Dispersion of molybdena on the surface of titania: the effect of potassium

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Molybdena/titania systems doped with potassium have been prepared by impregnation of the support with aqueous solutions of ammonium heptamolybdate and studied to assess the effect of the alkaline cation on their surface and structural properties. Simultaneous or consecutive (first potassium, then molybdenum) methods have been tested. Characterization has been carried out by X-ray diffraction, Fourier-transformed infrared and visible–ultraviolet (diffuse reflectance) spectroscopies and nitrogen adsorption at low temperature. It was concluded that both the relative amounts of Mo and K, and the method of preparation, determine the nature and dispersion of the species formed upon calcination at 773 K. Simultaneous incorporation of both cations favours formation of potassium polymolybdates, and if the amount of molybdenum is above the stoichiometric value for these Mo–K–O compounds, molybdena is also formed.

1. Introduction

Molybdena/titania systems have received great attention in the last few years, mainly due to their good activity and selectivity for several heterogeneous catalytic reactions, such as oxidation of propene [1], of butene and butadiene [2], and of methanol [3], as well as in hydrodesulphurization processes [4]. Characterization of these and related systems includes evaluation of the nature and dispersion of the supported phase that depend, among other factors, on the preparation method, the nature of the precursor salt, pH during impregnation (if the samples are obtained using this method), pretreatment of the support, etc. On the whole, the nature of the active phase and the surface acidity can be considered as the main properties controlling the catalytic properties of such systems. Similarly to the nature of the active phase, the surface acidity can be modified by adding a doping agent able to increase or to decrease such a surface acidity, and thus modify the selectivity towards a given product in a catalytic reaction. In this way, we have previously shown that addition of sodium to vanadia/titania systems increases their selectivity towards acrolein during propene oxidation [5].

In the present paper, potassium-doped molybdena/titania systems have been studied. We have analysed the effect that several preparation methods have on the surface physico-chemical properties of these systems. Their performance for propene oxidation is under current investigation in this laboratory.

2. Experimental procedure

All samples have been obtained following an impregnation method [6], but using two alternative routes.

2.1. Samples $M_X K_Y$

Titania support (P-25 from Degussa) was doped with potassium (weight percentage Y), by impregnation of the support with aqueous solutions of KNO_3 in a rotary vacuum desiccator (Heidolph VV-60), to minimize formation of surface carbonates. The solid was dried in an oven for 24 h at 373 K, calcined at 773 K for 3 h and finally manually ground in an agate mortar. Supports containing 0, 1 or 3% K have been named as TK0, TK1 and TK3, respectively. The solid was then impregnated with an aqueous solution of ammonium heptamolybdate (AHM), in relative amounts that would lead to X monolayers of MoO_3 on the support, as calculated from the specific surface area (SSA) of the support, previously determined by nitrogen adsorption at 77 K (see below), and the surface covered by a "molecule" of MoO_3 [7]. The solvent was again removed as mentioned above, but at 353 K. Drying was performed as already mentioned for the K-doped support.

2.2. Samples $IM_X K_Y$

In this case, both molybdenum and potassium precursor compounds were mixed in solution and impregnation and drying was performed as above described.

All chemicals were from Merck (p.a.), of high purity levels. Naming of the samples and a summary of their main properties have been included in Table I.

Characterization of the samples was carried out using the following techniques. X-ray diffraction diagrams were recorded in a Siemens D-500 diffractometer provided with a Difract-AT system, Ni filters, and using CuK_α ($\lambda = 154.050$ pm) radiation. The electronic spectra in the visible–ultraviolet range were

TABLE I Surface properties of the samples studied

| Sample	Mo (%)	K (%)	S_{BET} (m^2 g^{-1})
TK0	–	–	53
TK1	–	1.0	50
TK3	–	3.0	41
M1K1	5.8	1.0	44
IM1K1	5.8	1.0	42
M2K1	11.6	1.0	38
IM2K1	11.6	1.0	37
M1K3	5.8	3.0	40
IM1K3	5.8	3.0	39
M2K3	11.6	3.0	35
IM2K3	11.6	3.0	34

Figure 1 X-ray diffraction diagrams of samples (a) M2K1, (b) IM2K1, and (c) M2K3. Designation of the peaks is as follows: A = anatase, R = rutile, M = molybdena, MK = potassium poly-molybdates.

recorded in a Shimadzu UV-240 spectrophotometer, by the diffuse reflectance technique (V–UV/DR), coupled to a Shimadzu PR-1 graphic printer, using a slit of 5 nm and MgO or the bare support (titania) as reference. The FT-i.r. spectra have been recorded in a Perkin–Elmer 1730 FT-i.r. instrument, connected to a Perkin–Elmer 3600 Data Station, using KBr pellets and a KBr/TiO$_2$ pellet, containing the same amount of titania as the sample pellet, as the reference. Finally, the nitrogen adsorption isotherms at 77 K were measured in a conventional high vacuum Pyrex system (residual pressure lower than 10^{-4} N m^{-2}), equipped with a silicone oil diffusion pump and grease-free stopcocks. Changes in pressure were monitored with a MKS pressure transducer. The system had been previously calibrated with helium (99.995%) and adsorption of nitrogen (99.99%) was determined after outgassing the samples in situ at 420 K for 2 h. Analysis of the isotherms for specific surface area (SSA) and mesopore size distribution were performed with the assistance of a computer program developed in this laboratory [8].

3. Results and discussion

3.1. X-ray diffraction

The X-ray diffraction (XRD) patterns recorded for the K-containing supports are rather similar to that of the undoped support. Contrary to the results reported by Busca and Ramis [9], no diffraction peak that could be ascribed to the presence of K$_2$O was recorded, but only those peaks due to anatase and rutile. The anatase content, as calculated from the intensities of the main diffraction peaks of both modifications of titania using the equation proposed by Criado and Real [10], was 55 ± 3%, fairly similar to the composition found for the original, undoped support. This behaviour is the opposite of that shown by Na–TiO$_2$ samples [11], where a rutilization process is undoubtedly detected.

The patterns for samples containing 1% K and one monolayer of molybdena (IM1K1 and M1K1) are very similar and, in addition to those peaks of the support, very weak diffractions are recorded at spacings of 683 and 480 pm, that can be tentatively ascribed to ternary Mo–K–O compounds, such as K$_2$Mo$_4$O$_{13}$ or K$_2$MoO$_4$. Nevertheless, the very low
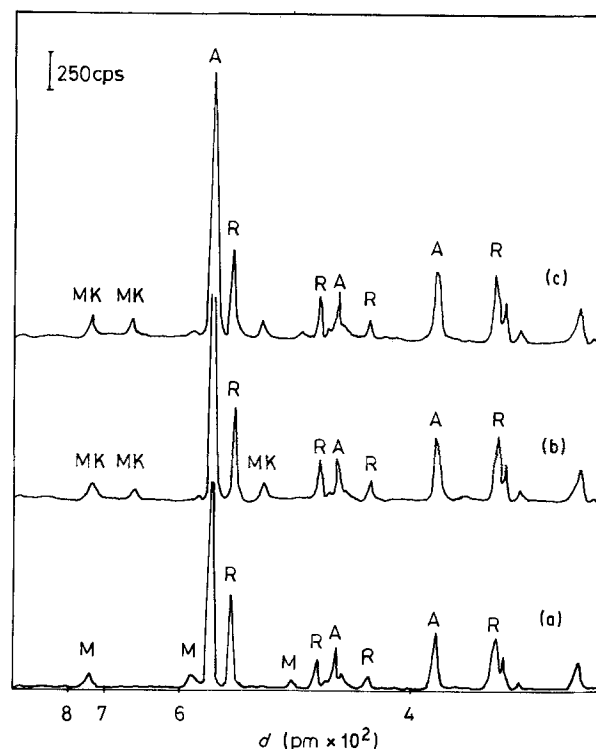
intensities of these peaks indicate a fairly good dispersion level of these compounds. Incorporation of both molybdenum and potassium has not favoured rutilization of the sample, the anatase content (52%) being very similar to that determined for the support and for samples containing the same amount of molybdena, but without potassium [11].

In contrast, when the molybdenum content is increased (samples M2K1 and IM2K1), rather different X-ray diffraction patterns are recorded (Fig. 1). For sample M2K1, the peaks recorded in addition to those of the support (690 and 380 pm) are due to crystalline MoO$_3$, while for sample IM2K1 the peaks recorded (in addition to those of titania) can be ascribed to polymolybdates (K$_2$Mo$_4$O$_{13}$) or simple molybdates (K$_2$MoO$_4$). So, it can be concluded that increasing the molybdenum content from one to two monolayers (the monolayer content corresponds to 5.8 % Mo weight, equivalent to 8.7% MoO$_3$), in the presence of low percentages of potassium, modifies the way in which molybdenum and potassium interact on the surface of titania, thus leading to ternary (Mo–K–O) or binary (Mo–O) species.

Finally, when the potassium content is increased (3%), (Fig. 1), such differences between the samples obtained by the two methods above described are not found, and in all cases only Mo–K–O species (K$_2$Mo$_4$O$_{13}$ or K$_2$MoO$_4$) are recorded, their crystallinity increasing as the molybdenum content increases.

3.2. V–UV spectroscopy

The V–UV/DR spectra for all supports, unloaded or doped with potassium, show a continuous absorption

below 420 nm that has been ascribed [12] to an $O^= \rightarrow Ti^{4+}$ charge transfer process. When molybdenum is present, the spectra are very similar (Fig. 2) and, in order to eliminate the strong absorption due to the support, the spectra have been recorded using parent titania as a reference. A medium intensity band, which strengthens as the molybdenum content in-
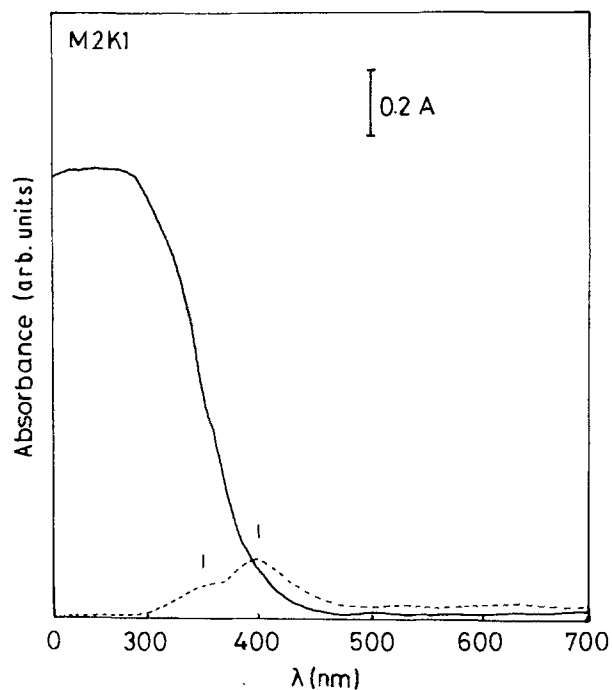
creases, is recorded at 350 nm, and has been ascribed [13, 14] to octahedrally oxygen-co-ordinated Mo(VI) species, [MoO_6], together with a more intense band close to 420 nm, that is not an instrumental artifact, and that has been previously ascribed [15, 16] to the presence of peroxide-like species, stabilized on the surface of titania by the presence of the molybdenum cations. No band is recorded in any case below 300 nm, thus indicating the lack of tetrahedrally co-ordinated Mo(VI) species, [MoO_4].

3.3. Infrared spectroscopy

The FT-i.r. spectra of samples M1K1 and IM1K1, in the 1100–800 cm^{-1} range, are nearly coincident (Fig. 3), with weak bands at 960, 937, 920, 904, 893 and 871 cm^{-1}. Bands in the 980–800 cm^{-1} range have been ascribed to the presence of different molybdates [17]. In solid compounds, such as Na_2MoO_4 and K_2MoO_4, the environment of molybdenum is tetrahedral, [MoO_4], while for $CoMoO_4$ and in aqueous solutions in the pH range 1–5 it is octahedral, [MoO_6]. Ng and Gulari [4] have reported a detailed study of the i.r. spectra of molybdates, concluding that [MoO_4] species are responsible for a strong band at 833 cm^{-1}, while for octahedral species two bands are recorded at 883 and 950 cm^{-1}. For supported, oxidized molybdenum compounds, containing low molybdenum loadings (lower than a monolayer) these authors ascribe a band at 950 cm^{-1} to the stretching mode of terminal Mo=O moieties, and a band at 990–885 cm^{-1} to the Mo–O–Mo stretching mode in polymeric molybdates. In MoO_x/TiO_2 systems with molybdena loadings below the monolayer, Ramis et al.

Figure 2 Visible–ultraviolet (diffuse reflectance) spectra of the molybdenum-containing samples. Reference used was MgO (solid line) or parent titania (dotted line).
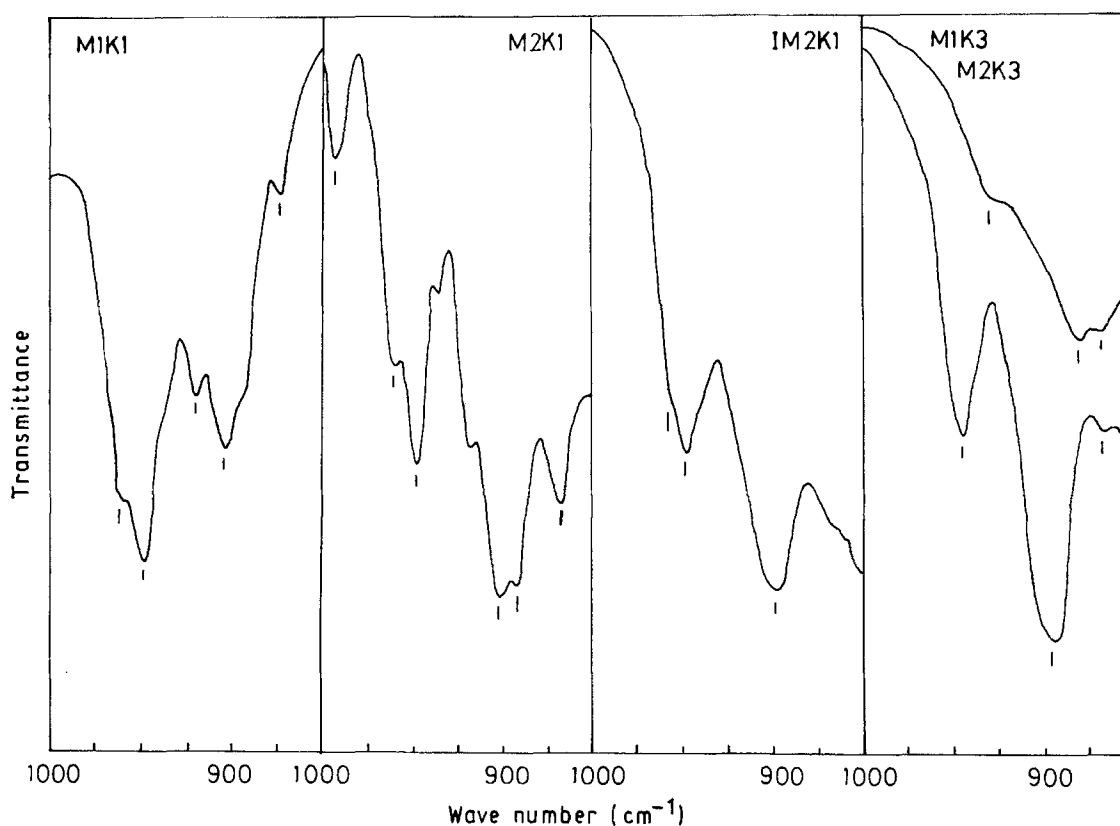

Figure 3 FT-i.r. spectra of samples M1K1, M2K1, IM2K1, M1K3 and M2K3.

[18] have reported, in addition to the band mentioned at 960 cm^{-1}, another at 890 cm^{-1}, which these authors have ascribed to the presence of small amounts of molybdate ions. According to all these results, we can ascribe the bands recorded for our samples to the presence of octahedral polymolybdates, as detected by XRD, such as $K_2Mo_4O_{13}$. The absence of bands close to 990 cm^{-1}, which are characteristic of the Mo=O stretching mode of orthorhombic MoO_3 [19, 20] and that are easily recorded for MoO_x/TiO_2 systems similar to those studied here but with no alkaline dopant [11], definitely demonstrates the absence of molybdena in these samples.

When the molybdenum loading is increased up to the amount equivalent to formation of two monolayers of molybdena (samples M2K1 and IM2K1) the FT-i.r. spectra differ according to the preparation method. So for sample IM2K1, only the bands corresponding to potassium polymolybdates are detected, while for sample M2K1, in addition to these bands, another is recorded at 993 cm^{-1}, that should be ascribed to the M=O stretching mode of bulk MoO_3 [19, 20]. That is, for fairly high molybdenum contents (11.6%, equivalent to two monolayers of MoO_3) the way in which potassium and molybdenum are incorporated on the titania surface (simultaneously or consecutively) strongly modifies the nature of the supported species. Small amounts of potassium cancel formation of bulk molybdena only in the case of simultaneous incorporation of both supported cations.

Samples containing 3% K show FT-i.r. spectra, Fig. 3, that seem to be independent of the preparation method, as happened with those samples containing only 1% K. Fairly weak bands are recorded at 929, 883 and 865 cm^{-1}, due to the presence of polymolybdates ($K_2Mo_4O_{13}$), as previously detected by X-ray diffraction. So in this case, the formation of molybdena is avoided by the presence of potassium, even with two monolayers of MoO_3 (equivalent to 11.6% Mo weight).

It should be mentioned that no band that could be ascribed to carbonate species has been recorded in the spectra of these samples.

3.4. Surface area and porosity

The nitrogen adsorption–desorption isotherms at 77 K were reversible on all samples studied, and the specific surface area (SSA) values calculated following the Brunauer–Emmett–Teller (BET) method have been included in Table I. No microporosity develops upon incorporation of molybdenum or potassium, all isotherms belonging to type II in the IUPAC classification [21]. A slight decrease in the adsorption capacity is observed as the potassium content increases, leading to a decrease in the SSA value, this effect being more clearly seen for those samples prepared by simultaneous impregnation (series I). The pore size distribution curves, as determined following the Cranston and Inkley method [22], indicate that all samples show only mesoporosity, with a maximum contribution to the surface area by pores with a diameter of 2–4 nm.

4. Conclusions

From the study carried out so far, it can be concluded that incorporation of potassium on the surface of titania P-25 and further calcination at 773 K does not favour the anatase → rutile phase change, but leads only to a slight sintering, resulting in lower specific surface area values as the potassium content is increased (up to 3%). The interaction of potassium with the support is not too strong, and no defined Ti–K–O species is detected by X-ray diffraction, neither is K_2O detected, as it has been by other authors [9].

The simultaneous presence of molybdenum and potassium again has no effect on the anatase → rutile phase change, although sintering of the support particles has also been observed. Incorporation of molybdenum on the surface of titania leads to formation of molybdena crystallites, as detected by X-ray diffraction [11], but the simultaneous presence of potassium avoids such a process, even with a MoO_3 content of 11.6% (by weight), but leads to formation of potassium polymolybdates ($K_2Mo_4O_{13}$), the crystallinity of which increases with the potassium and molybdenum content, and where Mo(VI) cations are always octahedrally co-ordinated. Only in sample M2K1 (i.e., that containing two monolayers of molybdena, equivalent to 11.6% weight, and 1% potassium), have molybdena crystallites been detected.

The behaviour found for these Mo–K–Ti–O systems should be related to the different acidity of these oxides: both molybdena and titania are acidic [23], and so their interaction during the thermal treatments given is somewhat difficult, thus leading to formation of separate crystallites of molybdena [11]. However, the simultaneous presence of potassium (which oxide is highly basic) leads to an acid/base reaction between MoO_3 and K$^+$, forming well dispersed polymolybdates, in most cases, on the surface of the titania crystallites. Such a reaction seems to be easier (compare the results for samples M2K1 and IM2K1) when both cations are simultaneously incorporated on the surface of titania than when potassium is incorporated before molybdenum.

Nevertheless, it should be mentioned that the results indicate that such a reaction between molybdena and potassium (and so the formation of MoO_3 or polymolybdates) is also dependent on the relative amounts of both oxides. The stoichiometric reaction between molybdena and potassium to yield $K_2Mo_4O_{13}$ requires c. 7.8 g MoO_3/1 g potassium (Fig. 4). So, the amount of molybdena existing in samples M1K1 and IM1K1 (one monolayer, equivalent to 5.8% Mo or 8.7% MoO_3) is only very slightly larger than that required to react with all potassium existing in these samples, thus yielding polymolybdates; there remains c. 0.1 monolayer of MoO_3 in a very well dispersed state. The same situation occurs for samples containing 3% K, as formation of $K_2Mo_4O_{13}$ starting from 3% K would require 23.4% MoO_3, a value very well above that existing in all samples. In contrast, for samples with two monolayers of molybdena and 1% K there is an excess of molybdena above the stoichiometric amount needed to react with all potassium: taking 100 g of sample, 1 g of
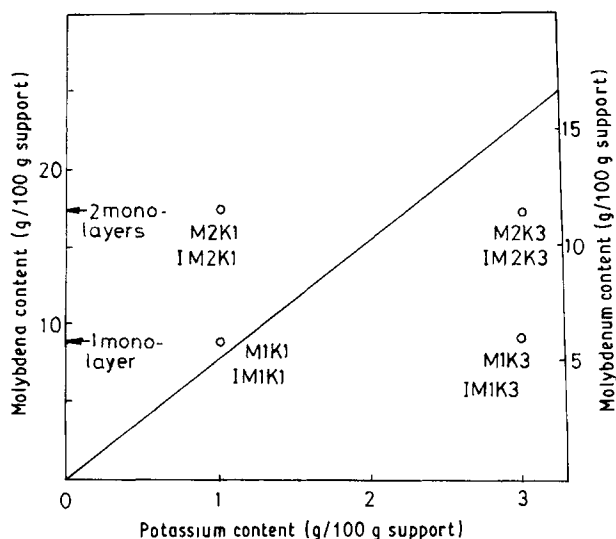
Figure 4 Amounts of Mo, MoO_3 and K existing in the samples prepared (in 100 g of support). The solid line corresponds to the stoichiometric amounts existing in $K_2Mo_4O_{13}$. Points above the solid line correspond to an excess of molybdenum. The amounts of MoO_3 corresponding to formation of one or two monolayers are indicated.

potassium would require 7.8 g MoO_3 to form $K_2Mo_4O_{13}$, and these samples contain 17.4 g MoO_3. So, for sample IM2K1, where both cations are incorporated simultaneously, the reaction is easy (it could be tentatively claimed that mobility of the cations in the liquid phase during impregnation would facilitate their reaction) and the amount of molybdena existing in addition to that reacted with potassium (c. 9.6%, equivalent to 1.1 monolayers) remains well dispersed and is not detected by X-ray diffraction. On the other hand, for sample M2K1, where the potassium ions are already attached on the titania surface when molybdenum is incorporated, their lower mobility would hinder formation of polymolybdates, thus molybdena crystallization takes place. For MoO_3/TiO_2 systems with no doping cation, formation of crystalline MoO_3 has been detected for molybdena contents of 7.15% [3], 7.5% [24], or even 17.3% [18], depending on the preparation method. The amount of molybdena in our samples IM2K1 above the stoichiometric amount to react with potassium is 9.6%, fairly close to these values given in the literature.

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