TiO_2-supported Mo model catalysts: Ti as promoter for thiophene HDS?

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Received 18 September 2001; accepted 3 January 2002

The combination of thiophene hydrodesulfurization (HDS) activity measurements and X-ray photoelectron spectroscopy on flat model systems of sulfided HDS Mo catalysts showed that sulfided Ti-species can act as a promoter in the same way as Co and Ni, although less effectively. This explains the higher thiophene HDS activity and hydrogenation selectivity of Mo/TiO_2 compared with Mo/Al_2O_3, while for Ni-promoted Mo catalysts the difference between the two supports is negligible.

KEY WORDS: hydrodesulfurization; X-ray photoelectron spectroscopy (XPS); thiophene; TiO_2; sulfidation; molybdenum.

1. Introduction

Sulfided CoMo and NiMo catalysts are widely used for hydrotreating processes [1]. Due to environmental legislation an increasing demand is put on these hydrotreating catalysts. One way to improve these catalysts is by optimizing the support. The strength of the metal sulfide–support interaction has a large influence on the dispersion and morphology of the active catalysts, while the support may also influence the electronic properties of the catalyst [2,3].

Al_2O_3 is the most commonly applied support for hydrotreating catalysts, due its strong interaction with the active phase leading to highly dispersed MoS_2 [1]. However, TiO_2 [4–7] and TiO_2-Al_2O_3 [8–10] mixed oxide supports have shown promising results. For example, it was found by several authors that Mo/TiO_2 catalysts are considerably more active (factor 1.6–4.4, depending on reaction and reaction conditions) in hydrodesulfurization (HDS) compared with Mo/Al_2O_3 [4–9,11]. More recent papers also report higher HDS activities on Mo/TiO_2 for (substituted) dibenzothiophenes [12–14]. Although there is general agreement on the superior catalytic activity of Mo/TiO_2, various explanations for this phenomenon are given. Most authors explain the difference in activity by differences in metal–support interaction, which leads to differences in *e.g.* dispersion [9,15,16], sulfidation [8,10,13] or morphology [5,7]. However, it still remains unclear what the real explanation is. Recent papers by Vissenberg *et al.* [11] and Ramirez *et al.* [17] concluded that differences in dispersion, sulfidability or morphology are not the cause of the difference in HDS activity between Mo/TiO_2 and Mo/Al_2O_3. These authors stated that most likely TiO_2 itself induces a synergistic effect that enhances the HDS activity [11,17]. Ramirez *et al.* [17] propose that partial reduction or sulfidation of TiO_2 leading to Ti^{3+} species can act as a promoter to the MoS_2 phase.

There also exists some confusion concerning the interaction of Mo with the various supports and the resulting reducibility or sulfidability of Mo. Some authors report a strong interaction of Mo with TiO_2, resulting in incomplete sulfidation at high temperatures [5,15,16,18]. However, Okamoto *et al.* [6] and Zhaobin *et al.* [8] observed that titania facilitates the sulfidation of Mo and as a result Mo is sulfided completely at 673 K. A recent paper by Vissenberg *et al.* [11] concluded that despite the strong Mo–TiO_2 interaction, Mo could be sulfided completely.

Another intriguing feature is the difference in promotion effect for Co- or Ni-promoted TiO_2- and Al_2O_3-supported catalysts. Ramirez *et al.* [5] found that CoMo/TiO_2 was more active in thiophene HDS than CoMo/Al_2O_3. However, compared with the unpromoted catalysts, the promotion effect of Co was strikingly lower for TiO_2 (factor ~3) than for Al_2O_3 (factor ~8). Ng and Gulari [4] found the same modest increase in activity of TiO_2-catalysts due to Co. Vissenberg *et al.* [11] found for both Co- and Ni-promoted Mo catalysts higher promotion factors for Al_2O_3 than for TiO_2. Due to the different values for promotion factors, some authors find promoted Mo/Al_2O_3 catalysts to be more active in HDS than promoted Mo/TiO_2 catalyst [11,19,20], while others find the opposite [5,21]. Different reactions and reaction conditions may explain these differences. The low promotion effect in the case of CoMo/TiO_2 catalysts supports the idea of TiO_2 acting as a promoter, as proposed by Ramirez *et al.* [17].

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1011-372X/02/0400-0149/0

In this paper we study the thiophene HDS activity of unpromoted and Ni-promoted Mo model catalysts supported on various substrates. Combining these results with activity measurements and angle-dependent XPS on Ti-promoted Mo catalysts, we come to the conclusion that Ti sulfides partially during sulfidation and these sulfided Ti-species act as a promoter in the same way as Co or Ni do. Furthermore, sulfided Ti-species increase the hydrogenation activity as evidenced by relatively higher amounts of butane after thiophene HDS.

2. Experimental

Catalysts were prepared on planar SiO_2, Al_2O_3 and TiO_2 model supports. Planar SiO_2 and Al_2O_3 model supports were prepared as described in earlier papers [22,23]. Alumina model supports were prepared in a UHV system ($P \approx 1 \times 10^{-7}$ mbar) by evaporation of Al in an O_2 atmosphere ($P_{O_2} \approx 1.2 \times 10^3$ mbar) on pre-cleaned Si wafers with a deposition rate of the oxide layer of 0.1 nm/s. XPS measurements on the alumina model supports gave an Auger parameter of 1461.5 eV, which corresponds to γ-Al_2O_3 [24]. TiO_2 model supports were prepared by evaporation of Ti in an O_2 atmosphere on an Si(100) wafer under similar conditions as Al_2O_3. The Ti $2p_{3/2}$ binding energy of the TiO_2 layer, i.e. 458.8 eV, indicated that TiO_2 was present [24]. UV–Raman spectra show that the TiO_2 mainly consists of anatase (not shown). The thickness of the evaporated layers is approximately 5 nm, with a surface roughness of 0.5 nm as obtained from AFM. After evaporation the model supports were kept in distilled water.

Nickel and molybdenum were applied by spincoating the model supports at 2800 rpm in N_2 with aqueous solutions of either nickel nitrate or ammonium heptamolybdate. The mixed-phase catalysts were prepared by spincoating with aqueous solutions containing Ni and Mo. The concentrations of Ni and Mo solutions were adjusted to result in a loading of 2 at/nm^2 Ni and 6 at/nm^2 Mo. The dried catalysts were calcined in air at 450 °C for 30 min.

Ti-promoted catalysts were prepared by spincoating the SiO_2/Si substrate with an ethanol solution containing Ti(IV)-isopropoxide (98+%, Acros), resulting in a Ti loading of 2 at/nm^2. Ti-promoted Mo catalysts were prepared by consecutive spincoating of Mo and Ti respectively.

Sulfidation was carried out in a glass reactor under flow of 60 ml/mm of 10% H_2S/H_2 at 1 bar. The catalysts were heated at a rate of 5 °C/min to the desired temperature and kept there for 30 min. After sulfidation the reactor was cooled to room temperature under a helium flow and brought to a glove box, where the samples were mounted in a transfer vessel for transport to the XPS under N_2 atmosphere. XPS spectra were measured on a VG Escalab 200 Mk II, equipped with a standard dual source, a monochromatized Al K_α source and a five channeltron detector. Measurements were done at 20 eV pass energy. Charge correction was performed using the Al 2p peak of Al_2O_3 at 74.4 eV and the Ti $2p_{3/2}$ peak of TiO_2 at 458.8 eV as a reference [24].

Model catalysts were tested in batch mode thiophene HDS. The thiophene HDS reaction has been proven to be a useful model reaction for the sulfur removal from crude oil [1]. The reaction is carried out under standard conditions for thiophene HDS (1.5 bar, 400 °C, 4% thiophene/H_2) [*e.g.* 6,11]. Model catalysts were presulfided at 400 °C for 30 min as described above. For more details on thiophene HDS on model catalysts, see references [22,23].

3. Results and discussion

Table 1 shows the thiophene hydrodesulfurization (HDS) activity after batch reaction at 673 K of unpromoted and Ni-promoted Mo model catalysts, supported on SiO_2, Al_2O_3 and TiO_2. The activity is expressed as total yield (%) of products per 5 cm^2 of catalysts after 1 h of batch reaction in 4% thiophene/H_2 at 673 K.

Table 1 clearly shows that for both unpromoted and promoted catalysts the activity increases in the order $SiO_2 < Al_2O_3 < TiO_2$. Unpromoted Mo/TiO_2 is almost twice as active in thiophene HDS as Mo/Al_2O_3, while for the promoted catalysts the activity is almost equal for Al_2O_3 and TiO_2. As a result the promotion factor of Ni is significantly lower for TiO_2 than for Al_2O_3, respectively a factor 5 and ~8 (see table 1). These results are in good agreement with those of Ramirez *et al.* [5] and Vissenberg *et al.* [11] on high surface area Co(Ni)Mo catalysts. Both unpromoted and promoted SiO_2-supported catalysts show significantly lower HDS activities compared with the other two supports. As a result of the very low HDS activity of Mo/SiO_2, the increase in activity due to Ni is the largest of all supports, *i.e.* a factor ~10.

Figure 1 shows the Mo 3d and S 2p XPS spectra of Mo/Al_2O_3 (A,B) and of Mo/TiO_2 (C,D) calcined at

Table 1

Thiophene HDS activity and promotion factors of unpromoted and Ni-promoted Mo-based model catalysts. Activity is expressed as yield of products after 1 h of batch reaction at 400 °C in 4% thiophene/H_2 per 5 cm^2 of catalyst

	Mo	NiMo	NiMo/Mo
SiO_2	0.11	1.07	9.7
Al_2O_3	0.37	2.84	7.7
TiO_2	0.6	3.2	5

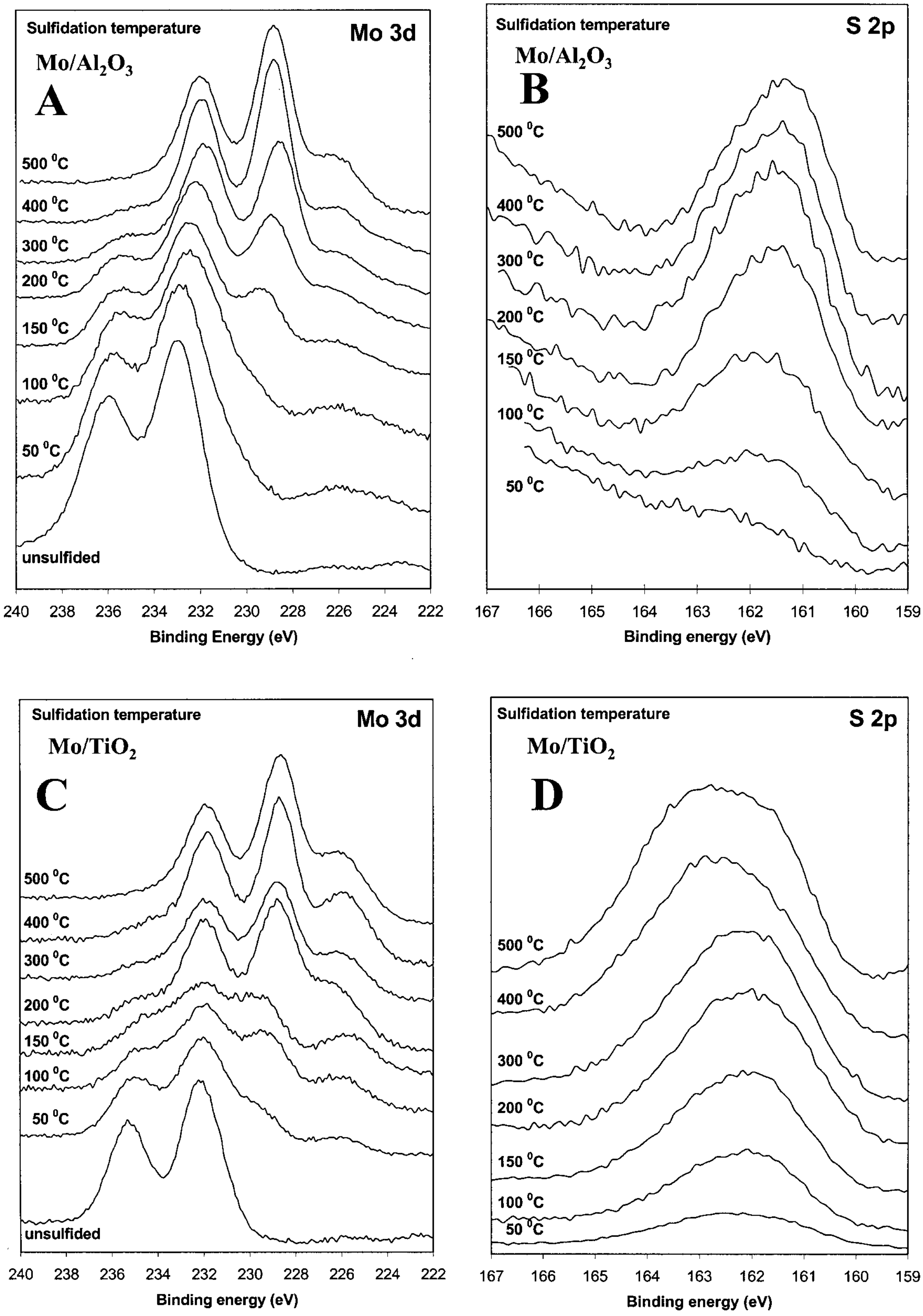

Figure 1. Mo 3d and S 2p XPS spectra of Mo/Al_2O_3 (A, B) and Mo/TiO_2 (C, D) model catalysts as a function of sulfidation temperature.

723 K and sulfided at various temperatures in 10% H_2S/H_2. The XPS spectra of Mo/SiO_2 have been described earlier [22,23,25]. The sulfidation of Mo starts around 323 K and is completed at 473 K. Due to the weak interaction of Mo with the SiO_2 support, the sulfidation of Mo is relatively easy and large particles and low dispersion of MoS_2 can be expected. Figure 1(A) and 1(B) show that the sulfidation of Mo/Al_2O_3 is much more

Table 2
Mo $3d_{5/2}$ and S $2p_{3/2}$ binding energies, degree of sulfidation, absolute S/Mo intensity ratios and Mo/support atomic ratios of oxidic and sulfided Mo model catalysts on various supports

	Mo_{ox} (eV)	Mo_{sulf} (eV)	S 2p (eV)	S 2p/Mo 3d	S 2s/Mo 3d	Mo 3d/X[a] 2p
Mo/SiO_2	232.8	228.9	161.8	0.40	~0.27	0.04
Mo/Al_2O_3	232.8	228.8 (86%) 230.8 (14%)	161.7	0.38	~0.25	0.13
Mo/TiO_2	232.6	228.6 (82%) 230.6 (18%)	161.8 163.6	0.9	~0.7	0.14

[a] X = Si, Al or Ti.

difficult. The sulfidation now starts around 473 K and is only complete at 773 K. Note that the sulfidation of Mo is incomplete at 673 K, the temperature at which the HDS activity is carried out. Fitting of the Mo 3d spectra at 673 K, shows that the major part of Mo is present as MoS_2, while still a significant part of Mo is present as Mo^{5+} species in an oxysulfidic environment (see table 2). Muijsers *et al.* [25] also reported the presence of Mo^{5+} oxysulfides during the sulfidation of Mo/SiO_2, although these species were already present at low sulfidation temperature and had a significantly higher Mo $3d_{5/2}$ binding energy, *i.e.* 231.5–232.0 eV. However, in Mo/Al_2O_3 the Mo^{5+} species are still present at high temperatures and therefore are most probably still attached to the alumina support, thereby stabilizing the MoS_2 slabs. Due to the interaction with the support, the chemical environment of the Mo^{5+} species is different compared with the species reported by Muijsers *et al.* [25], which can explain the difference in binding energy. As a result of the strong interaction with the alumina support, the MoS_2 particles are well dispersed over the support [1–3]. This would explain the difference in HDS activity between Mo/SiO_2 and Mo/Al_2O_3 as observed in table 1. The S 2p spectra confirm that the sulfidation starts around 373 K and is complete at high sulfidation temperatures. The S $2p_{3/2}$ binding energy of 161.7 eV corresponds with S^{2-} ligands [24].

The sulfidation of Mo in Mo/TiO_2 proceeds similar as that of Mo/Al_2O_3. Figure 1(C) shows that although the sulfidation starts at a lower temperature for TiO_2 than Al_2O_3, *i.e.* 323 K *versus* 373 K, for both supports the sulfidation is incomplete at 673 K and only complete sulfidation is reached at 773 K. As can be seen also in table 2, after sulfidation at 673 K the degree of MoS_2 formation is 82% for Mo/TiO_2, which is almost equal to Mo/Al_2O_3, *i.e.* 86%. The remaining part of Mo can be fitted with an Mo 3d state with Mo $3d_{5/2}$ binding energy at 230.6 eV, which can be assigned to Mo^{5+} species in an oxysulfidic environment, as was also observed for Al_2O_3, as described above.

We attributed these species earlier to Mo species partially connected to the support. This incomplete sulfidation of Mo in Mo/TiO_2 agrees well with Ramirez *et al.* [5] and Leliveld *et al.* [15,16], who also found Mo–$O_{support}$ linkages at high sulfidation temperatures. However, other authors observed complete sulfidation of Mo [6,11]. In general, the sulfidation of Mo at higher temperatures of Mo/Al_2O_3 and Mo/TiO_2 is quite similar, from which we conclude that significant differences in dispersion are not likely. The almost equal Mo 3d/Al 2p and Mo 3d/Ti 2p atomic ratios in table 2 confirm this. Hence, the difference in HDS activity cannot be explained by differences in sulfidability or dispersion.

The Mo $3d_{5/2}$ binding energies of fully oxidic and sulfidic Mo do not show significant differences between the various supports (see table 2). However, the S 2s and

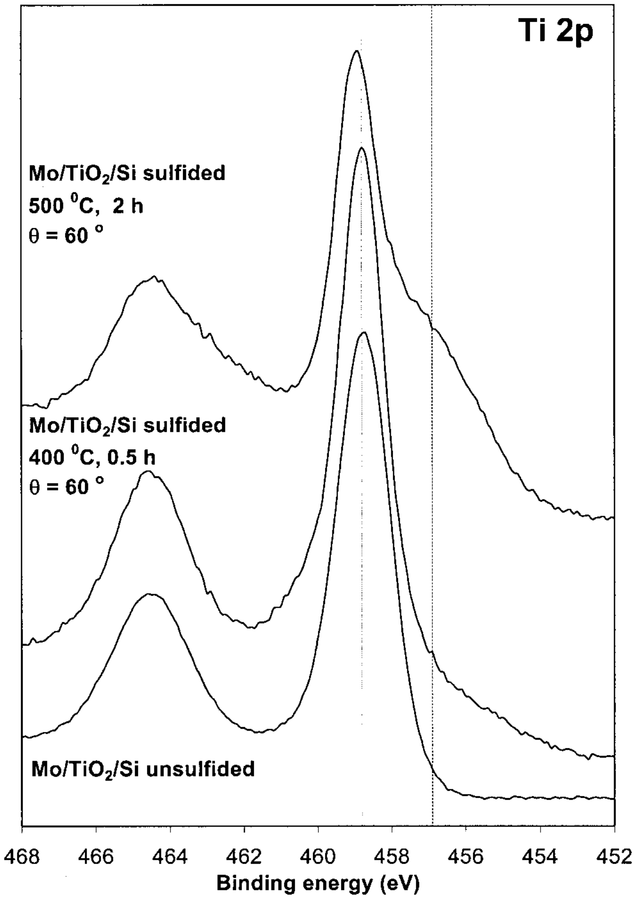

Figure 2. Angle dependent Ti 2p XPS spectra of Mo/TiO_2 model catalysts sulfided at high temperatures.

S 2p spectra of sulfided Mo/TiO_2 show some strange features (see figure 1). Although the positions of the S 2s peaks for the different Mo catalysts are equal at first sight, the relative contribution is significantly different. Table 2 shows that for Mo/SiO_2 and Mo/Al_2O_3 the absolute S 2s/Mo 3d peak ratio is ~0.25, while for Mo/TiO_2 this ratio is much higher, *i.e.* 0.7. The S 2p spectra in figure 1(B) and 1(D) and the fit results in table 2 show that for Mo/TiO_2 at higher temperatures more than one sulfur species is present. Besides the S $2p_{3/2}$ peak at 161.8 eV, corresponding to S^{2-} in MoS_2 [24], a second doublet with S $2p_{3/2}$ binding energy at 163.9 eV is present. These sulfur species are absent for either Mo/Al_2O_3 or Mo/SiO_2 [22,23] (see figure 1). While the support is the only difference between the catalysts, the excess of sulfur found with XPS must be caused by the TiO_2 support.

Figure 2 shows the Ti 2p spectra of Mo/TiO_2 after different sulfidation treatments. The XPS spectra have been measured at a high angle (*i.e.* 60°) between analyzer and sample, to increase the surface sensitivity [26]. The spectrum of unsulfided Mo/TiO_2 shows a single Ti 2p doublet with a Ti $2p_{3/2}$ binding energy at 458.8 eV, corresponding to TiO_2 [24]. After sulfidation at 673 K for 30 min a small shoulder at low binding energy is visible. This shoulder is more pronounced after sulfidation at 773 K for 2 h. For comparison, the Ti 2p spectrum of a bare TiO_2 support after sulfidation at 773 K for 2 h is shown in figure 3(A). In this spectrum the extra Ti 2p doublet at lower binding energy is even better visible. The corresponding S 2p spectra of the TiO_2 support in figure 3(B) show that after sulfidation of the bare TiO_2 support sulfur species are present with S $2p_{3/2}$ binding energy around 163.4 eV, which agrees well with the extra S 2p doublet observed in figure 1 and table 2 for Mo/TiO_2. The extra Ti 2p doublet at high sulfidation temperature has a Ti $2p_{3/2}$ binding energy of 456.7 eV, which can be ascribed to TiO_xS_y species possibly with a 3+ oxidation state [27]. Hence we can conclude that TiO_2 is able to sulfide partially at high temperatures. The small shoulder after sulfidation of Mo/TiO_2 at 673 K shows that sulfidation of TiO_2 also takes place for Mo/TiO_2 catalysts used for thiophene HDS measurements (table 1).

To elucidate the influence of the sulfided Ti species on the activity of TiO_2-supported catalysts, model catalysts were prepared by spincoating Ti or TiMo from solutions on to a SiO_2 support (see section 2). Figure 3(A) and 3(B) show the Ti 2p and S 2p spectra of Ti/SiO_2 and TiMo/SiO_2 model catalysts unsulfided and sulfided at 673 K. The Ti 2p spectra of the unsulfided catalysts show a

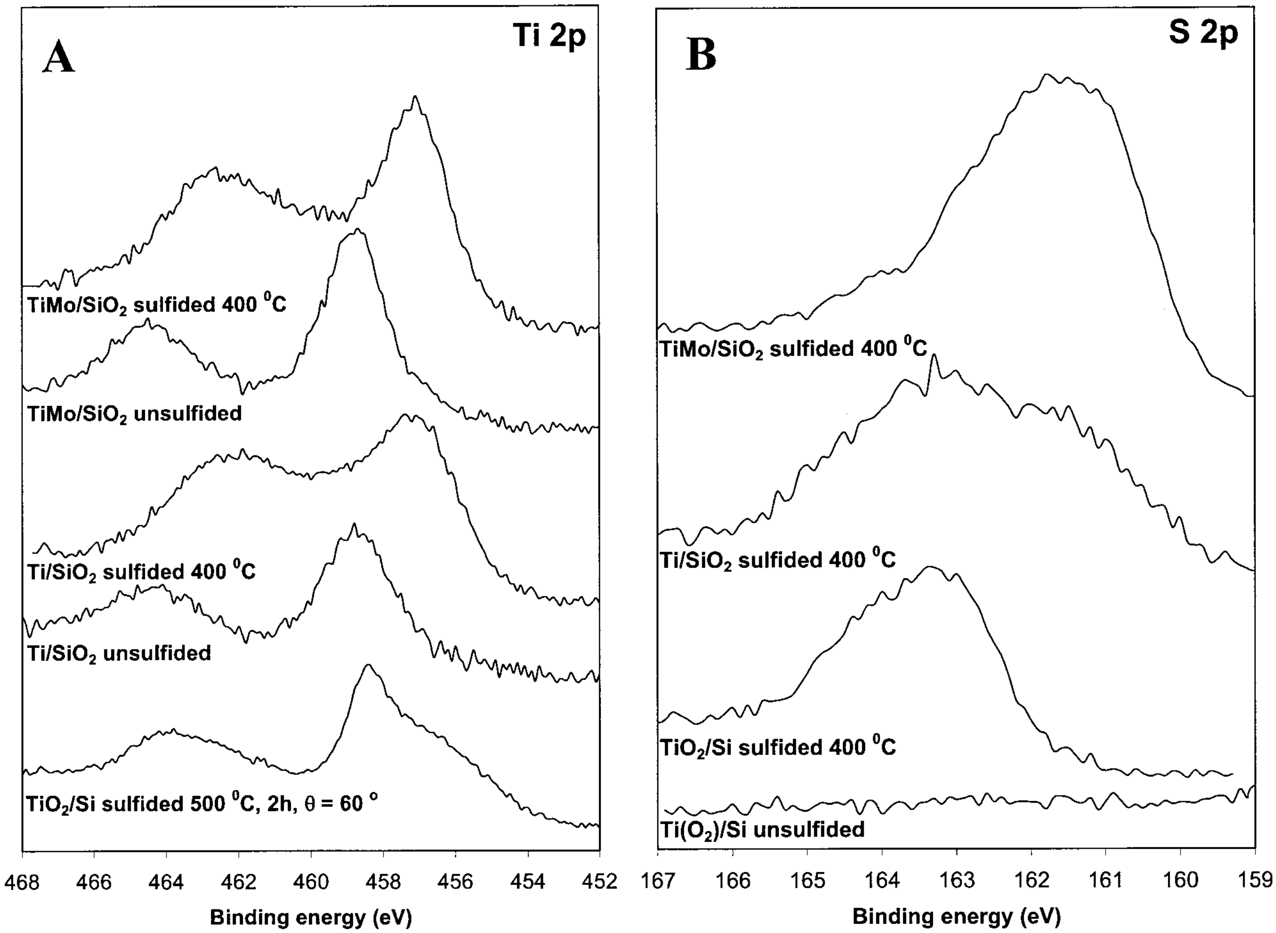

Figure 3. Ti 2p (A) and S 2p (B) XPS spectra of unsulfided and sulfided Ti/SiO_2 and TiMo/SiO_2 model catalysts.

Table 3
Thiophene HDS activity of Ti-containing model catalysts and some reference catalysts. HDS is the total yield of products after 1 h of thiophene batch reaction per 5 cm^2 of catalyst, HYD is the hydrogenation selectivity (n-butane/total products).

	HDS	HYD
Mo/SiC_2	0.11	0
$TiMo/SiO_2$	0.23	0.12
$NiMo/SiO_2$	1.07	0
Mo/TiO_2	0.6	0.08

Ti $2p_{3/2}$ peak at 458.8 eV, which can be ascribed to oxidic Ti species [22]. It can be clearly seen that, after sulfidation at 673 K, this doublet has shifted to lower Ti $2p_{3/2}$ binding energy, *i.e.* 457.0 eV. The S 2p spectrum of Ti/SiO_2 sulfided at 673 K shows two small peaks at ~161.5 and ~163.5 eV, respectively. The latter corresponds well with the sulfur species on sulfided TiO_2 (figure 3(B)). The S 2p spectrum of $TiMo/SiO_2$ after sulfidation shows a large peak at 161.9 eV, ascribed to S^{2-} in MoS_2, and a shoulder at higher binding energy (~163.5 eV), corresponding to sulfided Ti species. These results agree well with that of TiO_2-supported catalysts, indicating that Ti in TiO_2 behaves similarly to Ti as a Ti precursor in Ti-promoted Mo/SiO_2 catalysts. Note that the sulfidation of Ti is not complete at 673 K.

Thiophene HDS activity measurements on Ti-promoted catalysts were carried out to study the influence of sulfided Ti species on the activity of Mo-based catalysts. The results are shown in table 3. The HDS activity of $TiMo/SiO_2$ is twice as high as Mo/SiO_2, showing that sulfided Ti species have a promotional effect. Although the promotion factor is smaller compared with $NiMo/SiO_2$, the effect is significant. Ramirez *et al.* [17] stated that Ti^{3+} species are easily formed by reduction of Ti^{4+} under hydrogen atmosphere and are located at the surface of TiO_2. These Ti^{3+} species can easily inject electrons to the Mo 3d conduction band, which is according Harris and Chianelli [28] the requirement for MoS_2 promotion in HDS. Note that this is in good agreement with the Bond Energy Model [29] since injections of electrons from Ti to Mo will decrease the Mo–S bond energy.

This explains also the almost equal activity for promoted catalysts: apparently Ni has more affinity for the edges of MoS_2 than Ti and thus acts as a promoter instead of Ti. The activity of Mo/TiO_2 is however a factor 3 higher compared with $TiMo/SiO_2$. This difference is probably caused by a better dispersion of MoS_2 in Mo/TiO_2 due to a stronger interaction with the support. The higher Mo 3d/Ti 2p atomic ratio compared to Mo 3d/Si 2p confirms this. The hydrogenation (HYD) selectivity, which is expressed as the ratio of n-butane/total products, in table 3 shows that n-butane is only found as a product in Ti-containing catalysts. Clearly sulfided Ti species also increase the hydrogenation selectivity.

4. Conclusions

The thiophene HDS activity of Mo/TiO_2 is twice as high as Mo/Al_2O_3, while the HDS activity of Ni-promoted Mo catalysts is almost equal. From combination of thiophene HDS measurements and angle-dependent XPS, we conclude that the difference in HDS activity of the unpromoted catalysts is due to partial sulfidation of the TiO_2-support leading to Ti^{3+} species. These species can act as a promoter in the same way as Co or Ni, although to a lesser extent. Due to the higher affinity of Co and Ni to the edge sites of MoS_2, Co and Ni acts as a promoter in promoted Mo catalyst, instead of Ti. As a result the promoter effect of Ti is absent in Ni-promoted Mo catalysts. Sulfided Ti species also increase the hydrogenation selectivity.

Strong interaction of Mo with both TiO_2 and Al_2O_3 retards the sulfidation of Mo and leads to incomplete sulfidation at high temperatures. However, the sulfidation of Mo for both supports is similar and therefore the difference in activity could not be ascribed to differences in dispersion.

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