Catalytic activity of Co, Mo and CoMo supported on NaY zeolite: hydrodesulfurization of gas oil at high pressure

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Three series of Co/NaY, Mo/NaY and CoMo/NaY zeolite catalysts with variable metal content, prepared by a conventional impregnation method, were characterized by XRD, IR spectroscopy (oxide state) and acidity measurements (sulfide state), and tested in hydrodesulfurization (HDS) of gas oil at high pressure in the temperature range 275–350°C. The combined results of surface area, XRD and IR showed that in the catalysts with high metal loading a small loss in crystallinity and a partial blockage of the zeolite supercages were produced by Mo oxide species. The number of acid sites, which was lower for the Co/NaY than for the Mo/NaY catalysts, increased with increasing Co or Mo loading, but the strength of the acid sites was stronger for the Co/NaY series. HDS specific activities of the Co/NaY and Mo/NaY monometallic catalysts reached a maximum at very low loadings of Co (~ 0.10 at. nm^{-2}) or Mo (~ 0.16 at. nm^{-2}) by the double action of the metal sulfide species and the strong acid sites generated on the zeolite by the Co or Mo incorporation. In the binary CoMo/NaY catalysts, the synergy between Co and Mo species was significant for high Mo contents only.

Keywords: Zeolites; hydrodesulfurization; sulfide catalysts; cobalt/zeolite; molybdenum/zeolite; cobalt–molybdenum/zeolite; gas oil hydrotreating

1. Introduction

The use in hydrocracking processes of bifunctional catalysts based on ternary combinations of metal sulfides over alumina and zeolites has stimulated fundamental research on the binary metal sulfide–zeolite systems. The study of the metal sulfide–zeolite catalysts can help to understand the catalytic behaviour of the more complex ternary catalysts, in which it is very difficult to separate the contributions of the various active components, including that corresponding to the metal-modified zeolite component. In line with this, several studies on characterization and catalytic activity, especially for hydrodesulfurization (HDS) of thiophene, over Mo/zeolite and Co(Ni)Mo/zeolite catalysts have been reported (see, e.g. refs. [1–10]). In such studies the HDS activity was measured generally at atmospheric pressure and using thiophene as model compound representative of the sulfur compounds in industrial feedstocks. Under such operating conditions this type of zeolite-based catalysts underwent very rapid and continuous deactivation [6–11], which does not permit, in most of the cases, an appropriate comparison of catalysts. On the other hand, Qusro and Massoth showed that for alumina-supported molybdenum catalysts the atmospheric pressure test is less sensitive to catalyst HDS activity, i.e. it gives smaller differences in relative activity among catalysts than does the high-pressure test [12]. However, Ledoux et al. [13] have recently shown that, if the kinetics of the reaction is carefully applied, the HDS of thiophene at atmospheric pressure can correlate satisfactorily with the HDS of dibenzothiophene under industrial reaction conditions as long as the test is carried out under perfect kinetic conditions and, also, without mixing different families of catalysts.

In this study, the catalytic behaviour of three series of Mo/NaY, Co/NaY and CoMo/NaY catalysts for HDS of gasoil, measured under a high pressure of H_2 in order to minimize catalyst deactivation, was measured, and the suggested synergism between Co and Mo over NaY zeolite [4,6] under such reaction conditions was studied.

2. Experimental

2.1. CATALYST PREPARATION

The Co/NaY and Mo/NaY catalysts were prepared by wet impregnation of the starting NaY (Linde zeolite LSZ-52, Si/Al = 2.5) with appropriate solution concentrations of cobalt nitrate or ammonium heptamolybdate. Excess of solvent was removed by a rotary evaporator at 36°C for 3 h under reduced pressure. The binary CoMo/NaY catalysts were prepared by simultaneous impregnation of both cobalt nitrate and ammonium heptamolybdate solutions at the same conditions as the monometallic samples. Coprecipitation during simultaneous impregnation of Co and Mo was not observed. All impregnation solutions were adjusted to pH 6.0. The impregnated samples were dried at 120°C for 12 h and then calcined at 550°C for 4.5 h in air. The catalysts are designed as Co(#), Mo(#) and

Co(#)Mo(#), where the number in parenthesis is the nominal metal oxide content relative to 100 g of NaY.

2.2. CHARACTERIZATION

BET surface areas (0.005–0.1 p/p_0 range used) of the calcined catalysts were measured with a Micromeritic analyzer. X-ray diffraction (XRD) profiles of calcined catalysts were recorded on a Philips PW 1730 instrument using Ni-filtered Cu K_α radiation and standard conditions. Relative crystallinity was estimated by comparison of the peak intensities for *d*-spacings of 3.76, 3.28 and 2.285 Å of the catalysts to those of the starting NaY. Fourier transform infrared spectra (FTIR) of the calcined catalysts in the zeolitic framework vibration region (1400–400 cm^{-1}) were recorded with a Nicolet ZDX Fourier transform infrared spectrometer. The wafers used were prepared by mixing the catalyst with a definite amount of KBr powder and pelletizing.

Total surface acidity of sulfide catalysts was measured by a potentiometric method using *n*-butylamine in acetonitrile as titration solution and Ag/AgCl as electrode. The initial electrode potential indicates the maximum acid strength of the sites. Further details can be found in ref. [14].

2.3. HDS ACTIVITY MEASUREMENTS

Catalytic activity of the sulfide catalysts for HDS of gas oil (0.76 wt% sulfur) was measured in a fixed-bed flow microreactor operating at 20 kg cm^{-2} pressure, 16.4 h^{-1} liquid space velocity and several temperatures in the 275–300°C range. The catalyst was diluted in a 1/75 ratio with inert SiC particles of similar size, and presulfided in situ with a 10% (v/v) CS_2/gas oil mixture under 20 kg cm^{-2} for 2 h at 275°C. Liquid products were periodically collected, generally at 2 h on-stream at steady-state conditions. Sulfur analyses in the feedstock and products were obtained by volumetric titration with a Leco analyzer.

Catalytic activity, expressed in terms of apparent rate constant per catalyst volume (k), was calculated from the HDS conversion (% of sulfur removed) assuming second-order kinetics in the reactant. Specific rate (k_s) and intrinsic rate (k_i) were also calculated by dividing k by the surface area and the metal loading (at. nm^{-2}), respectively.

3. Results and characterization

3.1. CATALYST CHARACTERIZATION

The compositions and BET surface areas of the calcined catalysts are given in table 1. Although the BET surface areas of zeolites cannot be considered as absolute and correct values, they are satisfactory for a relative comparison since all sam-

Table 1
Composition, surface area and crystallinity of the catalysts in oxide state

Catalyst	Loading of cobalt		Loading of molybdenum		Surface area ($m^2\ g^{-1}$)	XRD crystallinity (%)
	CoO (%) [a]	Co (at. nm^{-2}) [b]	MoO_3 (%) [a]	Mo (at. um^{-2}) [b]		
NaY	–	–	–	–	770	100
Co(0.25)	0.25	0.026	–	–	750	n.d. [c]
Co(0.50)	0.50	0.052	–	–	740	n.d.
Co(1.0)	1.0	0.104	–	–	722	82
Co(2.0)	2.0	0.209	–	–	685	76
Co(3.0)	3.0	0.313	–	–	665	73
Co(4.0)	4.0	0.418	–	–	622	n.d.
Co(5.0)	5.0	0.522	–	–	610	n.d.
Mo(1)	–	–	1	0.054	710	98
Mo(2)	–	–	2	0.109	615	86
Mo(3)	–	–	3	0.163	568	75
Mo(6)	–	–	6	0.325	470	76
Mo(9)	–	–	9	0.488	376	67
Mo(12)	–	–	12	0.651	336	75
Co(1) Mo(3)	1	0.104	3	0.163	535	78
Co(2) Mo(12)	2	0.209	12	0.651	331	n.d.
Co(4) Mo(12)	4	0.418	12	0.651	479	n.d.
Co(5) Mo(12)	5	0.522	12	0.651	460	42

[a] Relative to the weight of NaY.
[b] Relative to the S_{BET} of NaY.
[c] n.d. = not determined.

ples are based on the same type of zeolite. A progressive reduction in surface area with increasing Co or Mo loading was observed. For samples with the highest Co or Mo loading, the surface area decreased down to ~ 21 or 56%, respectively, in comparison with the original NaY, which suggests, in principle, some breakdown of the framework and/or a partial blocking of the zeolite cavities.

In the XRD patterns no phase of Co or Mo, and only lines due to the original NaY, were observed. The relative crystallinity of the Co/NaY and Mo/NaY catalysts decreased moderately with increasing metal loading, especially for the latter catalysts. But these changes in crystallinity were not equal to the relative variations in surface area. As can be seen in fig. 1, in the case of the Co/NaY catalysts all data points lie above the line representing equal relative surface area and crystallinity, while for the Mo/NaY catalyst the contrary occurs, i.e. most of the points lie below that line. These disagreements between relative surface area and crystallinity values indicate that: (i) the loss in surface area is due mainly to the partial blockage of the zeolite cages by molybdenum oxide species, and also, in some cases (for very high Mo-containing samples), to some partial breakdown or perturbation of the zeolite lattice; and (ii) the loss in XRD crystallinity is to some extent apparent, and probably due to a dilution effect caused by the introduction of metal, particularly of Mo, into the zeolite. This conclusion is supported by the FTIR spec-

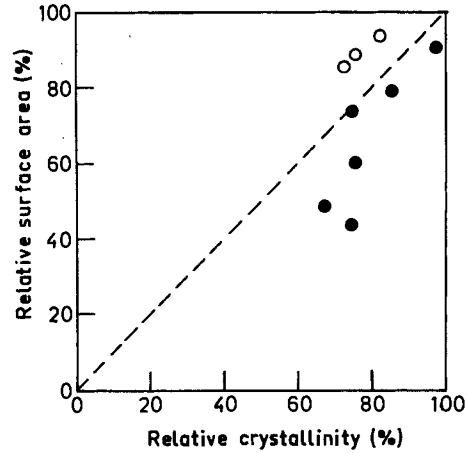

Fig. 1. Relative surface area versus relative crystallinity of (○) Co/NaY and (●) Mo/NaY catalysts.

tra (not shown) in the framework region of the calcined Co/NaY and Mo/NaY catalysts. For all samples the position and intensity of the structure-sensitive bands did not change significatively, suggesting that the loss of XRD crystallinity, if any, is rather a perturbation of the zeolite lattice by the Co or Mo introduction. In contrast to the present FTIR results, in the spectra of high Mo-containing NaY-supported catalysts apparently similar to these, but prepared without pH-control of the impregnation solutions, the structure-sensitive bands were very weak or nearly absent [2,6,7]. In these cases the presence of a higher amount of acid sites [6,7], which favor the interaction of molybdate anions with the zeolite framework, caused certain perturbation and loss of crystallinity. This difference in results shows the importance of the pH of the impregnation solution.

The results of total surface acidity of some sulfide Co/NaY and Mo/NaY catalysts are given in table 2. The acid site density, expressed as meq of *n*-butylamine per m^2 of catalyst, was much higher for the Mo/NaY catalysts than for the Co/NaY ones, and for both series acidity increased with Mo or Co loading. However, the Co/NaY catalysts presented sites with stronger acidity, i.e., higher initial electrode potential, E_i (mV), than the Mo/NaY catalysts. These differences in the number of acid sites and strength between the two series of catalysts are probably related to the origin and nature of the acid sites. It is noted that some Co^{2+} and NH_4^+ ions could be introduced into the zeolite by cation exchange during the impregnation step, which upon calcination would generate zeolite acidity. Such a process of cation exchange will very likely occur to a different extent for the Co/NaY and Mo/NaY catalysts. Furthermore, all catalysts except the Mo(12) exhibited two types of acid sites, very strong and less strong. The stronger sites are presumably Brønsted acids of the zeolite, and the less strong or with moderate strength are probably SH^- groups associated to the metal phase [9,10,15,16]. The acid sites

Table 2
Surface acidity of sulfided Co-, Mo- and CoMo-containing NaY catalyst

Catalyst	Total acidity (meq m^{-2}) × 10^3	Acid strength E_i [a] (mV)
Co(0.25)	2.27	+200 (vs) [b]
Co(0.50)	1.80	+200(vs)
Co(1.0)	3.40	+170 (vs)
Co(3.0)	4.15	+171 (vs)
Co(4.0)	5.05	+182 (vs)
Mo(1)	5.30	+ 70 (s)
Mo(2)	5.41	+ 47 (s)
Mo(12)	8.06	+108 (s)
Co(1)Mo(3)	8.31	+ 75 (s)

[a] Initial electrode potential.
[b] vs = very strong, s = strong.

density of the binary Co(1)Mo(3) catalyst was practically equal to the sum of the corresponding monometallic catalysts, the maximum acid strength being only moderately strong.

3.2. CATALYTIC ACTIVITIES

3.2.1. The effect of Co and Mo loading

Figs. 2a and 2b show the measured HDS activity for the Co/NaY and Mo/NaY series as a function of Co and Mo loading, respectively, at various reaction

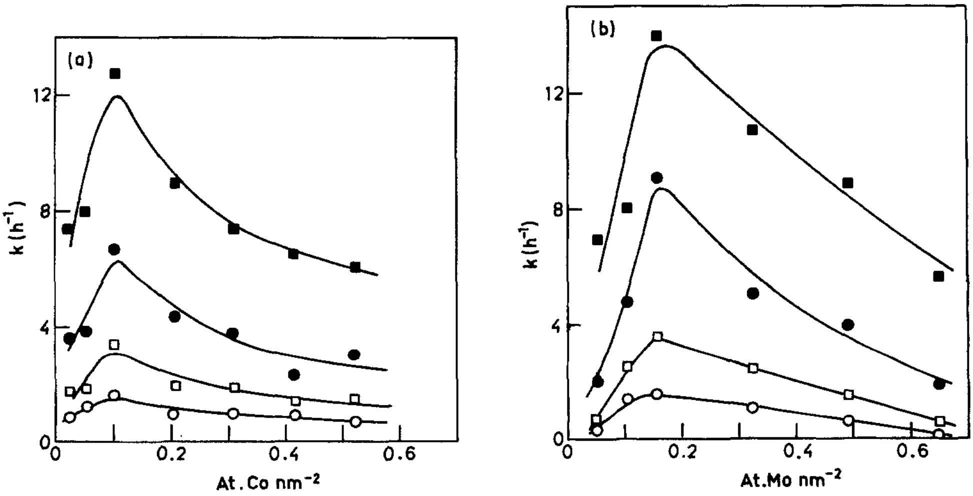

Fig. 2. The activity (per catalyst volume), k, for the HDS of gas oil at various reaction temperatures of (a) Co/NaY and (b) Mo/NaY catalysts as a function of the surface concentration of Co and Mo (atoms per nm^{-2} of support). Reaction temperatures (°C): (○) 350, (□) 325, (●) 300 and (■) 275.

temperatures. These results correspond to 2 h on-stream at steady state conditions. No appreciable deactivation was observed during ~ 20 h of testing, which is in contrast with the considerable catalyst decay found for HDS of thiophene at atmospheric pressure over similar Co- and Mo-containing zeolite catalysts [6]. The variation of the HDS activity (per catalyst volume), k, with metal loading was similar for both Co/NaY and Mo/NaY catalysts, with the appearance of a maximum in HDS activity, of a similar magnitude, at very low metal loadings (~ 0.10 at. Co nm^{-2} and ~ 0.16 at. Mo nm^{-2}), as compared to those generally reported for alumina-supported catalysts [17–20].

Comparison of the specific HDS activities (per m^2 catalyst), k_s, of the Co/NaY and Mo/NaY catalysts allows a clear distinction to be made between the two catalyst series. In fig. 3 the k_s values for 350°C are plotted against the metal loading. The two catalyst series show, in general, similar curves with a maximum, but at different metal loading and with different level of activity. Consequently, at low metal loadings (< 0.12 at. nm^{-2}) the Co/NaY catalysts are slightly more active for gas oil HDS than the Mo/NaY catalysts, whereas above this metal value, on the contrary, the latter catalysts are about a factor 2 more active than the former catalysts.

This crossingover in activity of the two catalyst series suggests different combinations of active sites, such as the associated to metal sulfides and the Brønsted acid sites of zeolites, for each of the series. Previous studies [6,7] have shown the ability of zeolite acid sites to catalyze the HDS of thiophene, and recent results over both

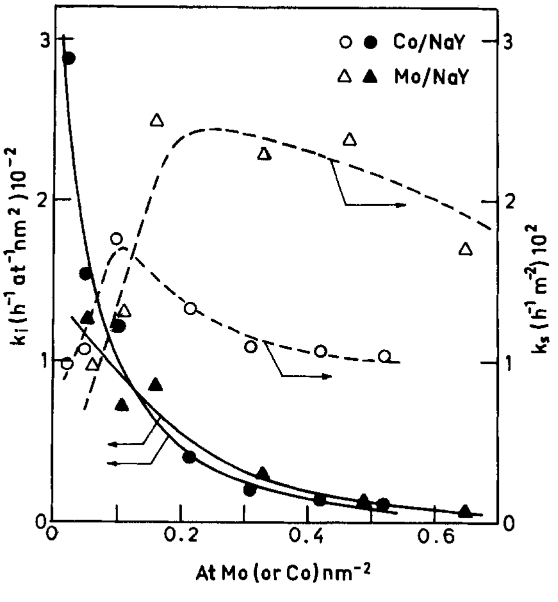

Fig. 3. The (- - -) specific activity, k_s, and (——) intrinsic activity, k_i, for HDS of gas oil at 350°C of Co/NaY and Mo/NaY catalysts versus surface concentration of Co and Mo.

acid and NaOH-treated ultrastable Y zeolites have confirmed the effect of zeolite acidity on such reaction [21]. Thus, the relatively higher specific HDS activity of the low Co loading catalysts is attributed to a negligible contribution of the metal sulfides to the HDS reaction at this metal loading, the measured specific HDS activity being mainly due to the stronger acid sites of the zeolite. The Co/NaY catalysts showed stronger acidity and higher relative rate of increase in total acidity than the Mo/NaY catalysts (table 2). With the increase in metal loading, the contribution of the metal sulfides to the HDS reaction became more important, especially for the Mo-containing catalysts. In the Co/NaY catalysts, this contribution of the cobalt sulfide to the HDS reaction may be minor since some Co^{2+} ions into zeolites are reduced [22], and possibly also sulfided, with difficulty. The observed decrease in specific HDS activity at high metal loading can be related with a decrease in metal sulfide dispersion and/or a minor accessibility of the reactants to the zeolite supercages caused by blockage of the metal phase, as the surface area and XRD crystallinity results suggested.

Considering intrinsic HDS activity k_i (irrespectively that a part of the reaction may occur over the acid sites, but these are associated to the metal loading), a monotonic decrease is observed with increasing metal loading (fig. 3). This activity trend is similar to that reported for thiophene HDS on Mo/TiO_2 [19,23] and Mo/ZrO_2 [19] catalysts, and significantly different from that found on Mo/Al_2O_3 [17–19] and Mo/SiO_2 [19] catalysts in which a maximum in intrinsic activity was observed at around 1.5 Mo at. nm^{-2}. This difference in activity trends of the various supports has been attributed: to differences of reducing molybdenum oxide, at low contents, on the different supports [20,23]; and also to differences in the morphology of MoS_2 structures, standing mainly vertically on Al_2O_3 and SiO_2 or lying flat on the surface of TiO_2 and ZrO_2 [19]. Similarly, the higher intrinsic activity of the Mo/TiO_2 catalysts as compared to the Mo/Al_2O_3 and Mo/SiO_2–Al_2O_3 catalysts has been attributed to smaller MoS_2 particles and their edge up binding on the TiO_2-supported catalysts [24]. Thus, by analogy with TiO_2-supported catalysts, the continuous decrease in intrinsic activity of fig. 3 suggests that the Co and Mo sulfided species formed in the zeolite have small size, and they may be homogeneously distributed and not strongly interacting with the zeolite lattice.

3.2.2. Synergetic effect

Fig. 4 shows the HDS activities (per catalyst unit volume) at 350°C of the binary CoMo/NaY catalyst in comparison with those for the single Co/NaY and Mo/NaY catalysts containing equal amounts of Co and Mo. Similar differences between the monometallic and binary catalysts were obtained for the other reaction temperatures. At low metal loading, the binary Co(1)Mo(3)/NaY catalyst was only slightly (~ 18%) more active than the unpromoted counterpart catalyst Mo(1)/NaY, and clearly less active than the sum of the individual Co and Mo catalysts separately, indicating that practically there was no cobalt promotion on HDS activity. This is probably because Co and Mo species are located in different

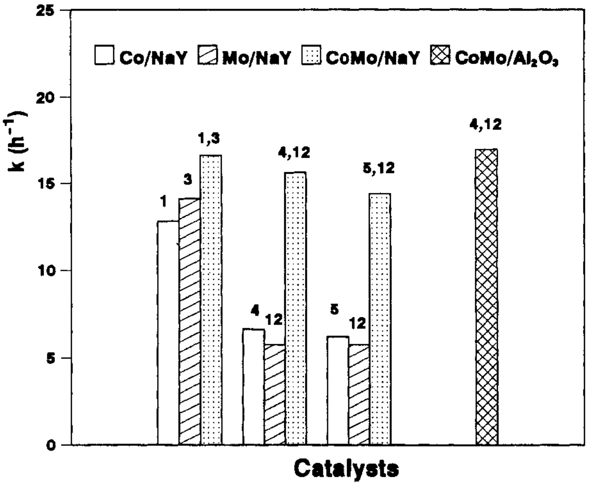

Fig. 4. The activity (per catalyst volume), *k*, of Co/NaY, Mo/NaY and CoMo/NaY catalysts, at comparable metal loadings, for gas oil HDS at 350°C. Comparison with a commercial CoMo/Al_2O_3 catalyst. Numbers on bars are oxide metal contents.

sites of the zeolite and, therefore, no interaction between the Co and Mo sulfided species may occur. It is noted that if in the catalyst preparation a part of the loaded Co were incorporated via exchange, at low loadings most of Co should be in the sodalite cage and the hexagonal prism according to the coordination preference of Co^{2+} ions [25]. However, for high Co and Mo loadings, i.e. 4–5 wt% CoO and 12 wt% MoO_3, the activities of the binary CoMo/NaY catalysts were almost threefold higher than those for their single Co- and Mo-counterparts, and slightly higher (~ 22%) than the sum of the individual Co and Mo catalysts separately. In this case, there was an appreciable synergism between Co and Mo, which might result because a part of Mo and Co are probably into the supercages and/or on the external surface of the zeolite and are, therefore, able to form a CoMoS phase upon sulfidation.

Finally, the HDS activity, *k*, of a commercial alumina-supported CoMo catalyst containing 4 wt% CoO and 12 wt% MoO_3 is also shown (for comparison purposes) in fig. 4. It is seen that the HDS activity (per catalyst volume) of the commercial CoMo/Al_2O_3 catalyst is comparable to those of the binary CoMo/NaY catalysts. However, if the comparison is done in terms of intrinsic activity (*k* per Mo at. nm^2) then the CoMo/NaY catalysts appear almost three times as high as that of the commercial CoMo/Al_2O_3 catalyst. The lower activity of the CoMo/Al_2O_3 catalyst reflects the much lower surface area of the alumina. The higher intrinsic HDS activity of the zeolite-supported catalysts could be attributed to a better dispersion and a more homogeneous distribution of the sulfided metal phase, as well as to some contribution of the zeolitic acid sites.

4. Conclusions

Our studies have shown that:

(i) Co, Mo and CoMo supported on NaY zeolite are active catalysts for HDS of gas oil at high pressure, not showing appreciable deactivation;

(ii) maximum HDS activity for the Co/NaY and Mo/NaY catalysts is reached at relatively very low metal loadings, in the 0.10–0.16 at. nm^{-2} range, due to the double action of the metal sulfide species and the strong acid sites on the zeolite catalysts;

(iii) synergetic effect between Co and Mo is observed only for samples containing high Mo loading, at low metal loadings Co and Mo species seem to be in different locations into the zeolite;

(iv) the HDS activity of the CoMo/NaY, in terms of catalyst volume is comparable to that of a commercial CoMo/Al_2O_3 catalyst, whereas in terms of intrinsic activity (per Mo at. nm^2) the zeolite-based catalyst appears more active than the alumina-based one.

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