	HY-3	3.5	7.0	472	0.213	1.44
NiMo	HY-5.3	3.8	12.4	526	0.223	3.50
NiMo	HY-17	2.8	14.7	518	0.216	3.60
NiMo	Al_2O_3	3.5	14	214	< 0.01	3.85

spectral data appear in [9]. The catalytic flow reactor was pressurized with hydrogen (8 MPa). Each catalyst (0.16 g) was first sulfided at 320 ° C under feed A made of dimethyldisulfide (DMDS, 2% mol), benzene (24%) and heptane (74%).

1. Benzene as the only reactant

In this part, the reactant was benzene containing 2% DMDS (feed B). Earlier results obtained with catalysts using the HY-3 support [6] were complemented by measuring the initial rate of benzene hydrogenation over the NiMo/HY-5.3 and the NiMo/HY-17 catalysts, and at temperatures ranging from 250 to

Table 2
Product distribution (wt%) for the reaction of benzene and heptane over catalyst NiMo/HY-5.3

Reactant	Benzene (B)		Benzene + heptane (A)	
Temperature (° C)	280	320	280	320
W/F ($kg\ h\ mol^{-1}$)	0.084	0.067	0.134	0.125
P_{Be} (kPa)	69	74	10	10.4
P_{Hp} (kPa)	0	0	32.2	34.6
C_3	0.02	0.29	6.8	26.6
C_4	0.05	0.61	9.6	37.3
C_5	0.01	0.25	0.52	2.12
C_6	< 0.01	0.56	0.22	1.31
Total C_3-C_6 alkanes	0.08	1.71	17.1	67.4
MCP + CHX	0.9	2.0	0.56	0.67
Benzene	99.0	95.3	19.0	17.1
Iso-C_7	–	–	9.3	1.53
n-C_7	–	–	53.7	11.9
Alkylaromatics	< 0.01	1.02	0.32	1.48

Table 3
Reaction rates at 280 ° C (r, mmol h^{-1} kg^{-1}) and apparent activation energies (E, kJ mol^{-1}) for benzene hydrogenation. r_B and E_B: Benzene alone; r_A and E_A: Benzene + heptane

Catalyst/ support	Ni/ HY-3	Mo/ HY-3	NiMo (a)/ HY-3	NiMO/ HY-5.3	NiMO/ HY-17	NiMo/ Al_2O_3
Benzene alone						
r_B	10	36	116	104	242	331
E_B [b]	78	78	76	74	64	55
Benzene + heptane						
r_A	3	16	48	47	73	75
E_A [b]	8	82	104	105	78	76

[b] Estimated error on E is ±5 kJ mol^{-1}.

350 ° C. Over the latter catalyst, which has few acidic centers, benzene was converted into MCP and CHX only (yield x_{hyd}). Over the more acidic NiMo/HY-5.3, the yield of MCP and CHX regularly increased with temperature, but light alkanes, C_3 to C_5, appeared in low amount at 280 ° C (table 2) and developed rapidly above 300 ° C, together with alkylaromatics (toluene, ethylbenzene and xylenes) and open-chain hexanes.

These alkylaromatics arose mainly through methylation of benzene by the DMDS and, when the benzene partial pressure was lowered down to 10 kPa, they considerably decreased, as well as the cracked products, whereas the hydrogenation of benzene was not affected. Therefore, in the reaction at higher benzene pressure, ca. 70 kPa, a secondary transformation of the alkylaromatics is responsible for the major part of the C_3 to C_5 alkanes, and for some of the C_6 observed over the more acidic catalysts. This unfortunately made it almost impossible to determine to what extent the primary hydrogenation products, MCP and CHX, underwent hydrogenolysis at the highest temperatures.

Then, measurements were restricted to temperatures between 250 and 300 ° C, where products other than MCP and CHX were low. The activation energies were found similar for all zeolite catalysts (table 3), and exceeded the value 55 kJ mol^{-1} recorded for the NiMo/Al_2O_3. The rates of hydrogenation r_B measured at 280 ° C also appear in table 3. They were mainly a function of the metal sulfide (Ni, Mo or NiMo). In the series of NiMO zeolites, r_B also varied with dealumination. The catalyst with the lowest Al content was the most active, but the hydrogenation function of all NiMo zeolites appeared inferior to that of the NiMo/Al_2O_3.

2. Competition between benzene and heptane

When feed A was delivered onto the MeS/zeolite catalysts at the same flow rate as before (0.2 ml h^{-1}), heptane reacted much faster than benzene. At

340 ° C, heptane was almost completely cracked. Two product distributions observed with this feed are shown in table 2. The isomeric C_7 consisted mainly of methylhexanes and dimethylpentanes. Among the cracked products, propane and isobutane were dominant, and very little C_2 was formed, the molar ratio C_2/C_5 being 0.17. The whole of the C_3-C_6 was attributed to the cracking of heptane. The conversions of n-heptane into isomers (x_{iso}) and into cracked products (x_{cra}) over catalyst NiMo/HY-5.3 are plotted on fig. 1 for several temperatures, and at a constant flow rate. Compared with the Pt zeolite [10] the NiMo catalyst gave much less isomers. From the overall conversion ($x_{iso} + x_{cra}$), a first-order rate constant [11] could be deduced: the apparent activation energy for the conversion of heptane was found to be $E = 140$ kJ mol^{-1}.

For the catalysts with the lowest acidity, i.e. NiMo/HY-17 or Al_2O_3, the conversion of benzene into MCP and CHX increased with temperature in a regular way. However for the most acidic ones, including the NiMo/HY-5.3 (fig. 1) the conversion x_{hyd} kept constant above 300 ° C, or eventually decreased. Such a decrease of the primary hydrogenation products was not observed when benzene alone was reacted (feed B), but it may be noted that the conversions were then lower, due to a higher benzene flow rate.

In the range 250 to 290 ° C it was estimated that the secondary transformation of MCP and CHX did not substantially affect the rate of hydrogenation of

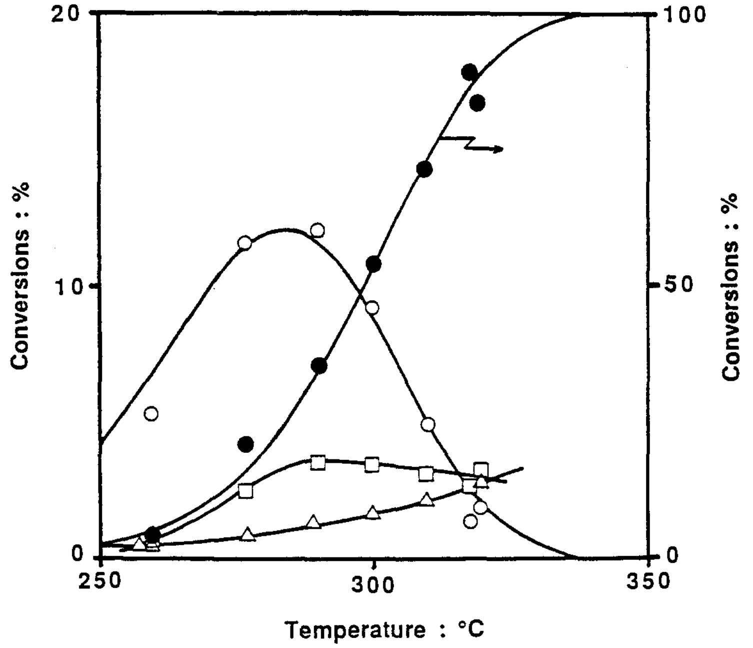

Fig. 1. Conversion of benzene and heptane (feed A) over catalyst NiMo/HY-5.3 at a constant flow rate: % heptane cracked (●); % heptane isomerized (○); % benzene hydrogenated (□). Conversion of benzene along (feed B): % benzene hydrogenated (△).

benzene in competition with heptane, r_A. As seen in table 3, the activation energies were nearly the same as in the absence of heptane, except for the Ni/HY-3 zeolite which was rapidly coked during the competitive reaction. But a comparison between the rates r_A measured at 280 °C and the values r_B recorded for benzene alone (table 3) shows that the hydrogenation of benzene is inhibited by heptane over all catalysts, including the $NiMo/Al_2O_3$. The inhibition factor r_B/r_A is slightly lower for the aluminium-rich zeolites, which are most acidic. Experiments performed with two further feed compositions agree with a rate law:

$$r_A = \frac{kP_{Be}}{P_{Be} + KP_{Hp}}.$$

Thus, heptane is likely to compete with benzene for the hydrogenation sites on the metal sulfide, whatever the acidity of the support. The inhibition of benzene by the alkane seems specific of the NiMo catalysts, since it was not observed when hexane reacted together with benzene over a Pt/Y catalyst [4].

3. Comparison between hydrogenation and hydrocracking

The rate of n-alkane hydroconversion over bifunctional catalysts such as Pt/zeolite usually depends on the metal loading or, more precisely, on the number of accessible metal sites [12]. For the MeS/zeolites investigated here, the rate constant for C_7 conversion may be plotted as a function of the rate constant for hydrogenation of benzene in competition with heptane (fig. 2). Both rates are measured at 280 ° C, and the conversion of heptane is strongly oriented toward cracking (85% selectivity).

For the catalysts using the same HY-3 support, and containing various sulfides (Ni, Mo, or two NiMo loadings), a linear relationship holds between the rates of hydrocracking and hydrogenation. The acidic function is largely predominant over these catalysts, and their activity is thus limited by the hydrogenation function, which is correctly evaluated by the competitive test with benzene. In the test with benzene alone, a synergy between Ni and Mo was found to occur [6]; it operates for hydrocracking as well.

Zeolites where the amount of NiMo is constant, but the Si/Al ratio rises from 3 to 5.3 are well placed on the same correlation. The acidic function remains predominant over these catalysts, because at moderate dealumination levels, the lower number of acidic sites is balanced by an increased strength [13]. As shown in table 1, the surface area and micropore volume increase upon introducing Ni in the HY-3 zeolite, and the decrease observed upon introducing Mo or NiMo may be accounted for by the mass increase of the zeolite catalyst. Then the crystallinity of the zeolite has not been damaged. It is even improved

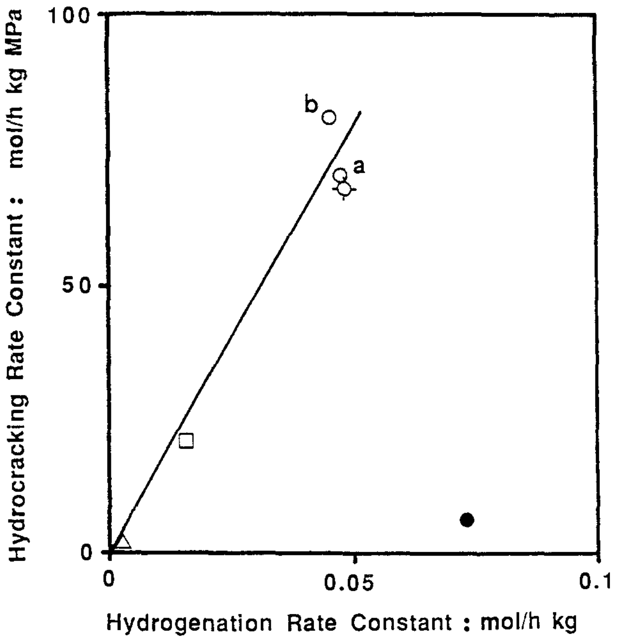

Fig. 2. Rate of n-heptane conversion versus rate of benzene hydrogenation for various catalysts (△) Ni/HY-3; (□) Mo/HY-3; (○) NiMo/HY-3 (a) and (b); (-ϕ-) NiMo/HY-5.3; (●) NiMo/HY-17.

by further dealumination and the circulation of the reactants is favoured by the creation of mesopores [8].

The NiMo/HY-17 catalyst presents a much lower rate of heptane conversion and stays well outside of the correlation. Its acidic function appears largely depressed. Yet the hydrogenating phase is likely to be well dispersed on account of the high rate of benzene conversion. For this particular catalyst the hydrogenation function is no longer limiting, but the low selectivity in heptane isomers (12% at the maximum) shows that it is still far from ideal hydrocracking [10] probably because the distance between acidic and hydrogenating centers is then large.

Acknowledgements

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