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γ -Al₂O₃-supported XMo₆ Anderson Heteropolyoxomolybdates: Adsorption Studies for X = Te^{VI}, Al^{III}, Co^{III}, Cr^{III} and Ni^{II} by DR Spectroscopy and TPR Analysis

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ABSTRACT: The support–overlayer adsorptive interactions, generated when solutions of Anderson heteropolyoxomolybdateswere supported as a monolayer on γ -Al₂O₃ by means of the equilibrium adsorption method, were studied by XRD analysis, DR spectroscopy, electron microscopy (SEM–EDAX) and TPR methods. The adsorption isotherms and corresponding adsorption parameters (number of active sites and adsorption constants) of the γ -Al₂O₃-supported ammonium heptamolybdate were obtained and discussed. The following sequence of adsorption strength was suggested: CoMo₆ > CrMo₆ > TeMo₆ ~ AlMo₆ > NiMo₆. The effectiveness of the TPR technique as a tool for elucidating interaction effects was clearly demonstrated. The formation of a γ -Al₂O₃-supported Te–Mo mixed valence oxide appears to provide new and interesting catalytic possibilities.

INTRODUCTION

Various different types of heteropolyoxomolybdates have been studied over the past few years in an attempt to analyse their applicability in a range of fields of chemistry, particularly catalysis (Mizuno and Misono 1994, 1998; Pope 1983, 1991).

The replacement of traditional Mo–metal/support catalysts (prepared by the equilibrium impregnation of a support with an aqueous solution containing ammonium heptamolybdate and a metallic salt) by ones involving supported heteropolyoxomolybdates offers a new approach and interesting possibilities (Mizuno and Misono 1994, 1998; Cabello *et al.* 2000). The use of heteropolyoxoanions as catalytic materials provides some advantages over the conventional catalyst. Such advantages are related to the structural characteristics of heteropolyoxoanions (an ordered arrangement of metallic elements which ensures uniformity of deposition), the redox and acid/base properties of such materials (associated with the presence of heteroatoms), the high concentration of active sites generated on the surface, good solubility of the impregnant and the preservation of the anionic structure in aqueous solution, easier control of the impregnation method leading to the elimination of the concentration profile of active sites as a function of depth in the support, etc.

And erson-type phases, possessing a heteropolyanion of general formula $[XMo_6O_{24}H_x]^{n-}$ (referred to hereafter as XMo₆) where X is a heteroatom and x = 0 or 6, have a hexagonal D_{3d} planar structure

in which the central X ion is surrounded by six octahedral MoO_6 groups. Each MoO_6 unit shares an edge with each of its two neighbouring MoO_6 units and another edge with the XO_6 or $X(OH)_6$ octahedron (Pope 1983, 1991; Nomiya *et al.* 1987). Such a planar structure has the advantage of providing efficient contact with the surface structure of the support material.

The spectroscopic and thermal behaviour of a series of pure ammonium salts of Anderson-type heteropolyoxomolybdates has been studied in our laboratory (Botto *et al.* 1992, 1994a,b, 1997, 2000). Thermal treatment involving the reduction of phases containing Cr^{III} , Al^{III} , Fe^{III} , Co^{III} , Te^{VI} and Ni^{II} has been studied by temperature programmed reduction (TPR) in order to analyse the possible application of such phases in catalysts for hydrotreatment and/or oxidation. In this regard, it has been shown that the TeMo₆ phase is a precursor of a Te–Mo mixed valence oxide which is of interest in olefin oxidation and ammoxidation catalytic processes (Botto *et al.* 1997; Vallar and Goreaud 1997), PtMo₆ has been applied in hydrogenolysis and NO/CO reactions (Tomishige *et al.* 1997) whereas the use of $CoMo_6/\gamma$ -Al₂O₃ catalyst has recently been tested in HDS and HYD reactions (Cabello *et al.* 2000). One of the most interesting features of the latter system is the elimination of the need for thermal pretreatment (which is essential for the traditional Co–Mo/ γ -Al₂O₃ catalyst), thereby preventing the formation of an inactive CoAl₂O₄ spinel oxide (Cabello *et al.* 2000).

Although Mo/ γ -Al₂O₃ and metal–Mo/ γ -Al₂O₃ catalysts have been extensively investigated, very little information regarding the XMo₆/ γ -Al₂O₃ catalytic system has been reported. The present work involved an analysis of the support–overlayer adsorptive interactions occurring when γ -Al₂O₃ was impregnated with aqueous solutions of XMo₆ to form a monolayer on the support surface. X-Ray diffraction (XRD), diffuse reflectance spectroscopy (DRS), electron microscopy (SEM and EDAX), thermal treatments under reducing conditions by temperature programmed reduction (TPR) methods and chemical analysis by atomic absorption were the main techniques used in this study. In this way the effect of various heteroatoms such as Te^{VI}, Co^{III}, Al^{III}, Cr^{III} and Ni^{II} on Mo–support interactions has been investigated. The corresponding adsorption isotherms as well as the magnitude of the K_{ad} adsorption constant have been determined and discussed as a means of establishing the potential of the XMo₆/ γ -Al₂O₃ catalytic system. Appropriate samples were prepared at toom temperature via the equilibrium impregnation method employing aqueous solutions of XMo₆ in the 1.5–20 mg Mo/ml range. TPR patterns of the supported phases were determined and compared with those of the unsupported heteropolyoxomolybdates, differences in the reduction capabilities being taken as a useful measurement of the interaction effects involved.

EXPERIMENTAL

Synthesis and characterisation of pure phases

Synthesis of the Anderson phases of $CoMo_6$, $CrMo_6$, $NiMo_6$, $AlMo_6$ and $TeMo_6$ was carried out by slow precipitation from aqueous solutions containing ammonium heptamolybdate (hereafter referred to as AHM) and stoichiometric amounts of the corresponding heteroatom salts [usually the sulphates but Te(OH)₆ for TeMo₆] according to the general method described previously (Nomiya *et al.* 1987). Characterisation of the species formed was carried out by X-ray powder diffraction (XRD) methods using a Philips PW 1714 diffractometer (Ni-filtered Cu K α radiation) and by IR and Raman spectroscopy using a Bruker IFS 66 FT-IR spectrophotometer (KBr pellet technique) and a Bruker FT-IFS interferometer (Nd–YAG laser, 1064 μ), respectively.

Catalyst preparation

Preparation of the XMo_{6}/γ -Al₂O₃ catalysts was by equilibrium impregnation of the support with

aqueous solutions of the ammonium salts of the respective Anderson phases employing concentrations in the range 1.5–20 mg Mo/ml. The upper limit of such solution concentrations was determined by the solubility of the respective salt. The γ -Al₂O₃ powder employed possessed a superficial surface area of 226 m²/g, a pore volume of 0.65 cm³/g and a grain size of 200 µm. All impregnations were performed at room temperature employing an excess of solution with continuous stirring for 24 h. The solid was then separated by centrifugation and dried at 80°C. Chemical tests of the solutions before and after impregnation were made using an IL-457 atomic absorption spectrometer. This enabled the values of C_i (initial concentration of the impregnant solution) and C_f (final concentration of the impregnant solution) expressed as mg metal/ml solution to be calculated. From these values and the use of a simple material balance equation, it was possible to calculate C_a (the concentration of adsorbed metal, i.e. Mo, Co, Cr, Ni and Al — but not Te) expressed as g metal/g support.

Similar studies were performed with aqueous solutions of ammonium heptamolybdate(VI) tetrahydrate (obtained from Aldrich) for comparative purposes.

Adsorption isotherms

The adsorption isotherms for the different Anderson phases were measured at room temperature using the values of C_i , C_f and C_a determined for M = Mo. When the concentration of Mo adsorbed (C_a) was plotted against the Mo concentration in solution at equilibrium (C_f), the shape of the resulting curves was found to follow the Langmuir model (Giles *et al.* 1974a,b). Hence, by plotting the linearised form of the Langmuir equation, i.e.

$$\frac{C_{f}}{C_{a}} = \frac{1}{K_{ad}S} + \frac{C_{f}}{S}$$
(1)

and extrapolating the subsequent straight line obtained, it was possible to calculate the total number of active sites present on the surface (S) expressed in g Mo/g γ -Al₂O₃. The equilibrium adsorption constant (K_{ad}), expressed in ml/g Mo, could be obtained from the slope of the line.

Temperature programmed reduction (TPR) analysis

The TPR patterns for the various XMo_6/γ -Al₂O₃ catalytic systems prepared, whose C_a values corresponded to the presence of a monolayer on the support surface (6–8% Mo) (Cabello *et al.* 2000), were obtained by means of home-made equipment. The reactor was fed with a gaseous stream consisting of 10% H₂ in N₂ gas at a rate of 100 cm³/min and the temperature range was varied between 20°C and 1000°C at a rate of 10°C/min. Similar TPR conditions were used in order to compare the results obtained in the present study with those determined previously for the pure phases (Botto *et al.* 1994a). The amount of H₂ consumed in the various experiments was determined by means of a conductimetric cell.

Diffuse reflectance spectroscopy (DRS) analysis

Characterisation of the pure and supported phases as well as the pyrolysis products and intermediates was effected by means of a UV–vis Varian Super Scan 3 spectrophotometer employing a double-beam arrangement and a built-in recorder. The internal standard employed in all cases was γ -Al₂O₃, i.e. the catalyst support.

Electron microprobe analysis

The supported and unsupported samples, both before and after thermal treatment, were evaluated by SEM microscopy using a Philips 505 electron microscope equipped with an EDAX 9100 microsound and energy dispersive detector. Pure reagents were used in all cases for reference purposes.

RESULTS AND DISCUSSION

Adsorption isotherms of supported XMo₆ phases

Adsorption isotherms for molybdenum on γ -Al₂O₃ as obtained from AHM impregnating solutions (over the concentration range 5–20 mg Mo/ml) have been reported in the literature over the past decade (Rodriguez *et al.* 1989). The typically two-stepped isotherms obtained were attributed to several factors mainly related to the complex equilibria existing in aqueous AHM solutions. Thus, different molybdena species (monomers and polymers) and various distributions of such species on the alumina surface (monolayer, multilayer) have been considered (Cáceres *et al.* 1985). Monomeric tetrahedral species were observed at low concentrations (< 10 mg Mo/ml) while a preponderance of octahedral heptameric molybdate species occurred at higher concentrations (Cáceres *et al.* 1985).

Figures 1 and 2 depict the molybdenum adsorption isotherms obtained for the XMo₆/ γ -Al₂O₃ systems studied at room temperature in the present work for X = Te^{VI} and Al^{III} (Figure 1) and for X = Co^{III}, Cr^{III} and Ni^{II} (Figure 2), respectively. All these curves exhibit Langmuir-type behaviour since the value of C_a increased with C_f until a constant value was attained (Giles *et al.* 1974a,b). Regression analysis of the data obtained employing the least-squares method allowed the values of K_{ad} and S to be estimated. The corresponding values are listed in Table 1. Similar parameters for AHM were also calculated for aqueous solutions up to a concentration of 10 mg Mo/ml, i.e. corresponding to the first step in the adsorption isotherm where a preponderance of tetrahedral monomeric species would be expected in aqueous solution. However, it should be noted that an exact comparison between the behaviour for AHM and XMo₆ is not entirely valid since neither the symmetry nor the structure of the heptameric species, nor their stabilities in aqueous solution, are similar. Nevertheless, the improved adsorption of the XMo₆ phases relative to AHM is clearly demonstrated by the data recorded.

The advantages associated with the use of Anderson-phase solutions is linked to the presence of an unique molybdenum species in the aqueous solution employed, i.e. the planar XMo₆ heteropolyanion which is present in the concentration range 1.5–15 mg Mo/ml for X = Ni, Co, Cr and Al but not for Te where the range extends up to 20 mg Mo/ml. This may be demonstrated spectroscopically as described in detail below. The size and planar structure of the heteropolyanion ensures the formation of a monolayer on the support (certainly over the concentration range 6–8% Mo/g γ -Al₂O₃) and results in the coverage of all types of interaction sites on the alumina surface. At higher concentrations, the formation of clusters and multilayers is to be expected. Relative to Mo/ γ -Al₂O₃ and metal–Mo/ γ -Al₂O₃ conventional catalysts, the heteroatom plays an important role in the XMo₆/ γ -Al₂O₃ system. Differences among the various K_{ad} values observed for the supported Anderson phases will be discussed below on the basis of the structural, electronic and thermal properties of the latter.



Figure 1. Molybdenum adsorption isotherms for XMo_{6}/γ -Al₂O₃ samples (where X = Te, Al) as determined at room temperature.



Figure 2. Molybdenum adsorption isotherms for XMo_6/γ -Al₂O₃ samples (where X = Cr, Ni, Co) as determined at room temperature.

Phase	K _{ad} (ml/g Mo)	S (g Mo/g support)	10 ²⁰ S (atoms Mo/g support)
TeMo	980	0.09	5.6
CoMo	1374	0.09	5.6
NiMo	436	0.12	7.5
AlMo	840	0.09	5.6
CrMo ₆	1430	0.08	5.0
AHM	290	0.10	6.3

TABLE 1. Adsorption Parameters for XMo_6/γ -Al₂O₃ Systems^a

^aAHM/ γ -Al₂O₃ included for reference purposes; K_{ad} = molybdenum adsorption constant; S = number of active sites on alumina surface.

Temperature programmed reduction behaviour of supported XMo₆ phases

Figure 3 shows the TPR patterns for the various XMo₆ phases supported on γ -Al₂O₃, the pattern for AHM under similar conditions being included for comparative purposes. In general, the TPR behaviour of the condensed molybdates exhibits two typical regions of H₂ consumption with increasing temperature. These regions correspond to Mo^{VI}–Mo^{IV} and Mo^{IV}–Mo⁰ reactions, respectively (Janssen 1991). However, it will be seen from the figure that the peak temperatures and the shapes of the patterns for the supported phases differ appreciably from those of the bulk material.

The data obtained from the TPR studies of the bulk and γ -Al₂O₃-supported phases are listed in Tables 2 and 3, respectively, where the possible intermediates present in the various systems are also listed. The presence of such intermediates, i.e. MoO_x (x < 3) oxides (with Mo_4O_{11} species as minor and MoO_2 species as major components), metallic molybdates [e.g. $Cr_2(MoO_4)_3$, $Al_2(MoO_4)_3$, $CoMoO_4$ and NiMoO₄) and a probable Te–Mo mixed valence oxide in the case of TeMo₆, may be established by XRD studies despite the low crystallinity of the unsupported phases.

XRD analyses were more difficult for the supported phases due to the high dispersion of the adsorbed heteropolyanion (as a monolayer rather than as microcrystals) and also because of the presence of excess γ -Al₂O₃ which affects the resolution of the lines corresponding to minor constituents in the reduced samples. Thus, the presence of intense lines corresponding to minor constituents in the reduced samples. Thus, the presence of intense lines arising from monoclinic MoO₂ as well as broad bands corresponding to the γ -Al₂O₃ spinel, which in practice overlap those for the structurally related CoAl₂O₄ and NiAl₂O₄ phases, may be associated with the first signal in the related TPR spectra. However, with the supported TeMo₆ phase, the formation of a mixed valency Te–Mo oxide and its reduction to Te metal (~ 500°C) can be more readily identified from XRD analysis (Botto *et al.* 1997).

Since TeMo₆ was the most soluble phase studied, solutions with initial concentrations, C_i , ranging from 5 mg/ml to 20 mg/ml could be used in the impregnation stage and hence the effect of the concentration of the supported heteropolyanion on the reduction process could be examined in this case. The data listed in Table 4 indicate that substantial differences were observed for the temperature of the Mo^{VI}–Mo^{IV} reaction as the initial concentration increased. Such differences may be attributed to the formation of clusters as a result of the precipitation of microcrystals from the impregnating solution during the drying step in the process. Run 2 listed in this table may be considered to correspond to the conditions necessary for an ideal dispersion of the reducible species



Figure 3. TPR patterns for (a) $AHM/\gamma-Al_2O_3$ samples and for (b) $NiMo_6/\gamma-Al_2O_3$, (c) $CoMo_6/\gamma-Al_2O_3$, (d) $CrMo_6/\gamma-Al_2O_3$, (e) $AIMo_6/\gamma-Al_2O_3$ and (f) $TeMo_6/\gamma-Al_2O_3$ Anderson phases.

TABLE 2. TPR Signal Temperatures for γ-Al₂O₃-supported and Unsupported XMo₆ Anderson Phases

Phase	Supported (°C)	Intermediates ^a	Unsupported (°C)	Intermediates ^a
TeMo ₆	503, 843	TeMo ₅ O ₁₆ (~450°C), MoO ₂	391*, 473, 666, 937	TeMo ₅ O ₁₆ (~473°C), MoO ₂
CoMo ₆	467, 845	MoO ₂ , CoAl ₂ O ₄	430*, 500, 610, 848	MoO ₂ , CoMoO ₄
NiMo ₆	415, 818	MoO ₂ , NiAl ₂ O ₄	427*, 455*, 521, 769	MoO ₂ , NiMoO ₄
AlMo ₆	485, 801*, 862	MoO_2 , $Al_2(MoO_4)_3$, Mo_4O_{11}	400*, 586, 842*, 990	Mo_4O_{11} , $Al_2(MoO_4)_3$, MoO_2
CrMo ₆	510, 915	MoO ₂ , α -(CrAl) ₂ O ₃	337*, 468*, 516*,	MoO_2 , $Cr_2(MoO_4)_3$
0			574, 819*, 874	2 2 1 2
AHM	490, 872	MoO ₂	500*, 730, 850	MoO

^aIntermediates prevailing at temperature corresponding to first reduction process (stronger signal). *Weak peaks.

TABLE 3. Temperature Separation (in °C) Between TPR Signals for the Mo^{VI}-Mo^{IV} and Mo^{IV}-Mo⁰Processes in γ -Al₂O₃-supported (I) and Bulk (II) Anderson Phases and Between the First TPR Signal for
 γ -Al₂O₃-supported and Bulk Anderson Phases (III)

Phase	Supported Anderson phase (I) T(Mo ^{VI} -Mo ^{IV})-T(Mo ^{IV} -Mo ⁰)	Bulk Anderson phase (II) T(Mo ^{VI} -Mo ^{IV})-T(Mo ^{IV} -Mo ⁰)	First signal difference (III) T(Mo ^{VI} –Mo ^{IV}) TPR step
TeMo ₆	340	271	66
CoMo ₆	378	238	88
NiMo ₆	403	248	106
AlMo	377	404	101
CrMo ₆	405	300	64
AHM	382	120	240

TABLE 4. TPR Peak Maxima for Mo^{VI}–Mo^{IV} and Mo^{IV}–Mo⁰ Processes for TeMo₆/γ-Al₂O₃ Samples Prepared by Impregnation with Solutions of Different Concentration

Run	Conc. of initial	Conc. of metal adsorbed C _a (% Mo)	TPR peak maxima (°C)	TPR peak maxima (°C)	
	impregnant solution, C _i (mg Mo/ml)		Mo ^{VI} –Mo ^{IV}	Mo ^{IV} –Mo ⁰	
1	5	5	504	838	
2	10	8	503	843	
3	15	9	439, 474	845	
4	20	10	426, 476	847	

as a result of the formation of a monolayer as reported elsewhere (Cabello *et al.* 2000). Higher values of C_i did not lead to proportionately improved values for the amount adsorbed, C_a . The assumption that clusters were formed when C_a values of 8% were attained may be corroborated by the temperature data for the Mo^{VI}–Mo^{IV} TPR reaction (see Table 2). In contrast, the temperature necessary for the Mo^{IV}–Mo⁰ reduction step is independent of the concentration employed during the impregnant concentrations may be attributed to the size of the intermediate MoO₂ clusters formed. When these are of a sufficient size, the rate of the reaction must be controlled by that for diffusion whereas for smaller sizes or thin layers the reaction kinetics are likely to exhibit more complex behaviour (Rothhaar and Oechsner 1998).

The distribution of species on the support surface is complex and depends on chemical and structural factors which affect the strength of the support–overlayer interaction (Corá *et al.* 1997). The data listed in Table 3 show that the difference in temperature between the value for the first TPR signal for the various supported Anderson phases on γ -Al₂O₃ and for the bulk Anderson phase itself is close to 100°C (corresponding to D_{3d} symmetry) whereas the corresponding value for bulk AHM was 240°C (corresponding to C_{2v} symmetry). To a first approximation, this difference may be attributed to the charge and ionic radii of the heteroatoms as well as to their acidic properties and their redox ability. Such characteristics must influence the interaction between the heteroatom

and the support in addition to the interactions occurring with the basic OH groups on the γ -Al₂O₃ surface which have been the subject of several studies (Vit and Zdrazil 1997). The latter reactions, whose extent will depend on the basicity of the support surface and whose behaviour will be Brönsted in nature, also play an important role in the adsorptive interaction of the heteroatom. It is of interest to note at this point that di- and tri-valent heteroatoms generate hexa-protonated Anderson structures, where six protons are attached directly to the oxygen atoms associated with the central X polyhedral. However, there is no evidence to suggest that these protons are acidic (Carrier *et al.* 1997), whereas the TeMo₆ structure is deprotonated because of the high acidic character of the heteroatom.

There are serious difficulties in analysing the behaviour of transition and non-transition heteroatoms jointly because of the different factors governing their chemical properties. For this reason, we consider the two groups of elements separately below.

The Ni^{II} (d⁸), Co^{III} (d⁶, low-spin) and Cr^{III} (d³) transition elements exhibit charge-transfer activity in addition to Brönsted behaviour. This must surely occur through the $p\pi$ -donation of interface oxygen atoms to the unoccupied $d_{x^2-y^2}$ and d_{z^2} orbitals of trivalent Co and Cr (these orbitals are halfoccupied in the case of Ni^{II}). In the same manner, since trivalent heteroatoms have similar structural and chemical characteristics, a ready overlayer–support cationic interchange is possible. In practice, however, electron transfer may be ignored in the AlMo₆/ γ -Al₂O₃ case. Recent investigations regarding AHM adsorbed on to alumina have provided important conclusions regarding the reaction at the interface (Le Bihan *et al.* 1998). Thus, the high affinity of Al for an Anderson-type structure can be associated with an equilibrium involving the dissolution of alumina. This leads to the deposition on the support of AlMo₆ as an unique molybdenum-containing species. More recent studies carried out on the WO_x/ γ -Al₂O₃ catalyst have demonstrated the formation of Keggin-type aluminotungstic heteropolyanions at the interface (Carrier *et al.* 1999).

An analysis of the isotherm data for both the various heteroatoms and molybdenum is given in Table 5. It will be seen that for a constant amount of Mo adsorbed ($C_a = 6\%$), the corresponding values of C_a for the heteroatom, X, when the latter is Cr are peculiar. Table 5 includes the theoretical values of C_a for the heteroatom derived from stoichiometric considerations as well as the corresponding C_a values for X and Mo at the plateau of the isotherms. The different degree of adsorption for the supported CrMo₆ system suggests the establishment of a complex equilibrium involving adsorption, dissolution and cationic replacement reactions. The homogeneous and heterogeneous processes occurring may best be depicted as:

(1) Deposition

$$XMo_6(sol.) \Leftrightarrow XMo_6(ads.)$$

(2) Dissolution of support

 $Al^{III}(supp.) \Leftrightarrow Al^{III}(sol.)$

(3) Counter-diffusion

$$Al^{III}(supp.) + XMo_6(ads.) \Leftrightarrow AlMo_6(ads.) + X(supp.)$$

(4) *Cationic interchange*

 $Al^{III}(sol.) + XMo_6(ads.) \Leftrightarrow AlMo_6(ads.) + X^{III}(sol.)$

where sol., ads. and supp. depict the solution, adsorbed and supported nature of the species involved.

Phase	Isotherm beginning			Isotherm pla	Isotherm plateau		
	C _a (Mo)	$C_a(X)_{exp.}$	$C_a(X)_{theor.}$	C _a (Mo) _{exp.}	$C_a(X)_{exp.}$	$C_a(X)_{theor.}$	
CoMo ₆	6	0.61	0.61	8.30	0.80	0.84	
NiMo	6	0.59	0.61	7.05	0.67	0.71	
CrMo	6	0.70	0.54	6.50	0.60	0.58	
AlMo ₆	6	0.30	0.28	6.30	0.30	0.29	

TABLE 5. Concentration of Adsorbed X at Beginning of Isotherms and at Isotherm Plateaux for Mo and X for Various XMo₆/γ-Al₂O₃ Samples Prepared with 6% Mo Content. Theoretical X Values from Stoichiometric Considerations Included in Both Cases^a

^aData expressed in % element; those for TeMo₆ not included — see text.

Although adsorption would be directed by reaction (1), the Cr heteroatom appears to be adsorbed by a ca. 30% greater extent than Mo. Hence, in the system where X = Cr, reactions (2) and (3) must play an important role, with the dissolution of Al^{III} appearing to depend on the characteristics of the heteroatom. For X = Co and Ni, the exchange interactions and counter-diffusion reactions appear to be minimised, and may be considered to be totally absent for X = Al. We have not included TeMo₆ in this comparative analysis because of technical difficulties in determining Te. However, this phase would be expected to exhibit a different behaviour because of the chemical characteristics of the heteroatom, i.e. higher acidic character, charge and ionic radius. Such characteristics are also responsible for the attachment of the Te atom to ony oxygen atoms.

The K_{ad} data obtained in the present study for the protonated Anderson phases (Table 1) show that cationic counter-diffusion [viz. alumina dissolution in the terms of Carrier *et al.* (1997)] is favoured in the CrMo₆/ γ -Al₂O₃ system. The different rate of deposition observed for the NiMo₆ phase may be attributed to the larger size of the nickel ion, its lower valency and its electronic configuration. The comparable K_{ad} values observed for NiMo₆ and AHM suggest the simple model for the deposition of the protonated Anderson phases depicted in Figure 4. This would suggest an 'ideal' quasi-planar deposition for CoMo₆ and AlMo₆, a ready cationic interchange and diffusion of the trivalent species for the CrMo₆ phase and adverse conditions for these processes in the case of NiMo₆.

Finally, the similarity between the temperature for the first TPR signal for AHM and the AlMo₆ supported phase (Table 2) provides a new route for demonstrating alumina dissolution from the support on contact of the latter with a solution containing condensed octahedral molybdate(VI) species.



Figure 4. Simple model for the deposition of protonated XM_{0_6} Anderson phases: (a) X = Co, Al; (b) X = Ni; and (c) X = Cr.



Figure 5. Diffuse reflectance (DR) spectra for $CoMo_{c}$: (a) unsupported phase; (b) TPR product from unsupported phase (T = 500°C); (c) supported phase; and (d) TPR product from supported phase (T = 500°C).

Diffuse reflectance spectra of supported XMo₆ phases

Electronic structure in different ligand environments can be analysed by DRS methods since the d–d spectra of transition metals can be ascribed to two classes of processes: those involving electron transfer from one d-shell to another and those where an electron is transferred from (or to) the band state of the ligands (oxygen) to (or from) the d-shell. These excitations are important both for describing the optical properties of materials and also for analysing chemical properties such as catalytic activity (Tchougréeff 1997).

Figures 5 to 9 show the diffuse reflectance spectra obtained for the bulk and supported phase, both untreated and after TPR treatment. The spectra of both the untreated bulk and supported samples exhibit charge-transfer (CT) bands in the 200–350 nm region of the spectra. Such bands are typical of Mo^{VI}–O bonds in octahedral coordination (Rodriguez *et al.* 1989), the lower intensity of the bands arising from the supported phases being attributed to dilution by alumina.

The DR spectra for the $CoMo_6$ phase are depicted in Figure 5, the $Co^{III} d^6$ species in an octahedral configuration of oxygen atoms being characterised by the presence of two spin-allowed transitions from the ${}^1A_{1\sigma}$ ground state to the higher ${}^1T_{1\sigma}$ and ${}^1T_{2\sigma}$ states which occur in the 700–550



Figure 6. Diffuse reflectance (DR) spectra for $CrMo_6$: (a) unsupported phase; (b) TPR product from unsupported phase (T = 510°C); (c) supported phase; (d) TPR product from supported phase (T = 510°C); and (e) TPR product from supported phase (T = 1000°C).



Figure 7. Diffuse reflectance (DR) spectra for NiMo₆: (a) unsupported phase; (b) TPR product from unsupported phase (T ~ 500°C); (c) supported phase; and (d) TPR product from supported phase (T ~ 500°C).

and 500–400 nm ranges of the spectra, respectively (Gajardo *et al.* 1980). The spectra labelled as a and c in Figure 5 are similar, differing only in the intensity of the bands located at 610 nm and 416 nm, respectively. Such similarity clearly demonstrates that the adsorption of the CoMo₆ monolayer on to the support surface occurred without any alteration in the structure of the heteropolyoxoanion. On the other hand, the Co^{II} d⁷ ion exhibits three spin-allowed d–d transitions when it is in a regular octahedral environment, viz. ${}^{4}T_{2g} - {}^{4}T_{1g}$, ${}^{4}T_{2g} - {}^{4}A_{2g}$ and ${}^{4}T_{2g} - {}^{4}T_{1g}$, and ${}^{4}A_{2g} - {}^{4}T_{1g}$, ${}^{4}A_{2g} - {}^{4}T_{1g}$, and ${}^{4}A_{2g} - {}^{4}T_{1}(P)$. The spectrum of the cobalt aluminate spinel phase (where Co^{II} exists in both sites) shows typical bands at (1534–1367–1245), 671 and (620–580–546) nm, respectively (Gajardo *et al.* 1980). Comparative studies involving the traditional Co–Mo/ γ -Al₂O₃ catalyst and the CoMo₆/ γ -Al₂O₃ system demonstrated the stability of the supported heteropolyanion in that bands corresponding to the inactive spinel phase were absent from the DR spectrum (Cabello *et al.* 2000).

The spectra of supported and unsupported $CoMo_6$ after TPR treatment at 500°C (corresponding to the Mo^{VI} – Mo^{IV} step) are shown as curves b and d in Figure 5. Although they are poorly resolved, the decrease in the magnitude of the CT bands and their shift to lower energy values are in agreement with reduction of the heteropolyanion to MoO_2 . A similar behaviour for molybdenum was



Figure 8. Diffuse reflectance (DR) spectra for AlMo₆: (a) unsupported phase; (b) TPR product from unsupported phase (T ~ 450°C); (c) supported phase; and (d) TPR product from supported phase (T ~ 450°C).

observed in the thermal reduction of AHM. Likewise, the possibility of observing well-defined d-d bands is notably diminished since (1) the surface of the $CoAl_2O_4$ spinel does not present the bulk-like spinel structure (Bai *et al.* 1991) and (2) the Co is distributed in both tetrahedral and octahedral sites in the structure.

Figure 6 depicts the DR spectra for the $CrMo_6$ phase. Three d–d spin-allowed transitions are observed for Cr^{III} in an octahedral configuration (McClure 1962), i.e. from ${}^{4}A_{2g}$ to ${}^{4}T_{2g}$, ${}^{2}E_{g}$ and ${}^{2}T_{2g}$, respectively, although only two are usually observed because the third transition often overlaps with charge-transfer bands in the UV region. These two bands are located at ca. 600 nm and 450 nm (Ikeda *et al.* 1992). The spectrum of the unsupported $CrMo_6$ phase without thermal reduction (curve a) clearly shows two d–d transitions at 406 nm and 550 nm, in agreement with the reddish



Figure 9. Diffuse reflectance (DR) spectra for TeMo₆: (a) unsupported phase; (b) TPR product from unsupported phase (T ~ 450°C); (c) supported phase; and (d) TPR product from supported phase (T ~ 450°C).

colour of the sample. However, the supported CrMo_6 phase, which is green in colour, generates two bands at 470 nm and 606 nm, respectively (curve c in Figure 6). These values are similar to those observed in the spectrum of α -Cr₂O₃ which occur at 470 nm and 602 nm, respectively (Botto *et al.* 2000). This corroborates the existence of an interchange between Cr and Al in the interface, diffusion of the Cr towards the bulk of the support and the transformation of the metastable γ -Al₂O₃ phase to the corundum structure. Diffusion towards a greater depth in the support leaves the external layer depleted of Cr ions, increasing temperature assisting such diffusion with a consequent hindering of the development of crystallinity in the corundum structure. EDAX analysis of the supported CrMo₆ phase gave values corresponding to 71.75% Al, 26.58% Mo and 1.67% Cr, which correspond to an Mo/Cr ratio of 15.6 whereas the value for the unsupported phase was 11.07.

The spectra of the $CrMo_6$ samples treated thermally under reducing conditions at 510°C (curves b and d in Figure 6) gave results which were similar to those observed in the $CoMo_6/\gamma$ -Al₂O₃ system. EDAX analysis in this case revealed the presence of Mo and Al only with no Cr content being detected at the surface. It is interesting to note that the DR spectrum of the sample after TPR at 1000°C shows defined bands at 470 nm and 600 nm (curve e in Figure 6), whereas the corresponding XRD pattern revealed only the presence of the corundum-like phase. The spectrum also

presents a weak band at ca. 350 nm which is attributed to Cr–O charge transfer. For samples treated at temperatures below 800°C, this band must also overlap that corresponding to Mo^{IV}–O charge transfer.

Figure 7 shows the DR spectra observed for the NiMo₆ phase under various conditions. When in an octahedral configuration, Ni^{II} exhibits three spin-allowed transitions from ${}^{3}A_{2g}$ to the ${}^{3}T_{2g}$, ${}^{3}T_{1g}$ and ${}^{3}T_{1}(P)$ states, respectively, which fall within the 1400–780, 910–500 and 500–370 nm ranges of the spectrum (Stone 1983; Porta *et al.* 1974). Bands at 606 nm and 434 nm were observed in the spectra of both the unsupported and supported NiMo₆ phase (curves a and c in Figure 7), the formation of the blue NiAl₂O₄ spinel phase from the counter-diffusion of Ni^{II} and Al^{III} being unlikely since the original pale green colour of the sample remained unaltered. However, it should be noted that the spectra for the supported samples reduced at ca. 500°C (curves b and d in Figure 7) were similar to those observed for the CoMo₆ phase where the presence of the spinel phase has been suggested.

The spectra depicted in Figures 8 and 9, for AlMo₆ and TeMo₆ respectively, exhibit only typical Mo–O charge-transfer bands [Mo^{VI}–O in curves a and c in both figures and Mo (at an oxidation state < 6)–O in curves b and d in the two figures]. Bands at 320–360 nm as observed in curves b and d of Figure 9 are attributed to the formation of a mixed valence compound containing Te and Mo at ca. 450°C just before the maximum of the TPR peak which corresponds to the formation of MoO₂ at 503°C.

A comparison of all the DR spectra depicted in Figure 8 indicates the existence of a relatively intense uncommon band in the spectra of the reduced samples (curves b and d) located in the CT region and attributed to an unreduced Mo^{VI} species. This can only be explained as arising from a reaction between the deposited Mo^{VI} and the aluminium in the support. This suggests the presence of Al^{III} as a unique cationic species, thereby indicating that alumina can act as a true chemical reagent (Carrier et al. 1997, 1999; Le Bihan et al. 1998). Indeed, the formation of a well-dispersed aluminium molybdate can be inferred from the TPR results depicted in Figure 3 as well as by the XRD pattern. Thus, the intensity and temperature for the second TPR signal for the supported and bulk phases show appreciable differences, a result which appears to be consistent with the TPR data for supported MoO, which also depend on the AHM loading (Regabuto and Jin-Wook Ha 1991). In contrast, it is known that $Al_2(MoO_4)_3$ presents a single and intense TPR signal at the temperature corresponding to the second reduction step for molybdenum (Lopez Cordero et al. 1990), whereas the incorporation of Al into the MoO₂ (reduced rutile) structure has been established during the reduction of bulk AlMo₆ (Botto *et al.* 1994a). The intensity and temperature of the second TPR signal for the supported and bulk phases thus show appreciable difference. In our study (Botto *et al.* 1994a), the reduction pathway for AlMo₆ in bulk exhibited a shoulder at 842°C whereas the supported AlMo₆ species presented a band of medium intensity at 801°C. The slight difference confirms that the observed behaviour is related to the Al/Mo ratio and to the prevailing Mo species [for example, the MoO_4 tetrahedral species of $Al_2(MoO_4)_3$ are reduced simultaneously from Mo^{VI} to Mo⁰ (Regabuto and Jin-Wook Ha 1991)].

Whereas the decrease in the Mo^{VI}–Mo^{IV} reduction temperature indicates strong heteropolyanion– support interactions, different molybdenum-containing species (i.e. isolated tetrahedra vis-a-vis condensed octahedra) appear to exhibit different redox capacities towards the generation of Mo⁰.

Finally, the thermal reduction behaviour of supported $AlMo_6$ demonstrates that the TPR technique may be employed to characterise not only supported MoO_3 (Regabuto and Jin-Wook Ha 1991) but also other supported oxidic systems.

CONCLUSIONS

When XMo_e Anderson phases (X = Te^{VI} , Co^{III} , Ni^{II} , Al^{III} and Cr^{III}) were deposited as a monolayer on γ -Al₂O₃ by the equilibrium adsorption method, the sequence of adsorption strengths appears to be: $CoMo_6 > CrMo_6 > TeMo_6 > AlMo_6 > NiMo_6$. The values of K_{ad} obtained from the corresponding isotherms were several orders of magnitude greater than those observed for the AHM/ γ -Al₂O₃ system and even greater than that for the traditional Co-Mo/y-Al₂O₃ catalyst. The XMo₆-support interaction seems to be based on a planar structure, i.e. on the characteristics of the heteroatom. Differences in the $CrMo_{A}/\gamma$ -Al₂O₃ catalytic system result in the generation of a series of homogeneous and heterogeneous equilibrium processes during the initial impregnation steps. Dissolution of aluminium from the support as well as a different degree of counter-diffusion and exchange processes may be inferred from spectroscopic and microprobe analyses and from TPR measurements. The formation of $Al_2(MoO_4)_3$ was only observed in the case of $AlMo_6$ adsorption; this was attributed to the chemical properties of the heteroatom and to the absence of counter-diffusional processes. The TPR results were consistent with the existence of an XMo₆-support interaction, thereby corroborating that this method provides a good tool for the characterisation of this type of supported oxide phase. The different behaviour of the TeMo, deprotonated phase may be associated with the acidic character of the heteroatom in this case. The formation of a Te–Mo mixed oxide/ γ -Al₂O₃ system seems to offer interesting catalytic possibilities. Stabilisation of the α -(Cr,Al)₂O₂ corundum-like phase on the surface as a result of a counter-diffusion process is also suggested by the XRD results and the DR spectra.

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