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HDS and HDN activity of molybdenum and nickel–molybdenum catalysts supported on alumina–titania carriers

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Abstract

Alumina–titania supports containing 5–50 wt.% of TiO_2 were prepared by coprecipitation method using inorganic precursors (sodium aluminate and titanium chloride). DTA-TGA, XRD, SEM, TPD_{NH3}, and IR spectroscopy were used to characterise these materials. The study shows that the promoting effect of nickel on the HDS activity of molybdenum catalysts supported on $Al_2O_3TiO_2$ is significantly lower than that for molybdenum catalyst supported on Al_2O_3, and depends on the TiO_2 content. The SEM results show that in the case of rich Al support (20 wt.% of TiO_2) molybdenum was aggregated on the external surface of the catalyst, whereas it was uniformly dispersed on the external surface of alumina. Results also show that molybdenum is preferably supported on aluminum oxide. Application of $Al_2O_3TiO_2$ oxides enhances the HDN activity of nickel–molybdenum catalysts. The highest HDN efficiency was obtained for the $NiMo/Al_2O_3TiO_2$ catalyst containing 50 wt.% of TiO_2. HDN activity was found to depend on protonic acidity and anatase content.

Keywords: Hydrodesulphurization; Hydrodenitrogenation; Mo catalysts; NiMo catalysts; $Al_2O_3TiO_2$; Al_2O_3

1. Introduction

In recent years, the interest has been heightened in new supports for HDS catalysts, due to the need to produce ultra clean fuels in the refinery [1–4]. The use of oxides different from alumina such as TiO_2 [5–8] or ZrO_2 [9,10] has given promising results, although the low thermal stability and low surface area of these oxides have prevented their application as supports for industrial HDS catalysts. Due to these problems, considerable effort has been concentrated on the development of binary oxides. Recently, mesoporous TiO_2 with a high specific surface area of 120 m^2/g was used as a support for HDS catalysts [11–13]. Among mixed oxides, $Al_2O_3TiO_2$ systems were studied by number of investigators with respect to their physicochemical properties as well as supports for NiMo catalysts. The support characteristics depend on the preparation method and on the amount of Ti ions that are incorporated into γ-Al_2O_3. The reported investigations have been focused on the TiO_2 precursors, the TiO_2 incorporation method [14–18] and the content of TiO_2 in the $Al_2O_3TiO_2$ binary supports [19–23]. An overview of literature on the $Al_2O_3TiO_2$ binary oxides is given in [24,25]. To prepare effective HDS catalysts it is necessary to gain knowledge about the influence of the support nature on the promotional effect of Co/Ni on molybdenum catalysts.

In the present study, we examined $Al_2O_3TiO_2$ oxides prepared by coprecipitation of inorganic precursors (sodium aluminate and titanium chloride). The influence of the amount of titania (5–50 wt.%) on the HDS and HDN activity of the catalysts, as well as on their physicochemical properties was determined. The promoting effect of nickel on the $Mo/Al_2O_3TiO_2$ catalysts was also studied. The catalytic performance of molybdenum and nickel–molybdenum catalysts supported on $Al_2O_3TiO_2$ was investigated with reference to the Mo/Al_2O_3 and $NiMo/Al_2O_3$ catalysts. For preparation of Al_2O_3 and $Al_2O_3TiO_2$ supports the same precursor of alumina was used.

2. Experimental

2.1. Preparation of supports and catalysts

Al_2O_3 and $Al_2O_3TiO_2$ were synthesized using sodium aluminate and titanium chloride. The synthesis was carried out

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by the coprecipitation method at 70 °C and pH 9. After precipitation, pH was decreased to 7. Supports containing TiO_2 were coprecipitated by a two-step method. In the first step, titanium tetrachloride paralleled the dosage of sodium aluminate. In the case of supports containing 5 wt.% of TiO_2 (support 5N), 10 wt.% of TiO_2 (support 10N), and 20 wt.% of TiO_2 (support 20N), the excess amount of sodium aluminate was reacted with nitric acid, which was included as the third stream for this purpose. In the case of support containing 50 wt.% of TiO_2 (support 50N), ammonium hydroxide was used as the third stream for the precipitation of the excess amount of titanium tetrachloride. Aluminium hydroxide support 0N was synthesized by the same method as it was used for $Al_2O_3TiO_2$ oxides containing 5–20 wt.% of TiO_2. The precipitates were washed to remove NO_3^- and Cl^- ions. The hydroxides were dried at 110 °C, peptized with a HNO_3 solution and then extruded, dried and calcined. The thermal treatment of the supports and catalysts involved the following steps: drying (20 °C for 12 h, 50 °C for 2 h, 80 °C for 2 h, 110 °C for 8 h) and calcination (200 °C for 1 h, 300 °C for 1 h, 400 °C for 1 h, 450 °C for 3 h). The conventional two-step impregnation of the extrudates was performed with a water solution of ammonium heptamolybdate (loading of 16 wt.% of MoO_3) and nickel nitrate (loading of 3 wt.% of NiO). The thermal treatment of the molybdenum (0K-2, 5K-2, 10K-2, 20K-2, 50K-2) and nickel–molybdenum (0K, 5K, 10K, 20K, 50K) catalysts was carried out under the same conditions as for the extruded supports.

2.2. Methods

Thermal analysis was carried out using a J.G.Perkin-Elmer derivatograph at temperatures ranging from 50 to 1000 °C. The DTA and TGA signals were obtained at the rate of sample heating 10 and 40°/min, respectively. The reference substance was alumina.

XRD measurements were performed using a Siemens D500 line power diffractometer, with Cu Kα radiation.

The surface area and pore volume of the supports and catalysts were determined by nitrogen adsorption at 78 K, using a Sorptomatic 1900 apparatus.

Acidity of the samples was determined by temperature programmed desorption of ammonia (TPD_{NH3}), pyridine chemisorption and cumene cracking. The NH_3 adsorption was carried out for samples calcined in situ in the stream of argon up to 550 °C. The conditions for TPD_{NH3} were as follows: heating rate, 10°/min; argon flow, 20 cm^3/min; temperature range, 180–550 °C. Acid sites (defined as weak, medium and strong) were calculated in terms of the amount of ammonia desorbed up to 300 °C, over the temperature ranges of 300–450 and 450–550 °C, respectively.

For IR studies, the samples were pressed in thin wafers and pretreated in situ in the IR cell in vacuum at 530 °C for 1 h. In the IR experiments, pyridine was sorbed at 170 °C for 20 min. Physically adsorbed pyridine was evacuated under the same conditions. The extinction factors for the determination of the concentration of Brönsted (1545–1550 cm^{-1}) and Lewis (1445–1450 cm^{-1}) acid sites were 0.07 and 0.10 $cm^2/\mu mol$, respectively. The IR spectra were recorded using a Brucker 48PC spectrometer.

Cumene cracking was conducted at 370 °C. The catalysts were pretreated at 400 °C for 2 h before the reaction.

Hydrotreating of a diesel oil fraction containing 0.85 wt.% of S and 321 ppm of N (density, 0.8560 g/cm^3; IBP, 236 °C; $T_{360\ °C}$ = 90 vol.%) was carried out in a high pressure flow fixed bed reactor (temperature, 300–360 °C; pressure, 4 MPa; LSHV, 3 h^{-1}; H_2:feed ratio, 350:1 Nm^3/m^3). Before activity measurements, the catalysts (grain size of 0.75–1.02 mm) were activated via the following procedure: reduction followed by sulphidation, using a diesel oil fraction (S, 0.85 wt.%) at 340 °C, 4 MPa, 3 h^{-1}, 350:1 Nm^3/m^3.

The activity of the catalysts was also evaluated in terms of thiophene conversion at atmospheric pressure by the pulse method (400 °C, 4.5 vol.% of C_4H_4S, column: Reoplex 10% PNAW). Presulphiding treatment of the catalysts was performed with a H_2–C_4H_4S mixture over the temperature range of 250–400 °C.

3. Results and discussion

Fig. 1A shows the DTA and TGA profiles of the supports treated in oxidizing atmosphere. The curves have different plots for the supports containing TiO_2, and they strongly depend on the titania amount. Table 1 summarizes the weight loss of the supports calculated on the basis of the TGA results.

The aluminium–titanium and aluminium hydroxides showed a very strong endothermal effect centred at 100–110 °C, due to the elimination of the adsorbed H_2O. This effect was more pronounced for aluminium-titanium hydroxides. Considering the loss of weight at 200–500 °C, it was found that the incorporation of 10 wt.% of TiO_2 only negligibly influenced the surface dehydroxylation of the alumina. In the case of aluminium–titanium hydroxide containing 50 wt.% of TiO_2, the removal of structural hydroxyl groups was much lower. Increasing the TiO_2 content from 10 to 50 wt.% reduces the loss of weight from 13.8 to 9.5 wt.%.

Fig. 1B shows the XRD patterns for the supports calcined at the temperatures corresponding to the minima of the endothermal effects of the DTA curves. X-ray diffraction spectra of the samples calcined at the temperature corresponding to the endothermal effect at 260 °C show only the peak originated from the boehmite. The diffractograms of the supports calcined at temperatures corresponding to the next endothermal effect (370–400 °C) show lines confirming the presence of γ-Al_2O_3. The XRD results for the 50N support calcined at 400 °C can be explained in terms of the boehmite phase transformation and titania phase transformation from amorphous to the anatase one. From the DTA curves, it can be seen that TiO_2 strongly influenced on phase transformation at higher temperature range (above 600 °C). The comparison of the DTA of 0N sample with DTA of 10N sample shows that the addition of 10 wt.% of TiO_2 leads to shift of the endothermal peak to considerably higher values (about 100°).

Ramirez et al. [20] studied $Al_2O_3TiO_2$ prepared by the coprecipitation of isopropoxides. Their X-ray examinations

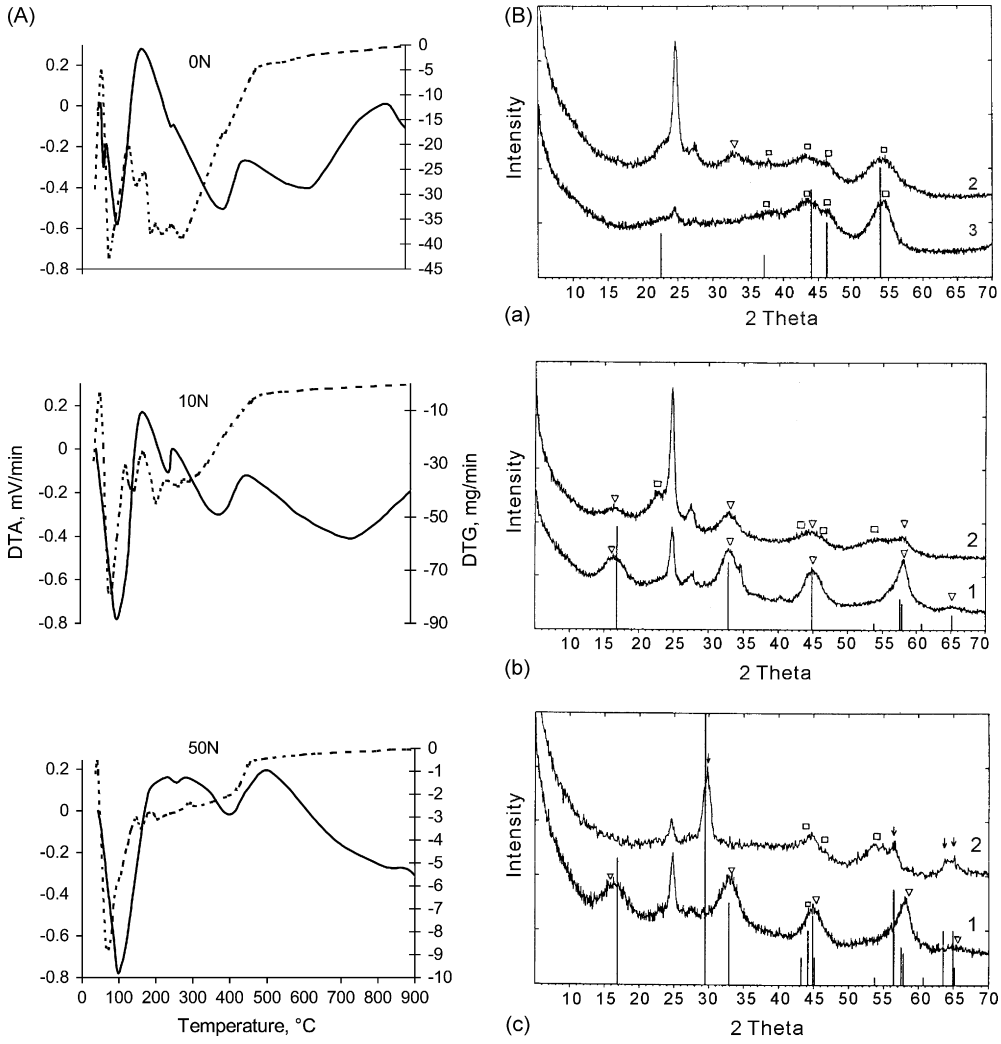

Fig. 1. Influence of TiO_2 content on phase composition of $Al_2O_3TiO_2$ supports. (A) DTA and DTG analysis of 0N, 10N and 50N supports. (B) X-ray diffractograms of the supports. (a) Support 0N calcined at 390 °C (2) and 650 °C (3), where □: γ-Al_2O_3; ∇: boehmite. (b) Support 10N calcined at 260 °C (1) and 370 °C (2), where □: γ-Al_2O_3; ∇: boehmite. (c) Support 50N calcined at 260 °C (1) and 400 °C (2), where □: γ-Al_2O_3; ∇: boehmite; ↓: anatase.

revealed that anatase was present in $TiO_2/Al_2O_3TiO_2$ samples with the molar ratios higher than 0.7. Considering the intensity of the anatase X-ray patterns, the authors suggested that only a small portion of the titania in the samples (including those with a high titania content) was present in the form of well crystallized anatase. When the alumina–titania supports were prepared using inorganic precursors, anatase was observed for $TiO_2/Al_2O_3TiO_2$ samples with molar ratio of 0.5 (Fig. 1B(c)). On the basis of the results obtained, it can be suggested that the influence of the TiO_2 content on the formation of anatase depends not only on the method of $Al_2O_3TiO_2$ oxides preparation, but also on the Al and Ti ions precursors as well as on the gelation conditions.

Table 1
Loss of weight obtained from TGA curves

Support	Loss of weight (%)		
	>200 °C	200–500 °C	500–800 °C
0N	11.9	14.8	1.6
10N	16.2	13.8	0.0
50N	16.9	9.5	0.7

The comparison of the Al_2O_3 and $Al_2O_3TiO_2$ supports indicates that the incorporation of TiO_2 has no influence on the pore volume distribution (pore radius of 1.5–100 nm). For all samples, the maximum of the mesopore volume corresponds with that of radius 3.2 nm.

It was also stated that the incorporation of 10 or 20 wt.% of TiO_2 had only a negligible effect on the specific surface area of the supports and catalysts (Table 2). When the TiO_2 content was increased to 50 wt.%, the support and catalyst surface areas were about 15% higher as compared to the samples containing lower amounts of TiO_2. It was found that with $Al_2O_3TiO_2$ binary oxides, the incorporation of molybdenum and nickel brought a decrease of the surface area to a greater extent than with Al_2O_3 (Table 3).

TPD of NH_3 results show that the incorporation of titanium dioxide by the coprecipitation method using $TiCl_4$ as a precursor yields supports and catalysts of a higher total acidity (Fig. 2A, Table 3). It is also evident that the variations in the

Table 2
Properties of supports and NiMo catalysts

Properties	Support				Catalyst			
	0N	10N	20N	50N	0K	10K	20K	50K
Surface area (m^2/g)	290	301	317	343	255	259	262	288
Pore volume (cm^3/g)	0.71	0.73	0.70	0.80	0.57	0.62	0.62	0.73
Mean pore radius (nm)	3.7	4.1	3.8	4.0	3.3	3.8	3.9	4.3
Acidity (mmol NH_3/g)	0.65	0.78	0.76	0.73	0.82	0.97	0.94	0.91

Table 3
Cumene conversion over NiMo catalysts

Catalyst	Conversion (%)	Yield (mol%)			Brösted acid sites (μmol/g)	Lewis acid sites (μmol/g)
		Propene	Benzene	α-Methylstyrene		
0K	10.88	0.11	3.16	7.61	35	560
10K	12.04	0.09	4.25	7.70	60	510
50K	15.25	0.02	9.80	5.43	70	390

titanium dioxide content have no significant effect on the total acidity and on the acid site strength distribution. A similar effect of the TiO_2 content on the specific surface area and acidity (TPD_{NH3}) of the supports obtained by the coprecipitation of aluminium and titanium isopropoxides has been reported by Olguin et al. [21].

Fig. 2B shows the results of pyridine adsorption experiments. The band between 1447 and 1460 cm^{-1} (typical of coordinately bonded pyridine) is present in all samples, but the Lewis acid sites concentration displays lower values for the catalyst 50K. From pyridine chemisorption it becomes evident that the amount of TiO_2 ranging from 10 to 50 wt.%, slightly influences the concentration of Brönsted acid sites. The concentration of Brönsted acid sites for catalyst 50K was higher than that for the alumina supported catalyst (catalyst 0K). Ramirez et al. [20] have found that $Al_2O_3TiO_2$ supports prepared by coprecipitation of titanium and aluminium isopropoxides do not show Brönsted acidity. The acidity evaluation by Lahousse et al. [26] showed that the $Al_2O_3TiO_2$ samples prepared by hydrolysis of alkoxides presented Brönsted acidity. In our study, the presence of Brönsted acid sites was estimated also in terms of catalyst activity in cumene cracking (Table 3). Benzene yield in the products of cumene cracking over the $NiMo/Al_2O_3TiO_2$ catalyst (50 wt.% of TiO_2) was three times as high (conversion of 15.25 mol%) as that over the $NiMo/Al_2O_3$ catalyst (conversion of 10.88 mol%). It can be therefore concluded that the alumina and titania precursors, as well as the TiO_2 content play a role in the formation of Brönsted acid sites.

Fig. 3 presents the catalytic activity results of $Al_2O_3TiO_2$ and Al_2O_3 supported catalysts. As shown by these data (Fig. 3A) a synergistic effect between nickel and molybdenum, well known for sulphided $NiMo/Al_2O_3$ catalysts, is not evident for the catalysts with higher amount of TiO_2. The conversion of

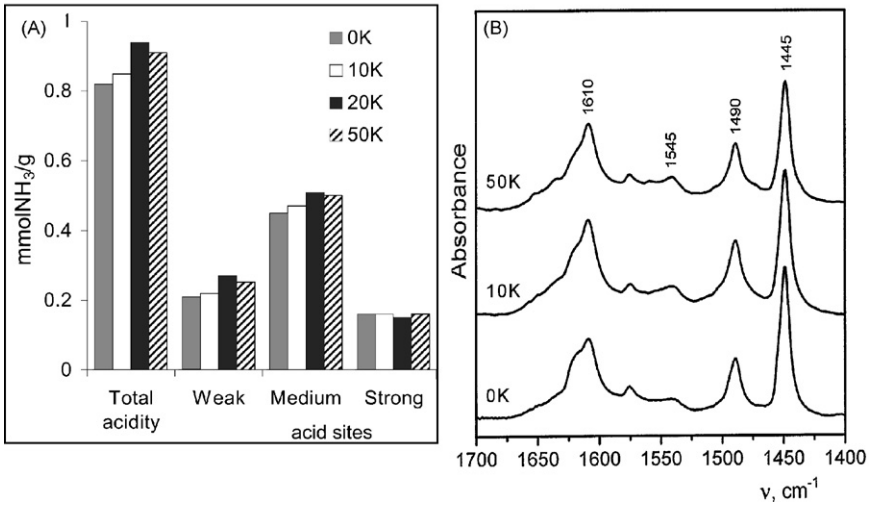

Fig. 2. The influence of the TiO_2 content on acidity of $NiMo/Al_2O_3TiO_2$ catalysts. (A) Total acidity and acid sites distribution—TPD NH_3. (B) IR spectra of pyridine adsorbed at 170 °C.

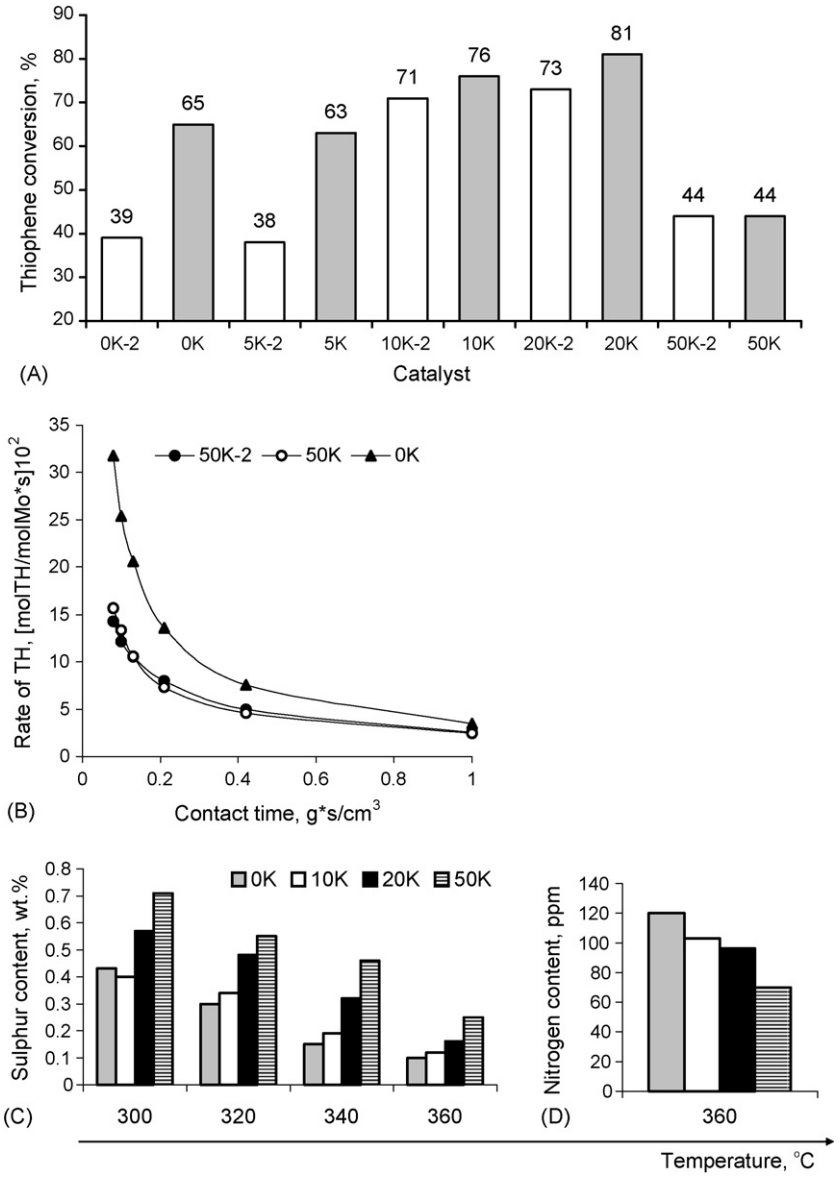

Fig. 3. The effect of TiO_2 content on the HDS and HDN activity. (A) Hydrogenolysis of thiophene over molybdenum and nickel–molybdenum catalysts. (B) Influence of the temperature on the HDS of diesel oil fraction. (C) Effect of time contact on the rate of thiophene HDS. (D) HDN of diesel oil fraction.

thiophene over Mo/Al_2O_3 (0K-2) and $Mo/Al_2O_3TiO_2$ (5K-2) amounts to 38%. The promoting effect of nickel on the 0K-2 and 5K-2 catalysts is evident. In this case thiophene conversion over nickel–molybdenum catalysts was found approximately 25% higher than over molybdenum catalysts. Thiophene conversion with $NiMo/Al_2O_3TiO_2$ catalysts containing 10 and 20 wt.% of TiO_2 was only slightly higher (5–8%) than with molybdenum catalysts. For the catalyst supported on Al_2O_3-TiO_2 containing 50 wt.% of TiO_2 (50K-2 and 50K) no synergistic effect was noticed. This observation is confirmed by detailed investigations of thiophene HDS rate versus contact time (Fig. 3B). The influence of contact time on the rate of thiophene HDS reaction for 50K catalyst is not as significant as in the case of 0K catalyst.

The same trend as we observed for Mo and NiMo supported on Al_2O_3 and $Al_2O_3TiO_2$ was described by Ramirez et al. [27] for cobalt promoted Mo/Al_2O_3 and $Mo/Al_2O_3SiO_2$. The authors proposed that difference in activity is related to the MoS_2 crystallite size and crystallite orientation on the Al_2O_3 and $Al_2O_3SiO_2$ support surface.

Recently Coulier [28] and Ramirez et al. [29] have reported that sulphided Ti-species can act as a promoter in the same way as Co and Ni, although less effectively. The results of our work (Fig. 3A) demonstrate that promoting effect of sulphided Ti-species depends on TiO_2 content in the supports. The activity of the $Mo/Al_2O_3TiO_2$ (10 wt.% of TiO_2) and $Mo/Al_2O_3TiO_2$ (20 wt.% of TiO_2) catalysts was higher than that of Mo/Al_2O_3 catalyst. Thiophene conversion over molybdenum catalysts decreases with the further increase of TiO_2 content from 20 wt.% (catalyst 20K-2) to 50 wt.% (catalyst 50K-2), but it is still remains slightly higher than the conversion obtained for Mo/Al_2O_3 (catalyst 0K-2). The results reported by Araki et al.

[30] evidenced that highest catalytic activity is due to high dispersion of edge-bonded MoS_2 clusters and that aggregation of edge-bonded MoS_2 clusters led to the reduction of activity.

Although limited data were obtained by scanning electron microscopy it could be observed that in the case of rich Al support (20 wt.% of TiO_2) molybdenum was aggregated on the external surface of the catalyst, whereas it was uniformly dispersed on the external surface of alumina support. Results show also that molybdenum on $Al_2O_3TiO_2$ is preferably supported on aluminium oxide (Fig. 4).

The results of HDS and HDN of diesel oil fraction are given in Fig. 3C and D, respectively. With the temperatures applied, the HDS activity of TiO_2 containing catalysts decreased as follows: 10 K > 20 K > 50 K. For example, at 340 °C, sulphur content in the products obtained over the 50K catalyst was about 0.14 wt.% higher than over the 20K catalyst and about 0.25 wt.% higher than in the presence of the 10K catalyst. According to a series of HDS tests, it was also found that the influence of the HDS temperature on the sulphur level in the products depend on TiO_2 content. The temperature exerted a highest influence on HDS efficiency when the support contained 50 wt.% of TiO_2 was applied. Among TiO_2-containing catalysts, the lower promoting effect of nickel established on the basis of thiophene hydrogenolysis may be an

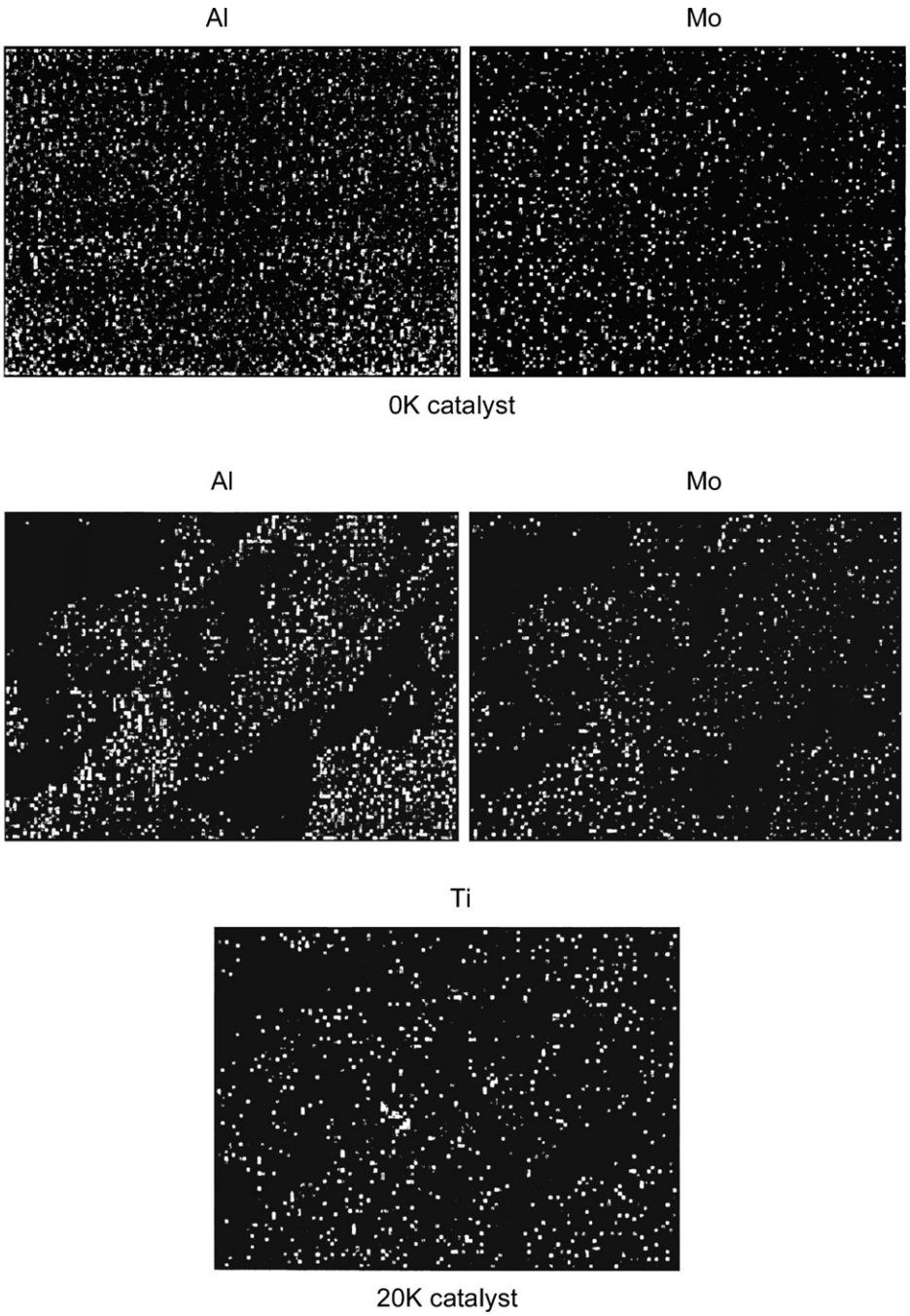

Fig. 4. Photomicrographs of the catalysts: distribution of aluminium, molybdenum and titanium on the surface of the catalysts.

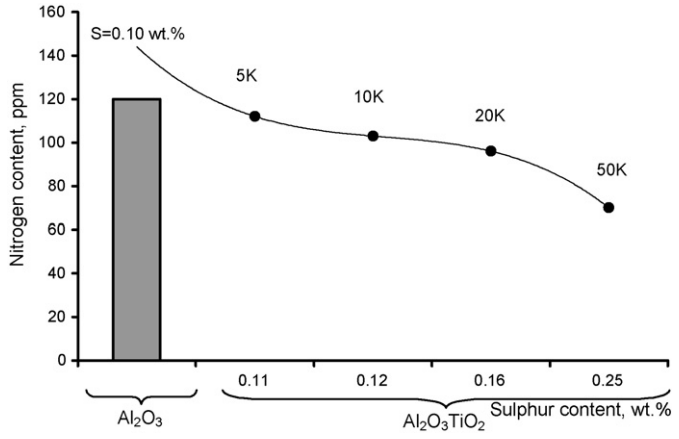

Fig. 5. The correlation between HDS and HDN activities (hydrotreating of diesel oil fraction at 360 °C) for the catalyst with different TiO_2 content.

important factor for the decrease in the HDS activity of the 20K and 50K catalysts.

The differences in the activities of the catalysts observed in the HDS of the diesel oil fraction and thiophene might be related to the nature of the feedstock, partial pressure of H_2 and H_2S [31] and activation temperature [30]. Bourgue et al. found that for CoMo and NiMo catalysts supported on $Al_2O_3TiO_2$, the HDS activity trends with support composition was completely different between thiophene and gas oil tests.

The influence of the support on the HDN activity of the NiMo catalysts (Fig. 3D) was studied at 360 °C (4 MPa, 3 h^{-1}, 350:1 Nm^3/m^3). The results indicate that the use of $Al_2O_3TiO_2$ binary supports increases the HDN activity of nickel–molybdenum. The highest HDN activity was that of the 50K catalyst (50 wt.% of TiO_2). Our results demonstrate that increasing both Brönsted acidity and anatase content account for the increase of HDN activity of NiMo/$Al_2O_3TiO_2$ catalysts. Hydroprocessing reactions such as hydrodesulphurization and hydrogenation are strongly inhibited by the nitrogen compounds naturally occurring in petroleum-derived fractions because of the competitive adsorption onto the catalyst surface, even at low concentration [32]. Wei et al. found that degree of the influence of nitrogen compound (pyridine) on HDS activity of NiMo/$Al_2O_3TiO_2$ and Al_2O_3 is different [16]. Results show that the correlation between HDS and HDN activities depends on TiO_2 content (Fig. 5). Comparing this with Fig. 3A, in which we demonstrate influence of TiO_2 content on promoting effect of nickel on thiophene conversion we can postulate that HDN and HDS over NiMo/$Al_2O_3TiO_2$ are carried out on different sites.

4. Conclusions

The purpose of this work was to investigate the influence of TiO_2 content on the HDS and HDN activity of molybdenum and nickel–molybdenum catalysts. The $Al_2O_3TiO_2$ oxides were prepared by coprecipitation of sodium aluminate and titanium chloride. The activity in thiophene conversion and hydrodesulphurization of diesel oil fraction on NiMo/$Al_2O_3TiO_2$ clearly indicates that promoter is less efficient for the molybdenum catalysts supported on $Al_2O_3TiO_2$ containing above 10 wt.% of TiO_2. This is a clear indication that the promoter is not well associated to molybdenum to form the NiMoS phase. The presence of titania was found to influence the molybdenum aggregation on the external surface of the catalyst supported on $Al_2O_3TiO_2$ rich in Al (20 wt.% of TiO_2) oxide. The promoting effect of sulphided Ti-species on activity is more pronounced for Mo/$Al_2O_3TiO_2$ (10–20 wt.% of TiO_2). Thiophene conversion for the catalysts supported on Al_2O_3-TiO_2 with the further increase of TiO_2 content from 20 to 50 wt.% becomes slightly higher than for Mo/Al_2O_3 catalyst. The highest HDN efficiency was obtained over the NiMo/$Al_2O_3TiO_2$ catalyst containing 50 wt.% of TiO_2. The HDN activity was found to depend on protonic acidity and anatase content. It has been also shown that the acidity of $Al_2O_3TiO_2$ oxides prepared by coprecipitation of inorganic Al_2O_3 and TiO_2 precursors was higher than that of Al_2O_3. Pyridine chemisorption evidently shows that the amount of TiO_2 ranging from 10 to 50 wt.%, slightly influences the concentration of Brönsted acid sites. The TiO_2 influences the phase transformation of boehmite and alumina.

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