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Synthesis and characterization of Ce-stabilized titania for NiMo HDS catalysts

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Abstract

With the aim of obtaining TiO_2-based catalytic supports with high surface area, pore volume and hydrothermal stability, in this work we study some of the synthesis parameters of the sol–gel preparation of Ce-modified titania, as: hydrolysis catalyst, solvent and titania precursor. The supports were used to prepare NiMo/TiO_2 catalysts, which were characterized and evaluated in the thiophene HDS reaction. It was found that the use of terbutanol as solvent, phosphoric acid as hydrolysis catalyst and a low acid/alkoxide ratio (0.05) lead to enhanced areas and hydrothermal stability. For catalysts loaded with the same surface concentration of active phase, the specific HDS activity increases with surface area suggesting that the dispersion of the NiMo active phase is similar for samples with different surface areas. However, it was also found that the variations in the synthesis parameters caused changes in the degree of sulfidation of the NiMo active phase, in the amount of CUS per Mo atom, and in the temperature at which the evolution of H_2S from non-stoichiometric sulfur (Sx) takes place.

Keywords: Cerium; Hydrodesulfurization; NiMo catalysts; Sol–gel; Synthesis; Titania; TPS; TPR-S

1. Introduction

Hydrodesulfurization has been used in refineries for over 50 years to reduce the sulfur content in diesel fuel to match the applicable legal specifications. Environmental considerations are the major drivers for the reduction of the maximum allowable sulfur content. In future, so called ultra low sulfur diesel (below 15 ppm S) will be required [1]. As a consequence, refineries need to increase again the conversion in their desulfurization processes. It was reported that to comply with the environmental requirements the catalytic activity needs to be increased by four to five times that of the present catalysts [2]. In order to achieve this goal many approaches have been followed among which variation of type of support has received important attention. The past two decades have seen an intense activity from several parts of the world on the development of different oxides and mixed oxides supports which help to enhance the activity of Mo, CoMo, NiMo, W and NiW HDS catalysts. Some of the oxides like titania showed outstanding activities but the low surface area and limited thermal stability prevented its commercial use. To overcome these disadvantages mixed oxides of titania with alumina have been used as supports hopping to take advantage of the favorable characteristics of both systems [3]. Mixed oxides supported catalysts have been found to perform better than commercial alumina supported catalysts but there is not sufficient data to arrive at a consensus regarding the factors that are responsible for such increase in activity. However, in general, activity increased with titania content [4] and in many cases the catalyst supported on pure titania was the most active [5–7]. The applications of titania as support for sulfides has been reported to provide some unique performances in the residue hydrotreating due to its highly dispersing ability and non polar surface [8]. It has also been proposed that the redox and semiconductor properties of titania help the sulfidation and reduction of the Mo oxide precursors [9]. In a previous work, Schacht et al. [10] reported results of characterization and catalytic behavior of different CoMo-based catalysts supported on titania modified with lanthanum and cerium. These results suggest that the catalysts supported on La or

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Ce-stabilized titania may be used in hydrotreating process for producing ultralow sulfur diesel (ULSD). However, the effect of the support synthesis parameters on catalytic activity was not explored. In this work we study the effect that hydrolysis catalyst, solvent and titania precursor, have on the textural and hydrothermal properties of sol–gel produced Ce-titania supports, and on the HDS activity of NiMo/Ce-TiO_2 catalysts. To this end, NiMo catalysts supported on these materials have been prepared, characterized and evaluated in the thiophene HDS reaction.

2. Experimental

2.1. Preparation of supports and catalysts

Cerium-doped titania supports were prepared by the sol–gel method. Titanium butoxide (or isopropoxide) dissolved in 2-propanol (ethanol or terbutanol) was used as titanium source. Nitric (or phosphoric) acid was employed as catalyst for hydrolysis reaction. The molar ratios of solvent/alkoxide and water/alkoxide were fixed at 65 and 10, respectively and the acid/alkoxide ratio was 0.05, 0.2 or 0.4. Calcination took place at 773 K during 3 h. Cerium nitrate, used as doping agent, was dissolved in the water used for hydrolysis, and added later to the solvent. A load of 2.8 atoms of Mo/nm^2 and a constant Ni/(Ni + Mo) ratio of 0.3 were considered as optimal according to the literature [11]. The catalysts were prepared by successive impregnation of $(NH_4)_6Mo_7O_{24}$ and $Ni(NO_3)_2 \cdot 6H_2O$ on doped titania. The impregnated samples were dried during 24 h at 373 K, and finally calcined at 773 K for 2 h. The supports were named as $\mathrm{S} - y\mathrm{A} - \mathrm{Ti} - X$, where; S is the solvent (IsoOH: isopropanol, TerOH: terbutanol or EtOH: ethanol), y is the catalyst/alkoxide ratio used (0, 0.05, 0.2 or 0.4) and A the nitric or phosphoric acid (N or P); Ti is titanium source (Butox: butoxide or Isop: isopropoxide) and X represents the Ce content expressed as the molar percent ratio (Ce/Ce + Ti) $\times$ 100 = 0.5, 2 or 5. Titania without Ce was used as reference; in this case X is equal to zero and is omitted in the formulation.

2.2. Catalyst characterization and activity test

Textural properties of supports and catalysts were evaluated in a Micromeritics ASAP 2000 sorptometer. The structural phases of supports were determined by X-ray diffraction (XRD). Particle-size determination by X-ray line broadening was performed using the FWHM of the (1 0 1) peak (anatase) or (1 1 0) peak (rutile) and by applying the Scherrer–Warren formula. The thermal evolution of the different phases was analyzed by differential thermal analysis (DTA) using a heating rate of 10 K/min from RT to 1073 K, under N_2 flow. Raman spectra were recorded in a Nicolet FT-Raman 950 spectrometer. The samples were pretreated at 373 K during 12 h in static air before taking the spectrum.

A conventional TPR apparatus with TCD and UV detectors was used for the study of the reducibility of calcined and sulfided (TPR-S) catalysts. The sulfided catalysts were analyzed by TPR-S before and after the reaction test, as described previously [9]. Catalyst samples were cooled under a nitrogen flow to room temperature immediately after the reaction and transferred, also in a nitrogen atmosphere, to the TPR-S apparatus. TPR-S was performed in a flow apparatus using an argon-hydrogen (30% H_2, v/v) mixture as reducing gas. The gas mixture flow was kept at 25 ml/min and the heating rate of the samples was 10 K/min. To measure the H_2S evolution a Perkin-Elmer 552 UV-spectrophotometer, set a 200 nm and equipped with a flow cell, was used. The spectrophotometer was operated in the absorption mode and was calibrated with H_2S–H_2 mixtures of different concentrations. It was found that at the usual concentrations of the experiment, the UV signal was directly proportional to the H_2S concentration.

Before the catalytic test, the samples were sulfided at 673 K for 4 h (heating rate of 10 K/min) using a stream of H_2S–H_2 (15% H_2S, v/v) in the same TPR apparatus to obtain temperature programmed sulfidation (TPS) results, as described in [5]. The catalytic activity tests for thiophene HDS, at 513 K, were carried out at atmospheric pressure in a typical continuous differential micro-reactor apparatus.

3. Results and discussion

3.1. Hydrolysis catalyst effect

The change of hydrolysis catalyst, phosphoric and nitric acid, has a marked influence on the properties of the synthesized titania. Table 1 shows the textural properties of titania, synthesized with different precursors, solvents and catalysts. A considerable increase in surface area is observed when phosphoric acid was used as hydrolysis catalyst. This increase can be related to the formation of TiP_2O_7 or $(TiO)_2P_2O_7$, detected by XRD (Figs. 1 and 2), which delay the growth of the anatase crystallites (Table 1). This result is not achieved with nitrates, and in this case the anion is eliminated from the gel during the washing of the precipitate. The acid, in contact with the pore walls

Table 1
Textural properties of the titania synthesized. Hydrolysis catalyst effect

Sample	Surface area (m^2/g)	Pore volume (cm^3/g)	Mean pore diameter (Å)	Particle diameter (nm)
TerOH–0.00–Butox	53	0.07	50	19.9
TerOH–0.05N–Butox	65	0.10	62	12.9
TerOH–0.05P–Butox	170	0.16	37	7.7
IsoOH–0.05N–Isop	72	0.12	69	13.9
IsoOH–0.05P–Isop	141	0.17	49	8.4
TerOH–0.05N–Isop	33	0.04	54	17.7
TerOH–0.05P–Isop	145	0.13	37	8.3

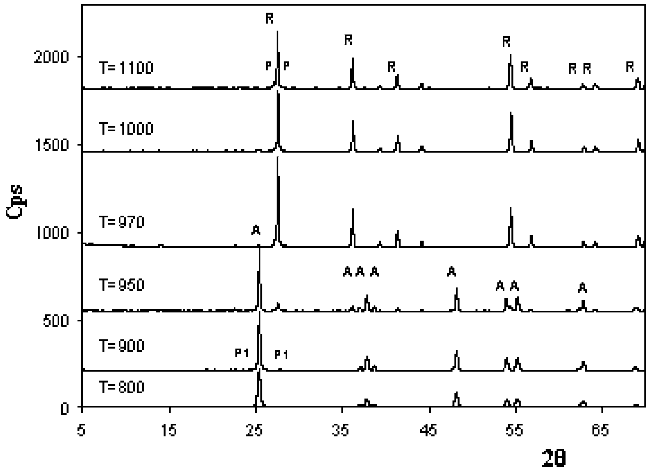

Fig. 1. X-ray powder diffraction patterns of TerOH–0.05P–Isop to different calcination temperatures. A: anatase, R: rutile, P1: TiP_2O_7, P: $(TiO)_2P_2O_7$.

generates structure degradation by partial dissolution, followed by a precipitation of the material during drying. HNO_3 is a strong acid while H_3PO_4 is of middle force. Therefore, it is expected that the former causes a bigger degradation of the pores. The results show that indeed the materials prepared with nitric acid present bigger pores, smaller surface area and larger particles (see Table 1). It is known that the presence of titania-phosphorus complexes delays the transition of anatase to rutile [12–14]. When nitric acid was used as hydrolysis catalyst, the resulting titania changed from anatase to rutile at temperatures above 1073 K, while in the material prepared with phosphoric acid this change occurred between 1223 and 1243 K. When the growth of the crystallites is delayed, it will also be delayed the phase transformation. In Table 2 it is clearly observed that the titania particles grow when the calcination temperature increases, but this increase is smaller for the preparations with phosphoric acid.

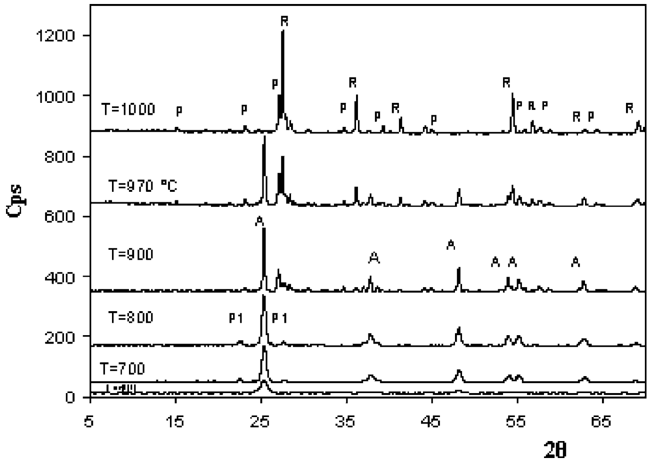

Fig. 2. X-ray powder diffraction patterns of TerOH–0.20P–Isop to different calcination temperatures. A: anatase, R: rutile, P1: TiP_2O_7, P: $(TiO)_2P_2O_7$.

Table 2
Average size particle (nm) as a function of calcination temperature for nitric and phosphoric acids as hydrolysis catalysts

Temperature (K)	TerOH–0.05N–Butox	TerOH–0.05P–Butox
773	12.9 (a)	7.7 (a)
1073	32.9 (a)	17.4 (a)
1173	40.8 (r)	28.6 (a)
1223	41.3 (r)	37.9 (a)
1243	n.d.	40.0 (r)
1273	n.d.	42.3 (r)
1373	n.d.	44.6 (r)

(a) Anatase and (r) rutile phases.

3.2. Catalyst/alkoxide ratio effect

Table 3 presents the textural properties of titania obtained with different amounts of hydrolysis catalysts, for acid/alkoxide ratios of 0.05, 0.20 and 0.40. When increasing the acid proportion, the surface area and pore volume diminishes drastically, while the pore diameter increases. The role of the acid is to give protons to alkoxide groups, increasing the rate of hydrolysis, however, high concentrations of acid diminish severely the condensation rate [15]. The decrease in titania surface area can be explained because the aging time during the sol–gel process (6 h) is not enough for the materials with high acid proportion to condense. This produces a precipitate with dispersed particles resulting in the formation of a smaller number of pores and a small specific area.

The XRD results obtained at different calcination temperatures and different acid/alkoxide ratios (Figs. 1 and 2) show that the anatase–rutile transformation shifts to higher temperatures when the amount of phosphoric acid is increased. This could be due to the presence of titanium-phosphorus compounds, which also appear in the diffractogram.

3.3. Solvent effect

The effect of the superficial tension of the solvent on the textural properties of titania was studied with ethanol (22.2 dyn/cm), isopropanol (20.6 dyn/cm) and terbutanol (19.3 dyn/cm) and the results are presented in Table 4.

Table 3
Catalyst/alkoxide relationship effect on textural properties of titania

Sample	Surface area (m^2/g)	Pore volume (cm^3/g)	Mean pore diameter (Å)
IsoOH–0.05P–Butox	139	0.11	33
IsoOH–0.20P–Butox	56	0.07	47
IsoOH–0.40P–Butox	19	0.05	103
TerOH–0.05P–Butox	170	0.16	37
TerOH–0.20P–Butox	164	0.15	35
TerOH–0.40P–Butox	128	0.14	43
EtOH–0.05P–Butox	105	0.08	30
EtOH–0.20P–Butox	79	0.06	32
EtOH–0.40P–Butox	19	0.06	117

Table 4
Solvent effect on the textural properties of titania

Sample	Surface area (m^2/g)	Pore volume (cm^3/g)	Mean pore diameter (Å)
TerOH–0.05P–Isop	145	0.13	37
IsoOH–0.05P–Isop	141	0.17	49
EtOH–0.05P–Isop	105	0.08	32
TerOH–0.20P–Isop	211	0.24	45
IsoOH–0.20P–Isop	81	0.08	41
EtOH–0.20P–Isop	34	0.04	46
TerOH–0.40P–Isop	175	0.29	66
IsoOH–0.40P–Isop	41	0.16	160
EtOH–0.40P–Isop	15	0.04	109
TerOH–0.05P–Butox	170	0.16	37
IsoOH–0.05P–Butox	139	0.11	33
EtOH–0.05P–Butox	105	0.08	30

Diminishing the superficial tension of the solvent improves the textural properties considerably, being reflected in a higher surface area and pore volume, which coincides with previous results [16–17] where replacing water for alcohol generates a smaller collapse of the pores during drying and calcination. However, many other factors, associated with the solvent could cause a variation in the characteristics of the material, i.e., the fact that the alkoxides dissolved in alcohols with different radical groups can generate alcoholysis reactions [15]. On the other hand, the hydrolysis of an alkoxide depends on the length of the chain of the alkyl group and it is possible to adjust the gelation rate of the alkoxide using a different solvent [18].

3.4. Titanium precursor effect

The use of different Ti precursors, titanium isopropoxide or butoxide, did not cause significant changes in the textural properties of titania or temperature at which the transformation anatase-rutile occurs. The DTA results show that the phase transformation occurs at similar temperature. Although, it is known that the alkoxides with bigger alkyl groups react and diffuse slowly, no marked differences in particle size were obtained from XRD (Table 5).

3.5. Ce incorporation effect

The addition of different amounts of Ce ((Ce/Ce + Ti) × 100 = 0.5, 2 or 5) to titania during the synthesis caused an important improvement in the textural properties of titania. This was more markedly when nitric acid was used as hydrolysis catalyst (Table 6). In spite of this, surface area and pore volume were higher for the materials prepared with phosphoric acid, for which the effect of Ce was not so important. This can be interpreted as the existence of a limit in the stabilization effect of the modifier.

Table 5
Average size particle (Å) as a function of calcination temperature for titania obtained from titanium butoxide and isopropoxide

Temperature, K	TerOH–0.05P–Butox	TerOH–0.05P–Isop
773	7.7 (a)	8.3 (a)
1073	17.4 (a)	20.8 (a)
1173	28.6 (a)	28.9 (a)
1223	37.9 (a)	38.2 (a)
1243	40.0 (r)	40.6 (r)
1273	42.3 (r)	42.6 (r)
1373	44.6 (r)	44.5 (r)

(a) Anatase and (r) rutile phases.

Table 6
Textural properties of stabilized titania with Ce

Sample	Surface area (m^2/g)	Pore volume (cm^3/g)	Mean pore diameter (Å)	Particle diameter (nm)
IsoOH–0.05N–Isop	72	0.12	69	13.9
IsoOH–0.05N–Isop–0.5C	114	0.19	67	9.1
IsoOH–0.05N–Isop–2C	141	0.23	65	7.1
IsoOH–0.05N–Isop–5C	140	0.21	60	7.8
TerOH–0.05N–Butox	65	0.10	62	12.9
TerOH–0.05N–Butox–0.5C	88	0.16	74	10.2
TerOH–0.05N–Butox–2C	91	0.15	65	10.9
TerOH–0.05N–Butox–5C	108	0.17	63	8.3
TerOH–0.05P–Isop	145	0.13	37	8.3
TerOH–0.05P–Isop–0.5C	178	0.19	42	7.4
TerOH–0.05P–Isop–2C	170	0.20	45	7.6
TerOH–0.05P–Isop–5C	173	0.21	47	7.5
TerOH–0.05P–Butox	170	0.16	37	7.7
TerOH–0.05P–Butox–0.5C	169	0.18	40	7.8
TerOH–0.05P–Butox–2C	177	0.19	41	7.2
TerOH–0.05P–Butox–5C	174	0.21	46	7.4
TerOH–0.20P–Isop	211	0.24	45	n.d.
TerOH–0.20P–Isop–0.5C	201	0.23	48	n.d.
TerOH–0.20P–Isop–2C	223	0.28	54	n.d.
TerOH–0.20P–Isop–5C	210	0.28	50	n.d.

The XRD of samples calcined at different temperatures show that the anatase-rutile phase transformation occurs at higher temperatures in presence of cerium. Moreover, in the DTA results we observe that the transition temperature increases with the quantity of cerium. A difference of up to 35 K (for phosphoric acid series and 60 K for nitric acid) respect to the material without Ce is observed. When the cations are introduced interstitially into the anatase phase, they fill the empty space in the matrix decreasing, concomitantly, the atomic mobility of the anions and cations of titania, making the anatase phase more stable [19]. Since Ce(4+) is bigger than Ti(4+), it fits more tightly into these interstices increasing the stability of the anatase phase. Consequently, it is possible to say that the dopant ionic radius and the specific characteristics of the matrix are important parameters for controlling the thermal properties of modified titania. In line with these results, Ce doped titania present smaller particle sizes, compared with those of titania without Ce (Table 6). According to previous studies [20], Ce addition to titania hinders the growth of the particles. The difference in the particles size between Ce doped titania and titania is more marked in the materials prepared with nitric acid.

In summary, the solvent and hydrolysis catalyst have a marked effect on the textural properties and the thermal stability of titania, anatase, while the Ti precursor has a

Table 7
Textural properties of supports and NiMo catalysts

Sample	BET surface area (m^2/g)		Pore volume (cm^3/g)		Pore diameter (Å)	
	Support	Catalyst	Support	Catalyst	Support	Catalyst
TerOH–0.05N–Butox	70	59	0.12	0.10	66	70
TerOH–0.05N–Butox-2C	91	80	0.15	0.13	65	63
TerOH–0.05P–Butox-2C	177	113	0.19	0.11	41	40
TerOH–0.05P–Isop-2C	170	123	0.20	0.14	45	45
TerOH–0.05P–Isop	145	103	0.13	0.10	37	36
TerOH–0.20P–Isop-2C	223	100	0.28	0.21	54	83
TerOH–0.20P–Isop	211	54	0.24	0.10	45	72
TerOH–0.05P–Isop-5C	173	112	0.21	0.12	47	44
TerOH–0.05P–Butox-5C	174	135	0.21	0.13	46	45

smaller effect. High values of surface area and pore volume are obtained with the solvent of low superficial tension (terbutanol), and when phosphoric acid was used as hydrolysis catalyst in the smallest acid/alkoxide ratio. Moreover, Ce incorporation to titania improves the textural properties and increases the thermal stability of anatase. The changes in surface area before and after the hydrothermal deactivation test (at 823 and 973 K during 2 h) were taken as a measure of stability of supports. Retention of area for Ce doped titania is higher than for pure titania. For the former series the area retention after hydrothermal deactivation was about 85 and 40% at 823 and 973 K, respectively, while for titania not doped, 67 and 35% retention area was obtained at the same temperatures.

3.6. Catalysts characterization

Titanias with the best textural properties were selected to prepare NiMo supported catalysts, Table 7 shows the textural properties of these catalysts. When Ni and Mo were impregnated on the supports with high surface area and therefore small pore diameters, the catalyst textural properties were severely affected, due to blockage of the small diameter pores by Ni and Mo compounds. The decrease of pore volume due to impregnation is less for the support having lower pore volume. However, NiMo catalysts presented surface areas between 54 and 135 m^2/g and average pore diameters of 40–83 Å, which are considered good for titania supported catalysts.

Table 8 presents the specific and intrinsic HDS activities of the catalysts in the thiophene HDS reaction. It is clear that the specific activity increases with surface area because all the catalysts had the same surface concentration of Mo and Ni. The trend of the intrinsic activity values was not clear. Since the activity of the catalysts must be related to the amount and state of the sulfided phase, TPS and TPR-S experiments were made with all catalysts in order to explain the observed differences in activity.

The TPS patterns of titania supported NiMo catalysts (Fig. 3) exhibited two H_2S consumption regions: region I from 300 to 475–575 (depending on the catalyst) and region II from 475–575 to 673 K. Between these two regions there is a small zone of H_2S production, which has been assigned to the reduction of Mo(VI) oxysulfides to Mo(IV) with H_2S liberation. Partial sulfidation of surface Mo(VI) is obtained in region I and in region II corresponding to Mo(IV) sulfidation. According to previous work [5] these TPS patterns can be explained in the following way: initially, an oxide of Mo(VI) is transformed (region I) into a Mo(VI) oxysulfide. This oxysulfide is subsequently reduced by H_2, with H_2S production, to an oxysulfide of Mo(IV). Finally this Mo(IV) species is completely sulfided to MoS_2 (region II). Clearly, in region I and II H_2S consumption is observed, while in the intermediate region H_2S is detected. Analysis of

Table 8
Thiophene HDS activities and quantitative TPS and TPR-S results of NiMo catalysts

Catalysts	Specific activity[a]	Intrinsic activity[b]	Sulfidation degree[c]	H_2S evolution[d]		T_{max}[e] (K)
				Before reaction	After reaction	
TerOH–0.20P–Isop	0.56	2.22	0.3974	0.0470	0.0152	473
TerOH–0.05P–Isop	0.64	1.37	0.6584	0.1935	0.0178	433
TerOH–0.05P–Butox-2C	0.86	1.68	0.4180	0.1420	0.0137	458
TerOH–0.20P–Isop-2C	1.11	2.46	0.3658	0.0799	0.0199	443
TerOH–0.05P–Isop-2C	1.41	2.64	0.5296	0.1122	0.0451	443
TerOH–0.05N–Butox-2C	1.49	4.13	0.9016	0.3490	0.1709	438

[a] Activity (thiophene mol/g of catalysts/s × 10^7) at 513 K.
[b] Activity (thiophene mol/m^2 of catalysts/s × 10^4) at 513K.
[c] Total H_2S uptake per mole of Mo from TPS patterns.
[d] H_2S evolution (H_2S mol/Mo mol) in the region 300–550 K from TPR-S patterns, before and after HDS reaction.
[e] T_{max} of 300–550 K peak in TPR-S patterns.

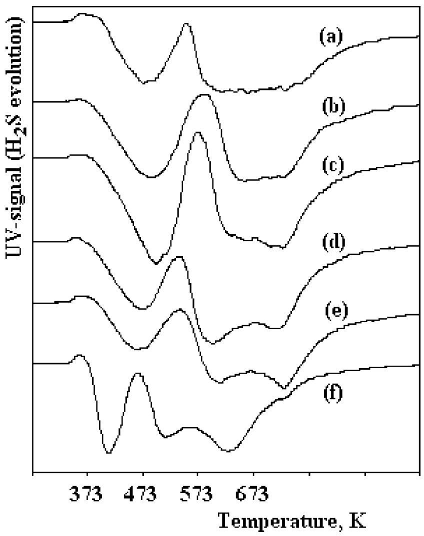

Fig. 3. TPS patterns of NiMo catalysts supported on (a) TerOH–0.05N–Butox2C; (b) TerOH–0.05P–Butox2C; (c) TerOH–0.20P–Isop2C; (d) TerOH–0.05P–Isop; (e) TerOH–0.20P–Isop2C and (f) TerOH–0.20P–Isop.

the experimental TPS patterns indicate that the incorporation of high amount of phosphoric acid and absence of Ce decreases the temperatures associated to the reduction of Mo(VI) to Mo(IV) species and the sulfidation of Mo(IV). Since HDS catalysts work in the sulfided state, one should expect a correlation between the changes in sulfidation degree of the catalysts and the catalytic activity. Quantitative results of the total H_2S uptake per mole of Mo (sulfidation degree) for the catalysts prepared at different conditions are presented in Table 8. These results are in good agreement with the intrinsic activity results (see Fig. 4), although for high concentration of phosphoric acid and Ce absence the correlation is not as good. This is possibly due to the formation of new Ti–O–P phases. The points corresponding to these preparations (TerOH–0.05P–Isop and TerOH–0.20P–Isop2C) were not included in Fig. 4. Since the amount of Ni and Mo was the same per square meter of support surface, the change in the degree of sulfidation of the NiMo phase must be related to changes in some of the synthesis parameters like amount of Ce or phosphoric acid.

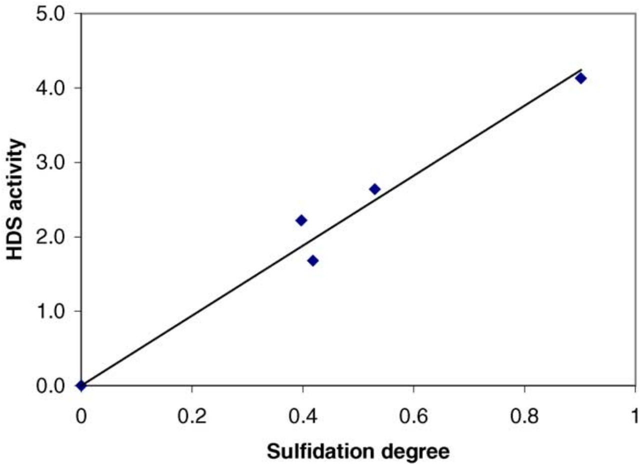

Fig. 4. Intrinsic HDS activity vs. sulfidation degree for NiMo catalysts.

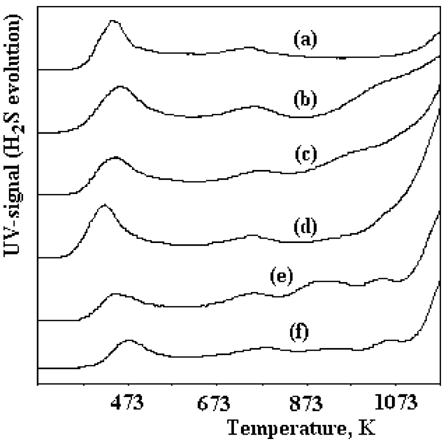

Fig. 5. TPR-S patterns of NiMo catalysts supported on (a) TerOH–0.05N–Butox2C; (b) TerOH–0.05P–Butox2C; (c) TerOH–0.20P–Isop2C; (d) TerOH–0.05P–Isop; (e) TerOH–0.20P–Isop2C and (f) TerOH–0.20P–Isop.

It has been generally accepted that the active sites in HDS consist of Mo sulfur vacancies (CUS). Therefore, in what follows an attempt will be made to correlate the catalyst activity trend with the number of sulfur vacancies created during TPR-S, for the catalysts before and after the thiophene HDS reaction. The changes induced by the presence of titania, on the molybdenum and nickel sulfided phases before and after the reaction test, can be assessed in part by the TPR-S technique. By means of this technique it is possible to follow the reduction of the sulfide phases. Fig. 5 shows the TPR-S patterns of the catalysts after HDS reaction. Here one can observe the presence of two main peaks, one between 373 and 573 K, and another in 573 and 973 K. According to [21–22], for Mo supported catalysts, the H_2S evolved in the temperature region 300–550 K can be ascribed to the reduction of sulfur species (Sx), chemisorbed on coordinately unsaturated (CUS) edge/corner sites, responsible for the HDS catalytic activity. The peak between 573 and 973 K has been associated by Mangnus et al. [22] with the recombination of –SH groups and reaction of –SH groups with hydrogen. This region is also associated to the Ni sulfides reduction, possibly segregated from the NiMoS phases [5]. At higher temperatures ($T > 973$ K), the observed H_2S evolution is related to the reduction of bulk MoS_2 species. In line with the above, the H_2S evolution peaks in these three regions are associated to hydrogen consumption peaks in the TCD signal (not shown). However, the observation of a hydrogen consumption peak at temperatures higher than 973 K without H_2S evolution reveals, in agreement with our previous results [23], the reduction of bulk TiO_2. A quantitative analysis of the H_2S UV signal in the region 300–550 K of the TPR-S patterns allows to estimate the number of sulfur vacancies created in the edge/corner sites of the MoS_2 crystallites [22], the results from this calculation are presented in Table 8. It is

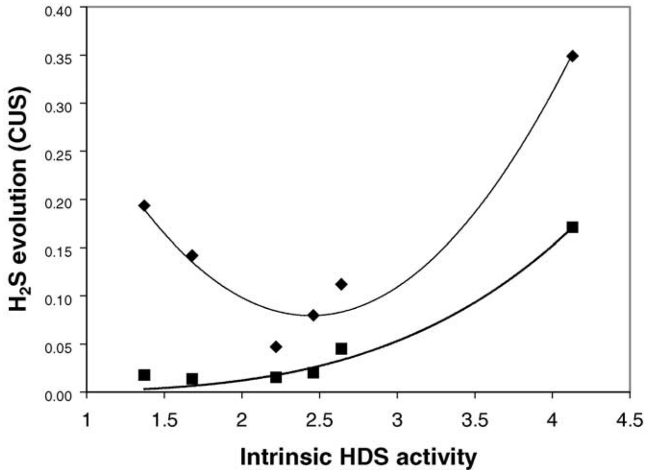

Fig. 6. H_2S evolution (H_2S mol/Mo mol) in the region 300–550 K of the TPR-S patterns, before (◆) and after (■) reaction test, vs. intrinsic HDS activity for NiMo catalysts.

interesting to note that the H_2S evolved from the catalysts is larger for the TPR-S test before than after HDS reaction. This result is in line with the higher H_2/H_2S ratio during reaction than during sulfidation. The HDS activity trend correlates well only with the CUS evaluated after reaction test (see Fig. 6), in agreement with previous results [5,9].

The TPR-S experiments not only give information on the amount of adsorbed sulfur, but they also give an indication of the ability of the catalysts to hydrogenate the adsorbed sulfur, by observation of the shifts in the temperature of the peak maximum of the Sx hydrogenation. This ability of sulfur hydrogenation, is equivalent to the ability of creating sulfur vacancies and therefore, must be related to HDS activity. These results indicate that higher peak temperatures are related to lower HDS activity (Table 8). In summary, the HDS activity trend of catalysts supported on stabilized Ce-titania is more accurately correlated with the degree of sulfidation and the ability of creating CUS after the reaction test.

4. Conclusions

The solvent and hydrolysis catalyst have a marked effect on the textural properties and the thermal stability of titania, anatase, while the Ti precursor has a smaller effect. The best textural properties are obtained with the solvent of low superficial tension (terbutanol), and when phosphoric acid was used as hydrolysis catalyst in the smallest acid/alkoxide ratio (0.05). Moreover, Ce incorporation to titania improves the textural properties and increases the thermal stability of anatase. It was found that the HDS activity trend of the catalysts supported on stabilized Ce-titania is more accurately correlated with the degree of sulfidation and the ability of creating CUS after the reaction test.

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