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The role of titania in supported Mo, CoMo, NiMo, and NiW hydrodesulfurization catalysts: analysis of past and new evidences

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Abstract

Previous results and new evidence on the role of titania in supported hydrodesulfurization catalysts are analyzed in order to construct a rational explanation for the different findings in Ti-containing HDS catalysts. Some of the important findings follow. The preparation method of Al–Ti oxide supports is important to catalytic activity. It is not the total amount of Ti but the Ti oxide surface structures that is relevant. TiO_2 is an electronic promoter in HDS catalysts. Ti^{3+} species formed under HDS reaction conditions act as electron donors. These electrons can be easily transferred, through the conduction band of the support, and be injected to the Mo 3d conduction band. This causes a weakening of the Mo–S bonds and helps the creation of more CUS. The addition of TiO_2 to the surface of alumina eliminates the most reactive surface hydroxyl groups and avoids the formation of tetrahedral Mo oxide species, causing an increase of well-sulfided active phase and hence in catalytic activity. This effect, although significant, is less important than the electronic promotion of Mo by Ti. TiO_2-containing catalysts are well suited for deep HDS because they facilitate the formation of a greater number of CUS in MoS_2 (or WS_2), favoring the hydrogenation–hydrodesulfurization route of transformation of 4,6-DMDBT.

Keywords: Titania; Titania–alumina; Hydrodesulfurization catalysts; Mixed oxide supports; CoMo; NiMo; NiW; Thiophene; DBT; 4,6-DMDBT; Naphthalene hydrogenation

1. Introduction

During the past years, the environmental regulations in the sulfur specifications for transportation fuels have became stricter, and will continue to do so. The current USA specification for sulfur in diesel is 500 ppm. However, for diesel fuel, the EPA Tier II indicates 15 ppm by 2006 and in Europe 10 ppm is expected for 2008. These restrictions in the sulfur content of transport fuels have created the need for better hydrodesulfurization catalysts. An additional problem facing the petroleum industry is that a significant part of the reserves of some petroleum producing countries consists of heavy petroleum with high content of contaminants like sulfur, nitrogen, aromatics and metals such as Ni and V. These heavier feeds will often contain a greater proportion of substituted dibenzothiophenes, and among them, 4-methyl dibenzothiophene (4-MDBT) or 4,6-dimethyl dibenzothiophene (4,6-DMDBT), which are very difficult to hydrodesulfurize [1–6]. It is clear that if the future environmental regulations are to be met, these refractory compounds must be hydrodesulfurized.

It is now known that compounds like 4-MDBT and 4,6-DMDBT can be hydrodesulfurized through several reaction routes [2,7]. The direct hydrodesulfurization route is a slow one for these compounds due to the steric hindrance of the methyl groups, which hinder an adequate interaction of the sulfur atom with the catalytic active site. The pre-hydrogenation route, in which one of the aromatic rings adjacent to the sulfur atom is hydrogenated, is the main route for hydrodesulfurization of these compounds. When the catalyst has an important acid function like in zeolite-containing

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catalysts, several other reaction routes are open. The acid function allows either the breaking of a C–C bond in the sulfur ring [8,9] or the isomerization or elimination of the methyl groups in the 4 and 6 positions, thus allowing a better interaction of the sulfur atom with the active site.

Several approaches are being used to develop new more active HDS catalysts with adequate functionalities to perform adequate HDS of refractory molecules. The use of new active phases such as carbides, nitrides, phosphides, or transition metal sulfides other than Mo and W, promoted by Ni or Co, has been proposed. The performance of these phases continues to be explored for practical applications. Other approach which appears promising and has been widely investigated is the use of modified γ-alumina supports. Modification of alumina with P, F or B has been studied in the past [10–13]. The use of oxides different from alumina such as TiO_2 [14] or ZrO_2 [15,16] has given promising results, although the low thermal stability and low surface area of these oxides has prevented their application as supports for HDS industrial catalysts. Because of these problems, considerable effort has been placed on the development of stable high surface area TiO_2 and ZrO_2 and on binary oxides containing Ti or Zr [3,17,18, and references therein, 19,20]. Among the possible binary oxides, Al–Ti oxides have shown interesting textural and chemical surface properties.

Mo or W-based catalysts supported on Al–Ti oxide supports have been successfully used for the hydrodesulfurization of refractory molecules such as 4-MDBT, 4,6-DMDBT, or real feeds. Several investigations have recently demonstrated that catalysts with Ti-containing supports are in general more active than those supported on alumina for the hydrodesulfurization of these refractory molecules [21–25]. These molecules are hydrodesulfurized through several reaction paths, being the pre-hydrogenation one of the most important. Thus, the explanation for the greater activity of Ti-containing catalysts has been given in simple terms saying that the presence of Ti increases the catalyst activity for the pre-hydrogenation path.

Many explanations like increased dispersion of the active phase, increased acidity, improved sulfurability or reducibility, induction of edge-on MoS_2 crystallites, state of the promoter, etc., have been suggested to account for the good performance of HDS Ti-containing catalysts [14,20,26–30]. Despite all these studies, a clear explanation of why Ti-containing catalysts are better has not been established. Also, the reasons of why some Ti-containing support preparation methods are better than others have not been well established. It is the object of this work to review and present in an orderly manner some previous results from our and other laboratories, and show some new evidence that hopefully will help to construct a more rational explanation for the different findings in Ti-containing HDS catalysts. In doing so, no attempt has been made to mention all the work previously published on this subject but only those publications which in our view are relevant to the above objective.

2. Catalysts supported on pure TiO_2 and Al_2O_3

Our interest for Ti-supported HDS catalysts started after the observation that changes in the nature of the support, originally conceived only as a means to disperse and stabilize the active phase, could lead to important improvements in the activity of Mo-based supported HDS catalysts. It was found that the intrinsic activity in thiophene HDS of Mo supported on TiO_2 was 4.4 times that of Mo supported on alumina [14]. The observed changes in catalytic activity could not be explained on the basis of increased dispersion of the TiO_2-supported catalysts. An additional interesting finding in the same study was that the promotion of Mo by Co was smaller for the TiO_2 supported catalyst. In spite of this, the activity of the TiO_2 supported catalyst was 2.2 times that of $CoMo/Al_2O_3$. These results suggested that TiO_2 was not an inert support for HDS catalysts and that its presence modified the activity of the catalyst. The main beneficial effect of TiO_2 being on the Mo phase rather than on the promoter.

Titania then appeared as a good support for HDS catalysts but the low thermal stability and specific surface area of TiO_2-anatase prevented its industrial use as support for HDS catalysts. The low surface area affects directly the Mo loading and thereby the specific catalytic activity. Because of this, many studies have been undertaken to obtain Ti-containing supports with textural and mechanical properties similar to alumina but with a surface chemistry close to TiO_2.

3. Behavior of HDS catalysts supported on Al–Ti mixed oxides prepared by co-precipitation

The studies on the HDS activity of Mo or W catalysts supported on Al–Ti mixed oxides made with model molecules like thiophene or benzothiophene indicated that the catalyst activity changes in a non-linear fashion with the Ti content. Studies on the HDS behavior of Mo catalysts supported on Al_2O_3–TiO_2 found that for alumina-rich formulations the activity in thiophene HDS at atmospheric pressure was similar or slightly lower than that displayed by the alumina supported catalyst. In contrast, in the Ti-rich side of the formulation ($TiO_2 > 80$ mol%) the intrinsic activity increased significantly with Ti content, reaching a maximum value for pure TiO_2 [14,28,29,31]. To explain the greater activity of Ti-containing catalysts it was proposed that the greater number of acid sites on the TiO_2 support caused a better dispersion of the Mo phase during the impregnation step, leading, after drying, calcination and activation, to an increase in the dispersion of the active MoS_2 phase. A correlation between the HDS activity and the number of acid sites was proposed. It was also mentioned without much explanation that the reactivity of the Mo active sites increased due to the presence of Ti in the catalyst.

It is known that the interaction of alumina with WO_3 is much stronger than with MoO_3. Therefore, the effect of Ti-containing supports on HDS activity will be more visible in W/Al_2O_3–TiO_2 catalysts. These W-based catalysts were studied by Ramírez and Gutiérrez-Alejandre [28,29]. It was found that the support composition influences the type of oxo-tungsten species present on the surface; tetrahedral species being present on alumina while octahedral ones on titania. A greater lateral interaction of the W oxide species on TiO_2 led to an increased population of polytungstates on the surface. The composition of the support also affected the degree of reducibility of the WO_3 phase. A similar trend with Ti content was found for activity and degree of reducibility. It was also found that during TPR the TiO_2 support is reduced and that this reduction occurs more easily if the W phase is already supported. For the promoted NiW/Al_2O_3–TiO_2 catalysts the HDS catalytic activity followed a similar trend to the unpromoted catalyst. It was also reported that the presence of TiO_2 in the support facilitated the reduction and sulfidation of the Ni–W phases, and decreased the interaction of the W oxide precursors with the support. In the Ti–containing catalysts a thin layer of the TiO_2 support surface was sulfided during sulfidation of the catalyst. This sulfided layer of Ti presents coordinatively unsaturated sites (CUS) capable of adsorbing NO. Analysis by XPS indicated that beyond a TiO_2 concentration of 70 mol% in the Al_2O_3–TiO_2 support, segregated TiO_2 was detected on the surface. For these catalysts, which were well sulfided, a HREM study allowed estimate the average size and staking of the WS_2 crystallites and using a geometrical model it was possible to find a good correlation between the catalytic activity in thiophene HDS and the fraction of edge and corner W sites in the WS_2 crystallites exposed by only one of the layers of each WS_2 crystallite. This indicated that during the adsorption of reactants on any given edge or corner tungsten atom, the tungsten atoms above and below in the same row would be sterically hindered for the adsorption of more reactants.

CoMo and NiMo catalysts supported on Al_2O_3–TiO_2 exhibited similar trends in HDS activity with respect to support composition. Below 80 mol% TiO_2 in the support, the catalysts displayed similar activity to the alumina supported catalyst [31]. In the same study, it was also found that the variations in catalytic activity with support composition were more pronounced in the thiophene than in the DBT test. These observations were related to the mechanism of transformation of the model molecule and to the experimental conditions, making evident the importance selecting the appropriate model molecule. Because of this, further studies were made with the same catalysts but now using a real feed (gas oil) [32]. In this new study it was found that the intrinsic activities of gas oil HDS and pyridine HDN increased significantly with the amount of Ti in the support, especially for the Ti-rich formulations. The activity trend with support composition for gas oil HDS differed from that obtained for thiophene at different hydrogen pressures. For gas oil contaminated with pyridine the HDS activity increased always with the Ti content, whereas for thiophene at different hydrogen pressures (3–30 bar) a minimum in activity was found at intermediate Ti content (TiO_2/Al_2O_3 = 1.0). The differences in activity trends with the model molecule in [32] were reported to be related not only to the different mechanisms of transformation of the different feed molecules (thiophene, DBT and gas oil), but also to the H_2S/H_2 ratio used in the activity test, which was different in each case, and affects not only the degree of inhibition but also the steady state degree of sulfidation of the catalyst. These results confirmed the importance of feed composition when choosing a catalyst formulation.

To explain the lack of sensitivity of HDS activity with Ti content for the catalysts supported on alumina-rich Al_2O_3–TiO_2 supports, two studies were made on the characterization of the bulk and surface properties of these binary oxides. The first study was devoted to Ti-rich formulations, while the second to Al-rich formulations [33,34].

For the Ti-rich samples, characterizations by nitrogen physisorption, XRD, FTIR, FTIR of adsorbed pivalonitrile (PN) and pyridine (Py), and FT-Raman, indicated that:

(i) At the concentrations of aluminum used in the binary Al_2O_3–TiO_2 no separate alumina particles are formed.
(ii) Anatase particles in Al_2O_3–TiO_2 mixed oxides prepared by co-precipitation of the corresponding alkoxides are largely covered by aluminum oxide ‘‘partial monolayers’’. Two aluminum species were detected, one that forms part of a surface monolayer and other bulk octahedrally coordinated.
(iii) The addition of small amounts of alumina to titania enhances the thermal stability of anatase to sintering and to phase transformation to rutile.
(iv) The surface chemistry of titania is significantly modified by mixing with alumina, giving rise to stronger Lewis acidity but also to weaker Brönsted acidity of the OH groups.

In the aluminum-rich Al_2O_3–TiO_2 samples, no important evidence of Ti oxide species was found at the surface suggesting that most of the Ti is dissolved in the bulk. Therefore, these Ti ions are essentially isolated. No evidence of TiO_2 particles was found. It appears then that in the Al-rich samples prepared by co-precipitation of alkoxides, Ti is almost absent from the surface and therefore contributes little or nothing to catalysis. So, these characterizations explain why the activity of HDS catalysts supported on Al-rich Al_2O_3–TiO_2 mixed oxides, prepared by co-precipitation of alkoxides, is very similar to that exhibited by the corresponding alumina supported catalysts. It is also evident that high HDS activity is obtained when Ti–O–Ti bonds, or rather TiO_2 structures are present at the surface. Therefore, impregnation of TiO_2 on the surface of alumina or any other support oxide should lead to more active Mo or W-based HDS catalysts. In what follows we discuss some of our findings with Mo catalysts supported on titania-covered alumina, with different Ti contents, stressing the differences with those supported on Al–Ti(x) mixed oxides prepared by co-precipitation of alkoxides.

4. HDS catalysts supported on TiO_2 covered alumina

According to the studies conducted on catalysts supported on Al–Ti mixed oxides prepared by co-precipitation, a different trend of activity versus Ti content should be found for catalysts supported on alumina covered with TiO_2. It should be interesting to analyze if HDS catalysts prepared by deposition of variable amounts of TiO_2 on the surface of alumina behave different than those supported on Al_2O_3–TiO_2 co-precipitated mixed oxides. To this end, we prepared a series of Mo catalysts supported on alumina covered with titania, Ti(x)/Al, where $x = TiO_2/(TiO_2 + Al_2O_3) = 0.0, 0.038, 0.087, 0.131$ (corresponding to about 0, 3, 7 and 11 wt.% TiO_2). Supports and catalysts were characterized by several techniques (nitrogen physisorption, FT-Raman, FTIR-NO, UV–vis-DRS, XRD, TPR) and evaluated in the hydrodesulfurization of thiophene. These results were compared with those obtained with catalysts supported on Al–Ti(x) mixed oxides prepared by co-precipitation of alkoxides.

Raman spectroscopy is a very sensitive technique for determining the presence of titanium dioxides, due to the strength of the Raman modes of these compounds. Figs. 1 and 2 show the FT-Raman spectra of the two series of supports. In the case of co-precipitated Al–Ti (x) mixed oxides (Fig. 1) only a very broad peak extending from 2200 to 100 cm^{-1}, which decreases in intensity as Ti is incorporated to the alumina, is observed. These features are assigned to fluorescence phenomena [35]. The lack of detection of peaks corresponding to titanium oxides strongly suggests that the Ti oxide species in these supports are isolated. In contrast, the Raman spectra of impregnated Ti(x)/Al oxide samples for x = 0.087 and 0.131 (Fig. 2), which correspond respectively to 7 and 11 wt.% TiO_2, show the characteristic peaks of titania-anatase [36,37]. For x = 0.038 (3 wt.% TiO_2) or below no evidence of TiO_2 was detected, and only the fluorescence signal of alumina was observed. So, the Ti oxide surface structures present in the co-precipitated samples are isolated forming Ti–O–Al bonds whereas in the impregnated samples TiO_2-anatase particles are evident on the surface.

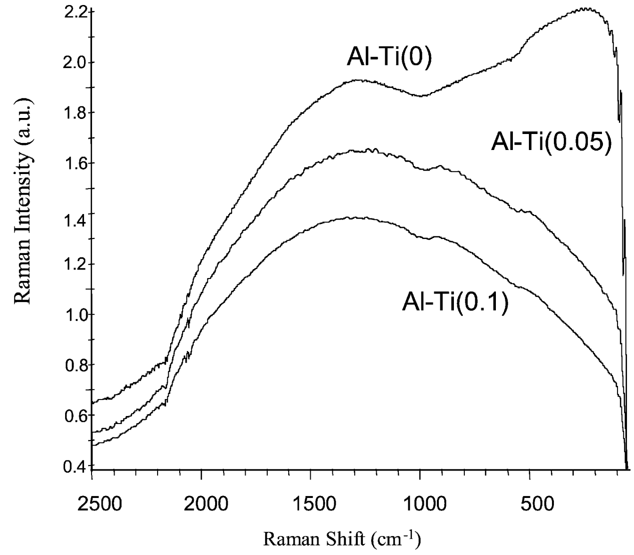

Fig. 1. FT-Raman spectra of Al_2O_3–$TiO_2(x)$ supports.

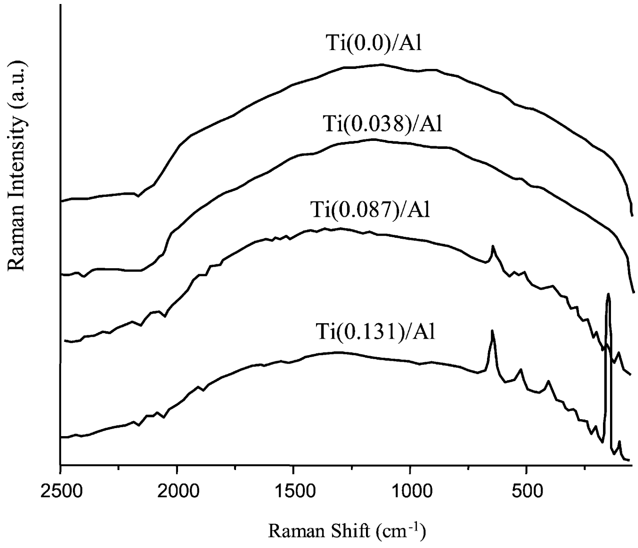

Fig. 2. FT-Raman spectra of $TiO_2(x)/Al_2O_3$ supports.

The electronic spectra of the two series of support samples, co-precipitated (Fig. 3) and impregnated (Fig. 4), show great differences between them. The Al–Ti(0.05) and Al–Ti(0.1) samples show a strong absorption centered at about 250 nm with absorption edges near 310 and 325 nm. In contrast, for the impregnated samples the absorptions are broader and the absorption edges are close to 400 nm for the samples Ti(0.131)/Al and Ti(0.087)/Al, indicating that in these samples TiO_2 particles exist. The Ti(0.038)/Al sample

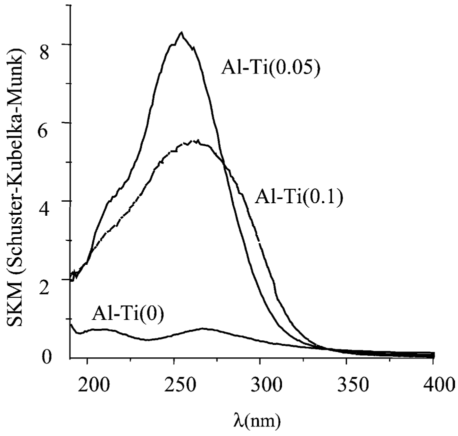

Fig. 3. Electronic spectra of Al_2O_3–$TiO_2(x)$ supports.

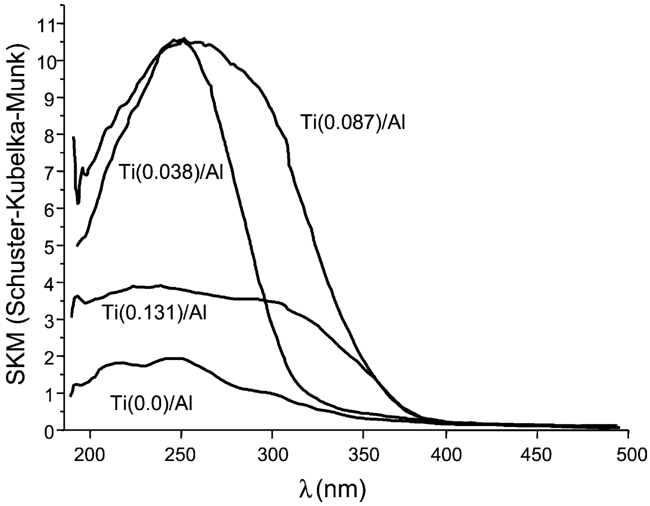

Fig. 4. Electronic spectra of $TiO_2(x)/Al_2O_3$ supports.

has a lower absorption edge more similar to those in the co-precipitated samples. These observations indicate that in the co-precipitated samples the Ti cations are isolated whereas in the impregnated samples a more polymerized form with characteristics close to TiO_2 prevails.

The catalytic evaluation of the Mo/Ti(*x*)/Al and NiMo/Ti(*x*)/Al samples in the hydrodesulfurization of thiophene showed that the HDS activity increases steadily with the titanium content. Figs. 5 and 6 compare the activity trend with Ti content for Mo and NiMo catalysts supported on co-precipitated Al–Ti(*x*) or impregnated Ti(*x*)/Al. It is clear that the activity trend changes completely with the type of support. For the samples supported on co-precipitated supports the activity at low titanium content ($x < 0.5$) remains similar or below that of the alumina supported catalyst, whereas in the impregnated samples the activity increases with Ti content. This result suggests that the presence on the surface of isolated Ti oxide species does not increase significantly the HDS activity and that to achieve high activity, the presence of surface TiO_2-like structures is necessary.

There are several effects that can contribute to the explanation of why the incorporation of Ti to the surface of the alumina support promotes higher HDS activity. One of them, mentioned in [38], considers that during the preparation of HDS catalysts, the reaction of aqueous molybdates with the highest frequency OH groups in alumina (type Ia and Ib) lead, at low Mo coverage, to stable tetrahedral molybdate species interacting strongly with the support. These Mo oxide species are difficult to convert to the active MoS_2 form. At higher Mo content (close or above monolayer coverage), a fraction of the Mo will still interact with these Ia and Ib type OH groups. As a result, the normalized HDS activity (per gram or atom of Mo) will be low. One way of increasing the amount of active Mo on the catalyst surface would be to eliminate the Ia and Ib hydroxyl groups from the alumina surface through titration with Ti isopropoxide, prior to the impregnation of Mo. Indeed, the results of this study indicated that the activity per gram of Mo increased when the most reactive alumina hydroxyl groups (Ia and Ib) were titrated with TiO_2. Recently, Segawa et al. [23] also showed evidence by IR of the substitution of Al–OH groups on alumina by Al–O–Ti in Al_2O_3–TiO_2 composites obtained by CVD of Ti on the surface of alumina. It was shown in this study that the stretching vibrations of alumina OH groups at higher wave numbers ($\sim$3762 cm^{-1}), were readily eliminated by deposition of Ti on the alumina surface. In a recent study about fluoride modification of Mo/Al_2O_3 catalysts, Cuevas et al. [13] showed beyond doubt that titration of the most reactive OH's

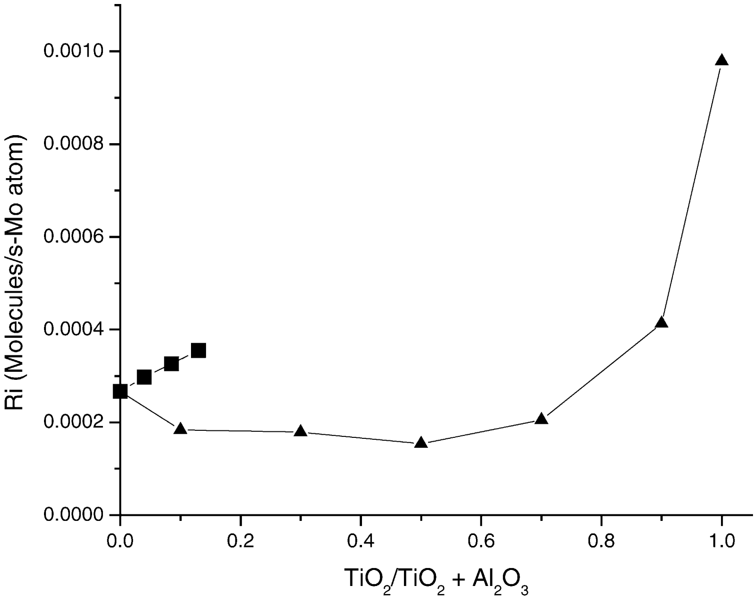

Fig. 5. Catalytic activity at 593 K in thiophene HDS for Mo catalysts supported on (▲) co-precipitated Al_2O_3–$TiO_2(x)$ and (■) impregnated $TiO_2(x)/Al_2O_3$ supports.

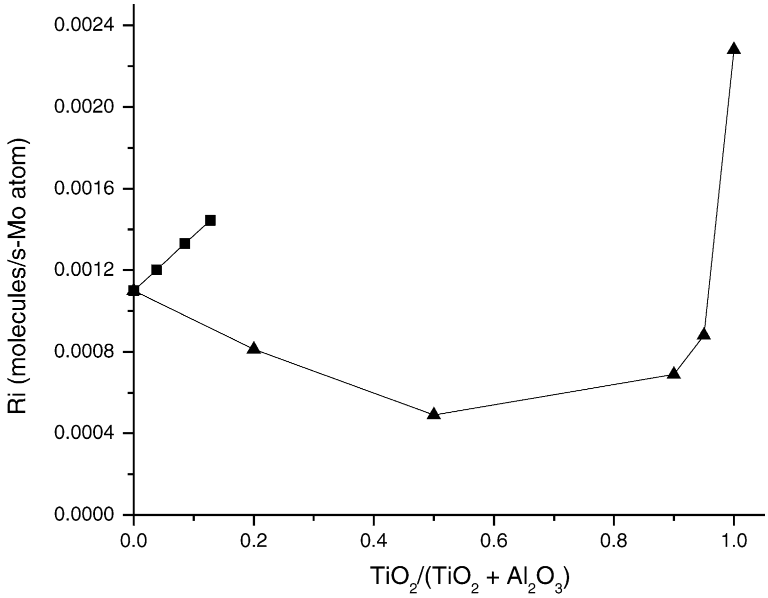

Fig. 6. Catalytic activity at 553 K in thiophene HDS for NiMo catalysts supported on (▲) co-precipitated Al_2O_3–TiO_2(*x*) and (■) impregnated TiO_2(*x*)/Al_2O_3 supports.

on alumina (Ia and Ib) with fluoride leads, after the subsequent impregnation of Mo, to a decrease in the population of Mo tetrahedral species strongly bound to the support, in favor of Mo octahedral polymeric species, which are readily sulfided, increasing in this way the number of molecular precursors for the active MoS_2 species. Titration of the OH groups with Ti should lead to similar results.

5. Mo species present on the surface

To analyze and compare the different Mo oxide surface species over alumina or titania we performed TPR tests on calcined Mo/Al_2O_3 and Mo/TiO_2 samples before and after washing the samples with an ammonium hydroxide aqueous solution (3 wt.% NH_4OH). This washing procedure dissolves great part of the octahedral Mo species, making more evident the presence of tetrahedral species that reduce at high temperature and which are water insoluble because they are strongly bound to the alumina support. Figs. 7 and 8 show the TPR traces of Mo catalysts supported on alumina and titania, respectively, obtained before and after washing with a solution of NH_4OH. The assignation of the different reduction peaks observed on Mo/alumina and Mo/titania has been made in the past [39,40]. The Mo/Al_2O_3 sample before washing presents one reduction peak at 740 K corresponding to the first stage of reduction of octahedral Mo species, an intermediate reduction region corresponding to reduction of octahedral polymeric species and an asymmetrical broad peak with maximum at about 1123 K, which contains contributions from the second stage of reduction of octahedral Mo species (low temperature side of the peak), and the reduction of tetrahedral Mo species in strong interaction with the alumina support (high temperature side of the peak). After washing, the TPR trace shows a small low temperature broad peak at 823 K, assigned to the reduction of some remaining polymeric Mo in octahedral coordination, and a high temperature symmetrical reduction peak (at about 1173 K) corresponding to the reduction of the tetrahedral Mo species bonded to the support. In contrast, the TPR of the Mo/TiO_2 sample before washing presents contributions from the first and second reduction stages of octahedral Mo species with different degrees of polymerization and from reduction of the titania support. The reduction of the latter occurs at about 837 K [28,29]. After washing, we observe the contribution of some polymeric Mo

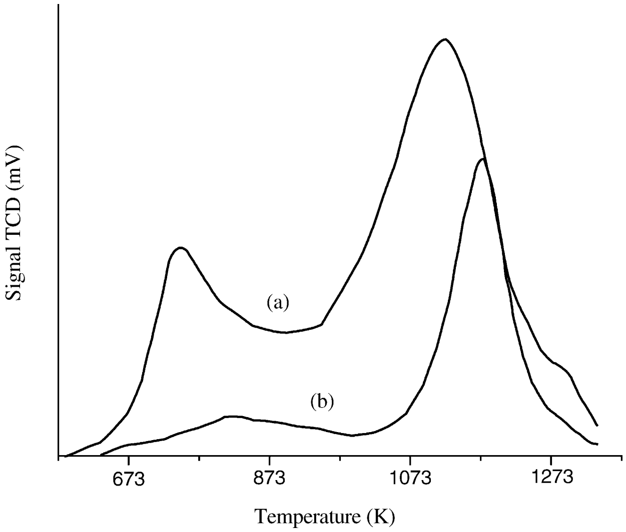

Fig. 7. TPR traces of Mo catalysts supported on alumina: (a) before and (b) after washing with a solution of NH_4OH.

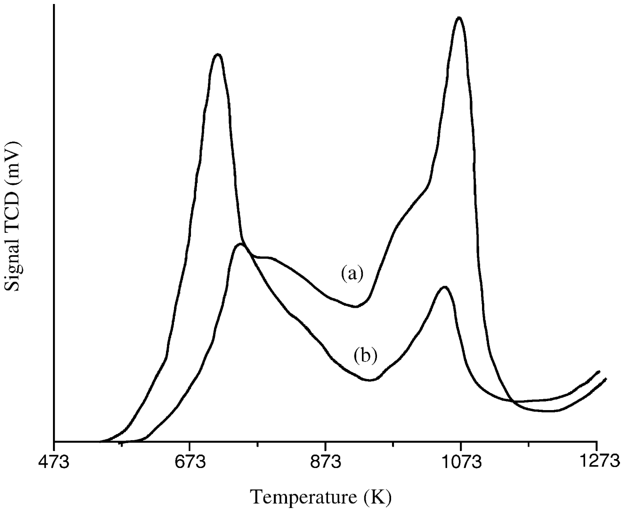

Fig. 8. TPR traces of Mo catalysts supported on titania: (a) before and (b) after washing with a solution of NH_4OH.

in its first and second stages of reduction and the reduction of TiO_2-anatase. So, our results show that the incorporation of TiO_2 to the alumina support of Mo-based HDS catalysts prevents the formation of Mo tetrahedral species interacting strongly with the alumina support, leaving therefore more Mo to form the active sulfided MoS_2 form.

6. Electronic properties of Ti-modified supports

Another important contribution of TiO_2 when it is incorporated to the alumina support of Mo or W oxide catalysts is the alteration of the electronic properties of the system. It is well known that alumina having a band gap of about 7.5 eV is an insulating material whereas TiO_2 with a band gap of about 3.2 eV is a semiconductor. A study of the electronic structure of tungsten oxide catalysts supported on various oxides was carried out by Gutierrez-Alejandre et al. [41]. In this study, tungsten oxide catalysts supported on pure oxides like Al_2O_3, TiO_2, ZrO_2 and mixed oxides such as TiO_2–Al_2O_3 and TiO_2–ZrO_2 were characterized by UV–vis spectroscopy. The data show that the electronic nature of the support can have an important effect on the electronic properties of the supported species. The addition of tungsten oxide to the surface of titania or titania-based mixed oxides, does not shift the UV–vis absorption edge of the support, indicating the location of the W 5d levels are within the conduction band of the overall solid. This assures the electric contact, through the conduction band of the support, between WO_3 particles located at different positions on the support surface. Titania-containing supports are easily reduced and in this reduced state the solid presents absorptions in the region above the edge, i.e., below the energy of the gap. This behavior was ascribed to the presence of Ti^{3+} species. It has in fact been reported that reduced titanias (i.e., non-stoichiometric TiO_{2}-x formally containing Ti^{3+}), strongly absorb in the visible region and have a quasi-metallic behavior [42]. It was later shown in [43] that for W supported catalysts below the monolayer, mono-oxo surface wolframyl species with similar low coordination largely predominate on the surface of alumina, titania and zirconia. However, the W=O bond length, the Lewis acidity, the charge transfer transition energies and the reducibility of the WO_x species, strongly depended on the support nature. In particular the wolframyl centers on alumina are more acidic, have higher charge transfer transition energies and are less reducible than those on titania. These findings mean that in spite of the similar geometrical "molecular" structure of the WO_x surface species, their reactivity varies considerably from carrier to carrier.

Several other benefits of titania over alumina supported catalysts have been published. Recently, it was reported in a study of titanium doped aluminas and sulfided NiMo/Al_2O_3–TiO_2 solids that titanium modification of alumina may fourfold increase the exchange capacity of pure alumina, and also that the Ti^{4+} ions in the alumina lattice are difficult to reduce but they act as dispersion centers for the supported sulfided NiMo phase [44]. This is in agreement with previous results that proposed that the greater number of acid sites in Ti-containing alumina supports increase the dispersion of the Mo supported phase.

All the above characteristics of titania and titania-modified alumina supports partially explain the increased dispersion, acidity, reactivity and reducibility of W and Mo oxide phases supported on Ti-based supports, and also point to the more efficient behavior of the supported phases in the performance of catalytic redox processes as found for SCR, oxidation catalysis and hydrotreating.

7. The role of TiO_2 as promoter of Mo supported phases

It is well accepted that the active sites of HDS catalysts are located on the edges of the MoS_2 crystallites. Therefore, the activity of these catalysts is normally proportional to the dispersion of the MoS_2 phase. However, some of the results obtained with Ti-containing catalysts have made explicit that the increased activity of these systems cannot be explained solely in terms of dispersion of the active phase [14], or its reducibility [30]. Also, the previous observation that the promotional effect of Co or Ni is greater for Mo catalysts supported on alumina than on titania was not explained satisfactorily. These problems were addressed by Ramírez et al. [45], in a study in which mechanical mixtures of MoS_2/Al_2O_3 and TiO_2/Al_2O_3 were tested in the hydrodesulfurization of thiophene. In this study, several of the questions about the role of TiO_2 in HDS catalysts were made clear, i.e. that (i) a fraction of the Ti^{4+} species present in the support become reduced under reaction conditions, (ii) Ti^{3+} species are formed in the reducing atmosphere prevailing under HDS reaction conditions, and (iii) the electron ‘‘in excess’’ in each Ti^{3+} has the tendency to be transferred and therefore the Ti^{3+} species act in effect as electron centers. Since in Ti-containing supports the different parts of the support are electrically connected through the conduction band of the support, as was demonstrated by Gutierrez-Alejandre et al. [41], then the 3d electron in Ti^{3+} can be easily injected to the Mo 3d conduction band. This, according to the calculations of Harris and Chianelli [46], is the requirement for MoS_2 promotion in HDS catalysts. In agreement with this, low valent Mo species were found by Shimada in Mo/TiO_2 catalysts [47], and it was suggested that these low valent species were produced by charge transfer from Ti^{3+} ions in the TiO_2 support. Moreover, in a recent study it was shown by ESR that a fraction of the Ti ions are reducible to Ti(III) by thermal treatment in vacuum and that, concomitantly, oxygen hole centers are formed [48]. Moreover, the charge transfer from Ti^{3+} centers to the MoS_2 phase must occur more easily under HDS reaction conditions due to the higher temperature and to the sulfidation of the titania surface [29,49], which increases the electrical conductivity of the support because TiS_2 has an almost metallic character [45]. Under these conditions, the empty orbital of Mo in MoS_2 should lie very near to the d orbital of Ti in TiS_2 [46,50], facilitating the charge transfer from the Ti^{3+} centers to Mo. Fig. 9 shows a simplified scheme of the promotional effect of Ti over Mo or W-based HDS catalysts showing that TiO_2 under reaction conditions gives rise to Ti^{3+} centers which can transfer electronic charge to the sulfided Mo or W active phases making more easy the formation of coordinatively unsaturated sites or sulfur vacancies.

Experimental evidence by TPR-S, showing that the number of CUS per Mo atom in the sulfided catalyst increases with Ti content was shown in [45]. This increased number of sulfur vacancies in the sulfided catalyst would be the result of an electronic promotion of Mo by Ti causing the weakening of the Mo–S bond due to injection of electrons, coming from Ti^{3+} centers, to the HOMO of Mo, occupying antibonding orbitals. This would be in complete agreement with the bond energy model [51], or the recent explanation given by Chianelli et al. [52], following the Sabatier principle, indicating that a medium value of sulfur metal bond energy optimizes the appropriate interaction between sulfur organic compounds and CUS active sites. The fact that the incorporation of Ni or Co to Mo/TiO_2 catalysts causes a further increase in catalytic activity, although to a lesser extent than in Mo/Al_2O_3 catalysts, indicates that the optimum value of the Mo–S bond energy is not reached by the sole incorporation of Ti and that additional promotion is required to obtain the value of the metal–sulfur bond energy which optimizes the interaction between sulfur organic compounds and CUS active sites. It is clear that the electronic promotion has a limit, or a maximum according to the Sabatier principle, because excessive weakening of the metal sulfur bonds in MoS_2 would lead to an inappropriate interaction between the sulfur compounds and the active phase.

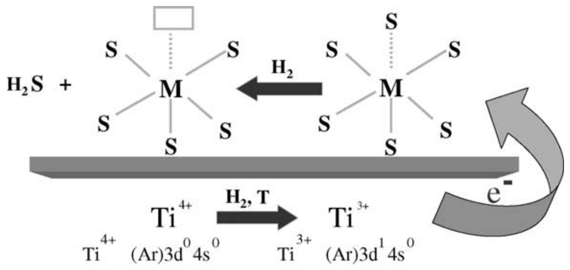

Fig. 9. Simplified scheme of the promotional effect of Ti over Mo- or W-based HDS catalysts; M = Mo or W.

Moreover, the weakening effect on the Mo–S bond strength by electronic promoters like Co is now accepted and has been confirmed theoretically and experimentally. A discussion on this subject is given in [52 and references therein]. All the previous results showing that the reduction of Mo or W oxide phases supported on TiO_2-containing supports takes place at lower temperatures than for alumina supported systems are in agreement with the above explanation.

In the case of mixed Al–Ti oxides with low Ti content prepared by co-precipitation or sol–gel, where Ti ions are isolated, the above electronic promotional effect by Ti-containing supports is not so efficient as in Ti-rich formulations because when Ti ions are surrounded by Al ions through Al–O–Ti bonds, the Ti^{3+} ions formed under reduction are stabilized [53], and therefore the transfer of the d electron in Ti^{3+} does not occur as easy as when there are Ti–O–Ti bonds. This would be in line with the observation that catalysts supported on Al–Ti mixed oxides, with TiO_2 loading below 50 mol%, have HDS activities similar or lower than alumina supported catalysts. In contrast, catalysts prepared by impregnation of TiO_2 on alumina, are more active at similar Ti loading. This is clearly observed in Figs. 5 and 6, where the activity in thiophene HDS as a function of Ti content is compared for NiMo/Al–Ti(x) and NiMo/($TiO_2(x)/Al_2O_3$) catalysts. It is clear that the activity trends in the two cases are completely different. For the NiMo/Al–Ti(x) catalyst, with support prepared by co-precipitation, at low Ti contents the activity decreases slightly with Ti, while for NiMo/($TiO_2(x)/Al_2O_3$) increases. This result corroborates that it is not the total Ti content that regulates the activity increase but the structure of the surface Ti oxide species.

In CoMo and NiMo catalysts supported on Al–Ti mixed oxides prepared by co-precipitation catalytic activity changes drastically with the titanium content. Therefore, these catalysts are good model systems to test if the number of sulfur vacancies or active CUS follows the same trend as catalytic activity with support composition. The number of CUS in the sulfided catalysts can be evaluated by performing TPR of the sulfided samples and quantifying the H_2S evolution in the 300–350 K temperature region of the TPR-S

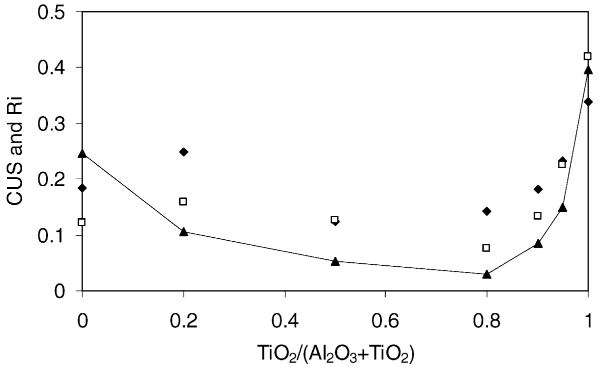

Fig. 10. Activity (▲) of CoMo/Al–Ti(x) catalysts at 513 K ($R_i \times 10^3$ = thiophene molecules, Mo atom^{-1} s^{-1}) and CUS vs. Ti content. CUS before (◆) and after (□) reaction test.

patterns, assigned to the presence of non-stoichiometric sulfur (S(x)). However, the number of CUS before reaction is not an accurate measure of the number of CUS existing during reaction. Because of this, TPR-S of the sulfided catalyst was performed before and after reaction for CoMo and NiMo catalysts supported on Al–Ti(x) mixed oxides prepared by co-precipitation. The number of CUS, estimated from the H_2S evolution in the 300–350 K region of the TPR-S patterns, before and after thiophene HDS are shown in Figs. 10 and 11 for CoMo/Al–Ti(x) and NiMo/Al–Ti(x) catalysts, respectively. For both catalysts, the evolution of H_2S, which is related to the number of sulfur vacancies created during TPR-S, coincides fairly well with the HDS activity trend. However, it was found that the variation of number of CUS with Ti content evaluated after reaction follows better the trend of catalytic activity.

So, it appears then that when the adequate Ti oxide surface structures are formed during preparation of Al–Ti binary oxide supports, several of the following factors lead to increased HDS activities: (i) under reaction conditions Ti acts as an electronic promoter of the MoS_2 (or WS_2) phase, (ii) induces higher acidity (greater number of acid sites), (iii) a higher dispersion of the sulfided phases is obtained and (iv) increased reducibility and sulfurability of the precursors is attained because the redox processes of the Mo (or W) phases are facilitated by the semiconductor character of TiO_2 in contrast to the insulating one presented by Al_2O_3 [14,28,29,40,41,48]. (v) An increased amount of MoS_2 (or WS_2) active phase is obtained because the addition of TiO_2 to alumina eliminates the most reactive hydroxyl groups (Ia and Ib) from the alumina surface, thus avoiding the formation of tetrahedral Mo oxide species, which are only reduced at high temperatures, and are therefore difficult to sulfide to the MoS_2 active form [38]. Among all these effects it appears that the electronic promotion of Mo by Ti is the most important.

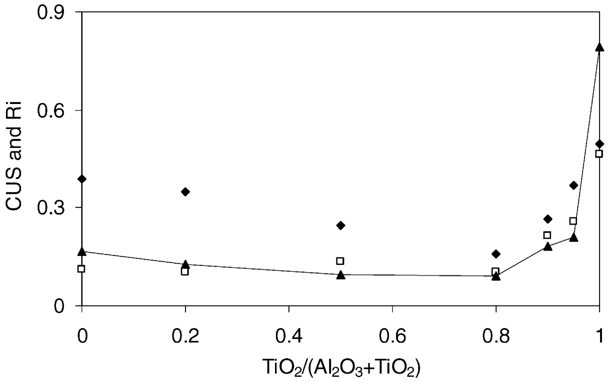

Fig. 11. Activity (▲) of NiMo/Al–Ti(x) catalysts at 433 K ($R_i \times 10^4$ = thiophene molecules, Mo atom^{-1} s^{-1}) and CUS vs. Ti content. CUS before (◆) and after (□) reaction test.

8. Repercussions to deep HDS

It is well known that sulfur compounds refractory to HDS such 4-MDBT or 4,6-DMDBT are hydrodesulfurized through several routes [2,7–9] and that the rate of transformation through a pre-hydrogenating route (HYD–HDS), leading to tetra or hexahydro DBTs, is greater than the direct hydrodesulfurization (HDS) one, leading to substituted biphenyl compounds. Hydrogenation of aromatics requires a greater number of CUS per catalytic site than HDS. Therefore, since the promotional effect of Ti causes an increase in the number of active CUS, Ti-containing catalysts must be good candidates for hydrogenation of aromatics and deep hydrodesulfurization. To test this proposal, a series of NiMo and NiW catalysts supported on Al_2O_3–TiO_2(x), were prepared and tested in the hydrogenation of naphthalene and the hydrodesulfurization of DBT and 4,6-DMDBT. As before, catalysts supported on Al–Ti(x) made by co-precipitation were used because they are good models to test changes of activity with support composition and not because they are the best supports.

The catalysts were prepared by sequential impregnation of Mo (or W) and Ni, using aqueous solutions of ammonium heptamolybdate (or ammonium metatungstate) and nickel nitrate. All catalysts were prepared with a surface concentration of Mo or W of 2.8 atoms/nm^2 and an atomic promoter ratio [Ni/(Ni + Mo (or W))] = 0.3. The activity tests for the HDS of DBT (5000 ppm S as DBT in hexadecane) were conducted in a continuous flow reactor operating at 800 psia and 573 K with a flow of hydrogen of 104 cm^3/min, while those of 4,6-DMDBT (5000 ppm S) were conducted in a batch reactor at 1000 psia and 573 K. In both cases 0.1 g of catalyst was used. The activity tests for the hydrogenation of naphthalene (3 wt.% in 40 ml of hexadecane) were conducted in a batch Parr reactor operating at P = 1000 psia and T = 573 K. The results from these tests are shown in Figs. 12-14, respectively. For comparison purposes the reported activities were calculated at low conversions (<10%).

For the hydrodesulfurization of DBT (Fig. 12), the activity for both NiMo and NiW increases with Ti content. In agreement with previous findings, the activity of catalysts with low titanium content is very similar to the catalyst

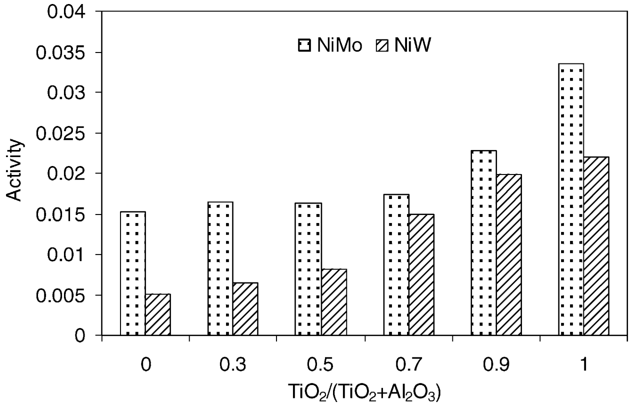

Fig. 12. Catalytic activity, expressed as pseudo-first-order rate constant (g h^{-1} m^{-2}) for NiMo and NiW catalysts supported on Al–Ti(x) in DBT HDS at 573 K and 800 psia.

supported on alumina, the activity increases only for the Ti-rich formulations. For all the catalyst compositions the activity of NiMo catalysts is greater than NiW, indicating that direct desulfurization, through which most of the DBT disappears, is performed better on NiMo than on NiW catalysts. In contrast for 4,6-DMDBT (Fig. 13), the activity of NiW catalysts is in general similar or greater than NiMo formulations. The difference in activity between NiMo and NiW catalysts is small for all the support compositions, except for the catalysts supported on pure TiO_2. In this case the activity of NiW is about 60% more than for NiMo. These results can be rationalized in terms of the greater hydrogenating capacity of NiW catalysts. It is well known that while DBT predominantly disappears through the direct hydrodesulfurization route, for 4,6-DMDBT the pre-hydrogenating route is more important. The difference between the activity of NiW supported on titania and all the other support formulations is a consequence of the greater promotional effect of pure TiO_2 with respect to Al_2O_3–TiO_2 mixed oxides. The presence of TiO_2 induces the formation of a greater number of CUS in the MoS_2 (or WS_2) active phase, favoring the hydrogenation–hydrodesulfurization transformation route of 4,6-DMDBT, which requires the hydrogenation of one of the aromatic rings before hydrodesulfurization. The greater hydrogenating capacity of TiO_2 supported catalysts is corroborated by the activity results from the hydrogenation of naphthalene (Fig. 14), which show that catalysts supported on TiO_2 have greater activity than those supported on Al–Ti mixed oxides or pure alumina. For this reaction the activity of NiW is greater than NiMo catalysts. These results are in good agreement with other studies performed on Ti-containing HDS catalysts using model molecules or real feeds [17,21–25,31,32].

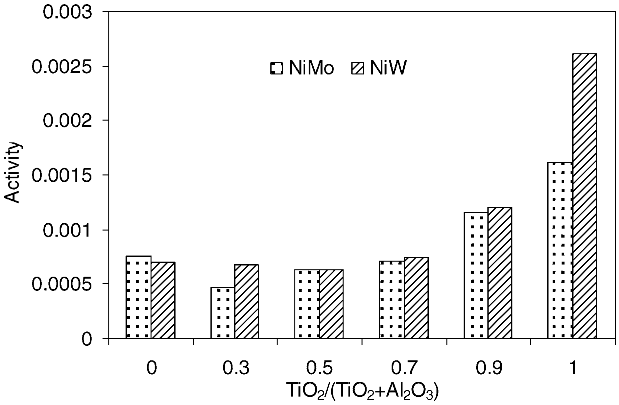

Fig. 13. Catalytic activity, expressed as pseudo-first-order rate constant (g h^{-1} m^{-2}) for NiMo and NiW catalysts supported on Al–Ti(x) in 4,6-DMDBT HDS at 573 K and 1000 psia.

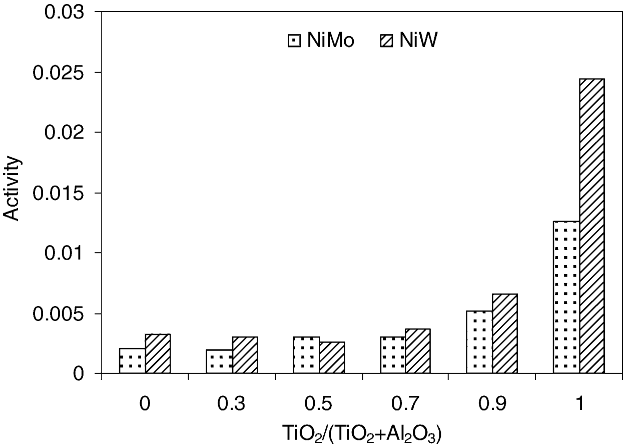

Fig. 14. Catalytic activity, expressed as pseudo-first-order rate constant (g h^{-1} m^{-2}) for NiMo and NiW catalysts supported on Al–Ti(x) in naphthalene hydrogenation at 573 K and 1000 psia.

9. Degree of sulfidation versus TiO_2 electronic promotion

The results with NiMo and NiW catalysts supported on Al–Ti(x) mixed oxides seem to indicate that the most important effect of Ti on the activity of the catalysts is of electronic nature. The decrease in the number of tetrahedral Mo or W oxide species in the catalysts precursor leading to better sulfided active phases does not appear to be so important. In fact, if the latter effect was the most important, an increase in HDS activity would be noticed at lower Ti contents because to obtain a well sulfided active phase one would only need to add enough Ti to suppress the most reactive hydroxyl groups, responsible for the formation of Mo or W oxide species interacting strongly with the support.

It is important to enquire further on the origin of the main differences in HDS activity between catalysts supported on TiO_2 and Al_2O_3, and in particular if these differences are due to the formation of a greater amount of well-sulfided MoS_2 or WS_2 phases over TiO_2-containing catalysts, or if the main beneficial effect is induced by the nature of TiO_2. To this end, we prepared two series of NiW/Al–Ti(x), x = 0, 0.5, 0.95, 1.0, catalysts using different W precursors. The first preparation used ammonium metatungstate (AMT) and $Ni(NO_3)_2$ as W and Ni precursor salts. The catalysts were prepared by the sequential impregnation (W first) of the precursor salts. After impregnation the catalysts were dried (373 K, 12 h) and calcined (673 K, 4 h). In this preparation the interaction between alumina and W oxide precursors is strong and sulfidation is expected to be difficult, except for the pure TiO_2 supported catalyst. For the second preparation the W precursor was $(NH_4)_2WS_4$, called hereafter ATT. This molecule already has sulfur in its structure and can be easily transformed to WS_2 by heating at 673 K under H_2–H_2S (15 vol.%) atmosphere. With this precursor the calcination step is not necessary and therefore there is no possibility of forming oxysulfides interacting strongly with the alumina support through W–O–Al bonds. For this preparation, an aqueous solution of ATT and $Ni(NO_3)_2$, was used to impregnate the Al–Ti(x) supports. In both preparations the metal content was 2.8 W atoms/nm^2 and a Ni/Ni + W atomic ratio of 0.3 was used. The catalysts were tested in the hydrodesulfurization of thiophene at atmospheric pressure and reaction temperatures of 553 and 573 K.

The results from the activity tests are shown in Table 1. In general, it is observed that the activity of the catalysts increases with Ti content. Comparing the activities of catalysts with the same support but different active phase precursor shows that the use of ATT produces catalysts with higher activity. However, the increase in activity due to the change of precursor salt becomes less important as the support contains more Ti. In fact, the difference in activity between the catalyst prepared with thiosalt (ATT) or with oxysalt (AMT) is only 17% for the catalysts supported on pure TiO_2, whereas for the catalysts supported on alumina is 60%. The change of support from alumina to titania leads in the case of the thiosalt precursor to a threefold increase in activity, and for the oxysalt precursor to four times the activity of the alumina supported catalyst. From these results it is clear that a thorough sulfidation of the catalyst, which in our case is obtained with ATT, can double the activity of an alumina supported catalyst. However, the change of support from alumina to titania can increase the activity three times in the case of thiosalt precursor, where the W phases are well sulfided. Therefore, the promotional effect caused by the nature of TiO_2 is more important to HDS activity than the increase in activity achieved through a better sulfidation of the W or Mo phases.

Table 1
Intrinsic HDS activities, $R_i \times 10^4$ (thiophene molecules, W atom^{-1} s^{-1}) of NiW/Al–Ti(x) catalysts prepared with $(NH_4)_2WS_4$ (ATT) or $(NH_4)_6W_{12}O_{40}$ H_2O (AMT)

Temperature (K)	Al_2O_3–TiO_2(x)							
	x = 0		x = 5		x = 0.95		x = 1.0	
	ATT	AMT	ATT	AMT	ATT	AMT	ATT	AMT
553	9.4	6.3	11.1	7.1	19.9	13.5	27.3	23.1
563	12.6	7.8	13.4	8.5	25.6	17.3	38.2	32.4

10. Conclusions

From the results of past studies and the new evidence presented here for Ti-containing HDS catalysts, several aspects can be highlighted:

1. The method of preparation of the support is of great importance to catalytic activity. It is not the total amount of Ti in the support that is relevant but rather the structures of the Ti oxide species on the surface. Isolated Ti oxide species do not increase significantly the HDS activity. To achieve high activity, the presence of reducible surface TiO_2-like structures is necessary.
2. The nature of the support modifies significantly the reactivity and properties of the supported Mo or W oxide phases. For example, the W=O bond length, the Lewis acidity, the charge transfer transition energies and the reducibility of the WO_x species, strongly depended on the support nature. In particular the Wolframyl centers on alumina are more acidic, have higher charge transfer transition energies and are less reducible than those on titania.
3. TiO_2 is an electronic promoter in HDS catalysts. Under HDS reaction conditions Ti^{3+} species are formed in the reducing atmosphere prevailing and the electron "in excess" in each Ti^{3+} has the tendency to be transferred. Therefore, these Ti^{3+} species act in effect as electron donors. These electrons can be easily transferred, through the conduction band of the support, and be injected to the Mo 3d conduction band. This charge transfer effect is the requirement for MoS_2 promotion in HDS catalysts.
4. It is proposed that as a consequence of the charge transfer from Ti^{3+} centers to the HOMO of Mo, occupying antibonding orbitals, the metal–sulfur bond in MoS_2 is weakened and the number of CUS per Mo atom in the sulfided catalyst increases with Ti content. This latter effect has been corroborated experimentally.
5. The electronic promotion of Mo by Ti has a limit, or a maximum according to the Sabatier principle, because excessive weakening of the metal sulfur bonds in MoS_2 would lead to an inappropriate interaction between the sulfur compounds and the active phase.
6. In the case of mixed Al–Ti oxides with low Ti content prepared by co-precipitation or sol–gel, where Ti ions are isolated, the electronic promotional effect is not effective because when Ti ions are surrounded by Al ions through Al–O–Ti bonds, the Ti^{3+} centers formed under reduction are stabilized, and therefore, the transfer of charge does not occur as easy as for Ti–O–Ti bonds.
7. The increased reducibility and sulfurability of oxide precursors in Ti-containing catalysts is related to the fact that the redox processes of the Mo (or W) phases are facilitated by the semiconductor character of TiO_2 in contrast to the insulating one presented by Al_2O_3.
8. The addition of TiO_2 to alumina eliminates the most reactive hydroxyl groups (type Ia and Ib) from the alumina surface, thus avoiding the formation of tetrahedral Mo

oxide species, which reduce at high temperatures and are difficult to sulfide to the MoS_2 active form. This causes an increase in the amount of MoS_2 (or WS_2) sulfided active phase and as a consequence to the specific activity of the catalyst. However, the impact of this effect on catalytic activity, although significant, is less important than the electronic promotion of Mo by Ti.

9. TiO_2-containing catalysts seem well suited for deep HDS because the formation of a greater number of CUS in the MoS_2 (or WS_2) active phase, favors the hydrogenation–hydrodesulfurization transformation route of 4,6-DMDBT.

Acknowledgments

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