Phase Transitions and Surface Stability of the WO_3–γ-Al_2O_3 System

P. TITTARELLI, A. IANNIBELLO, AND P. L. VILLA*

*Stazione Sperimentale per i Combustibili, Viale De Gasperi 3, 20097-S. Donato Milanese, Milano, Italy and *Istituto di Chimica Industriale del Politecnico, Piazza Leonardo da Vinci 32, 20133 Milano, Italy*

The solid state transitions of the WO_3–γ-Al_2O_3 system have been investigated in the temperature range 873–1323 K. The formation of α-Al_2O_3 and $Al_2(WO_4)_3$ phases and the thermal desorption of W(VI) attached to the γ-Al_2O_3 surface have been studied as function of the treatment time. The inhibition of the phase transition to α-Al_2O_3 and therefore the stabilization of the surface has been observed at 1323 K for samples with 7% WO_3 content. This stabilization is critically affected by the tungsten content. An explanation for the stabilization of the alumina surface is proposed.

Introduction

The mixed oxides of the group VIa elements and γ-Al_2O_3 hold a prominent position in industrial catalysis and have been the subject of a number of investigations (*1–6*): these systems are heterogeneous and their catalytic properties still pose several fundamental questions.

The chemisorption phenomena which take place when aqueous solutions of Cr(VI), Mo(VI), and W(VI) are contacted with γ-Al_2O_3 have been studied in a series of papers and the relevance of these phenomena in determining the surface structure of the oxides systems CrO_3–γ-Al_2O_3, MoO_3–γ-Al_2O_3, and WO_3–γ-Al_2O_3 has been pointed out (*7–11*). The results of these studies can be summarized as follows:

(i) Cr(VI), Mo(VI), and W(VI) interact selectively with the basic sites of γ-Al_2O_3.

(ii) The amounts of Cr(VI), Mo(VI), and W(VI) irreversibly chemisorbed onto γ-Al_2O_3 from aqueous solutions are, respec-tively, 3, 9, and 20% by weight of CrO_3, MoO_3, and WO_3.

(iii) The surface phase formed by chemi-sorption is stable up to 873 K as indicated by Raman and electronic spectroscopy.

(iv) The surface phase formed by chemi-sorption cannot be considered a homoge-neous phase because of the heterogeneity of the basic sites of γ-Al_2O_3.

The chemisorption process which occurs during the contacting of the γ-Al_2O_3 with the ammonium molybdate or tungstate so-lution allows the preparation of MoO_3–γ-Al_2O_3 and WO_3–γ-Al_2O_3 samples in a wide range of composition and with a controlled degree of surface dispersion.

We also studied the catalytic and physi-cochemical properties of the MoO_3–γ-Al_2O_3 and WO_3–γ-Al_2O_3 systems in the range 298–873 K and we proposed that Mo and W interacting with the support form isolated species with the degree of distor-tion increasing with the degree of coverage (*12–13*).

In this work we report a physicochemical study of the behavior of the W(VI) adsorbed layer and its interaction with the support in the range 873–1373 K, with particular attention to the formation of $Al_2(WO_4)_3$ and α-Al_2O_3 phases, to the thermal desorption of W(VI), and to the surface stability to high temperature treatment as a function of the degree of surface coverage.

In the experimental approach X-ray diffraction, electronic and Raman spectroscopy, and surface area measurements were used.

Experimental

Reagents. γ-Al_2O_3 (AKZO Chemie CK 300) (particle diameter 0.1–0.3 mm; surface area 180 m²/g), ammonium tungstate $5 \cdot (NH_4)_2O \cdot 12WO_3 \cdot 5H_2O$, aluminium chloride, and sodium tungstate, Carlo Erba pure reagent grade, ultra pure α-Al_2O_3, Research Chem. Corp. γ-Aluminas differing in surface areas and purity grade from various manufacturers were also tested.

Samples preparation. Aluminium tungstate was prepared by stoichiometric reaction between $AlCl_3 \cdot 6H_2O$ and $Na_2WO_4 \cdot 2H_2O$ solutions following Ref. (*14*). The stoichiometric composition of the compounds was confirmed through the determination of aluminium by atomic absorption and tungsten by X-ray fluorescence spectrometry. WO_3 was prepared by thermal decomposition of $5 \cdot (NH_4)_2O \cdot 12WO_3 \cdot 5H_2O$ at 823 K in air.

The samples of alumina with variable WO_3 contents were prepared by equilibrium adsorption adding 2 g of γ-Al_2O_3 to 200 ml of ammonium tungstate aqueous solutions with different initial concentrations as previously described (*9, 11*).

Solutions of $2 \cdot 10^{-3}$, $3.5 \cdot 10^{-3}$, $5 \cdot 10^{-3}$, $7 \cdot 10^{-3}$, $10 \cdot 10^{-3}$, and $60 \cdot 10^{-3}$ M ammonium tungstate were employed in order to obtain WO_3–γ-Al_2O_3 samples with a WO_3 weight content of 3, 4.7, 7, 9.5, 13, and 18%, respectively.

For brevity these samples are referred to with a number indicating the WO_3 content: e.g., W3 is the sample with 3% WO_3 b.w. calcined at 873 K.

Equipment. X-Ray diffractometer (Philips PW 1050) with copper X-ray tube and proportional counter. X-Ray fluorescence spectrometer (Philips PW 1540) with chromium tube. Cary 83 Raman spectrophotometer. Cary 15 spectrophotometer with the Model 1511000 attachment for diffuse reflectance spectra. Sorptomatic 1700 Carlo Erba automatic surface area analyzer.

WO_3 content determination. The determination of the WO_3 content in the samples was performed by X-ray fluorescence spectrometry using standards of γ-Al_2O_3 impregnated with known amounts of WO_3 in the range 0.3–2% WO_3 by weight. The samples were diluted with γ-Al_2O_3 to bring the WO_3 concentration within the working range. The samples and standards were thus pressed in pellets and analyzed.

Crystalline phases determination. Preliminary X-ray diffraction patterns were obtained in order to detect the crystalline phases of each sample. Standards with known amounts of the phases detected by X-ray diffraction were prepared mixing α-Al_2O_3, bulk $Al_2(WO_4)_3$, WO_3 dispersed onto γ-Al_2O_3, and ϑ-Al_2O_3 prepared by calcination of γ-Al_2O_3 at 1123 K.

The five most intense reflections were employed for the determination of $Al_2(WO_4)_3$ and the two most intense reflections were used in the case of α-Al_2O_3.

The standards were prepared with the same total WO_3 content of the samples to be analyzed, to correct the X-ray absorption interference of tungsten on aluminium. In this way α-Al_2O_3 and bulk $Al_2(WO_4)_3$ were determined down to 3 and 1% by weight, respectively.

Results

X-Ray Diffraction

Figure 1 shows the X-ray diffraction patterns of γ-Al$_2$O$_3$, W3, W7, W18 calcined at 1323 K for 15 hr and the sample W18 calcined at 823 K.

It can be seen that the sample treated at lower temperature shows nothing but γ-Al$_2$O$_3$ phase. This observation holds for the composition range investigated at this temperature (3–18% WO$_3$).

After treatment at high temperature ($T >$ 1173 K) the samples show different phase compositions depending on the WO$_3$ content and treatment time.

γ-Al$_2$O$_3$ is almost completely transformed in α phase within 15 hr, while in the samples containing W(VI) this transition is inhibited. It can be seen that, by increasing the WO$_3$ content, the formation of α-Al$_2$O$_3$ decreases and is almost completely suppressed at 7% WO$_3$ content; in fact in the range of 6–7% WO$_3$ only ϑ-Al$_2$O$_3$ forms. The formation of bulk Al$_2$(WO$_4$)$_3$ is observed when the content of WO$_3$ is greater than 7–8%.

We will see that result has its counterpart in the surface area. In fact in this range of composition (6–7%) the WO$_3$-γ-Al$_2$O$_3$ system exhibits maximum surface stability.

In Fig. 2 the rate of thermal desorption of W(VI) and the rate of crystallization of

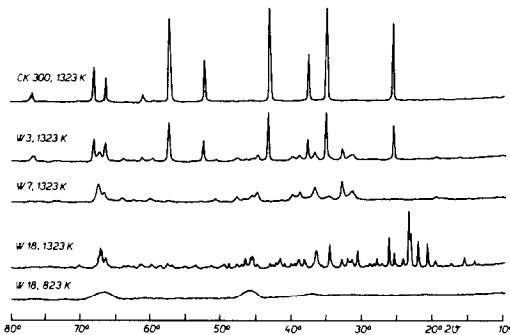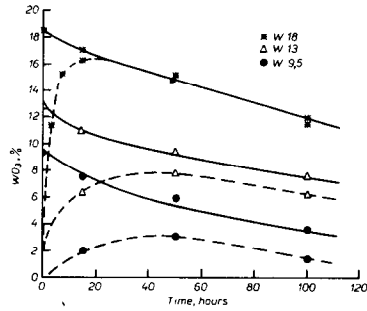FIG. 2. WO$_3$ total content (full line) and Al$_2$(WO$_4$)$_3$ content (dotted line) calculated as WO$_3$ at 1323 K.

Al$_2$(WO$_4$)$_3$ at 1323 K are plotted as a function of composition. The rates of the described processes are critically affected by the WO$_3$ content. Two regions of composition can be identified: the region with low WO$_3$ content (<7%) in which both thermal desorption and crystallization of Al$_2$(WO$_4$)$_3$ are completely suppressed (and therefore are not shown in the figure); the region with high WO$_3$ content (>7%) in which the processes, the loss of W(VI) via gas phase and the crystallization of Al$_2$(WO$_4$)$_3$, take place simultaneously. A careful examination of the figure indicates that the loss of W(VI) via gas phase is initially ($t <$ 15–20 hr) better described as a desorption process from the alumina surface, while after 20 hr it is a result of thermal decomposition of bulk Al$_2$(WO$_4$)$_3$. The combined effect of these two processes gives a maximum in the curve of the formation of the crystallization product. All W(VI) is present as a crystallographically well-defined phase after 15–20 hr treatment only in the sample with highest W(VI) content.

In Fig. 3 the rate of formation of α-Al$_2$O$_3$ in the WO$_3$-γ-Al$_2$O$_3$ system at 1323 K is shown. The data indicate the remarkable change of rate and mechanism of the transition depending on the W(VI) content of the system. Two regions of composition can be identified also in this case with a borderline situated in the range of 6–7% WO$_3$ content.
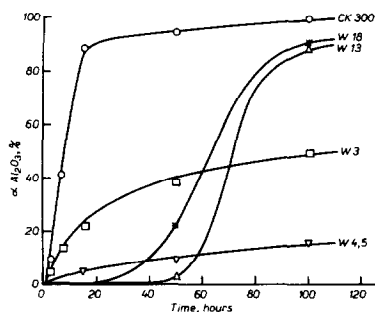

FIG. 1. X-Ray diffraction patterns of samples calcined at 1323 K for 15 hr and W18 treated at 823 K.

FIG. 3. α-Al$_2$O$_3$ formation at 1323 K.

Samples with this WO$_3$ content do not exhibit α-Al$_2$O$_3$ after 150 hr of calcination at 1323 K and exhibit the highest surface stability as shown later.

In the region of lower WO$_3$ content (<7%) the formation of α-Al$_2$O$_3$, when compared with the transition of γ-Al$_2$O$_3$ to α, is depressed and eventually suppressed when the WO$_3$ content approaches 7%. By contrast, in the samples with higher WO$_3$ content (>7%), the formation of α-Al$_2$O$_3$ is described by a sigmoid curve which indicates the formation of the α phase as a consecutive process and therefore the change in the mechanism of formation of the α phase. In this case the formation of α-Al$_2$O$_3$ follows the crystallization of Al$_2$(WO$_4$)$_3$ and the thermal decomposition process and takes place after the crystallization of Al$_2$(WO$_4$)$_3$ has reached the maximum (Fig. 2): these processes seem to be correlated.

In Table I the formation of α-Al$_2$O$_3$, bulk Al$_2$(WO$_4$)$_3$, and thermal desorption of W(VI) after 100, 200, and 400 hr are given at 1223 K. Samples W13 and W18 do not show the presence of α-Al$_2$O$_3$. The desorption of W(VI) is relatively favored compared with the other two processes at this temperature in samples W13 and W18.

Raman Spectroscopy

In Fig. 4 are reported the Raman spectra of γ-Al$_2$O$_3$, W7 and W18 at 823 K, W7 at 1323 K for 100 hr, W18 at 1323 K for 15 hr, and W18 at 1223 K for 200 hr.

Raman spectra of W7 and W18 treated at 823 K and W7 at 1323 K are characterized by a strong band at 970–990 cm^{-1} and a weak band at 860–880 cm^{-1}.

Although there are some controversies about the assignment of these bands (10, 11, 15), the general feature of the Raman spectra clearly show the absence of crystallographically well-defined phases such as WO$_3$ and Al$_2$(WO$_4$)$_3$. Moreover these spectra are in some ways similar to the spectra of aqueous solutions of W(VI) oxoanions and this similarity in turn suggests that W(VI) onto γ-Al$_2$O$_3$ is well dispersed, possibly as isolated species, as already proposed (11, 13). These findings are fully consistent with the X-ray patterns.

In agreement with the X-ray diffraction pattern the Raman spectrum of W18 calcined at 1323 K is almost identical to that of the bulk Al$_2$(WO$_4$)$_3$. More informative seems to be the Raman spectrum of W18 at

TABLE I

Content of α-Al$_2$O$_3$, Total WO$_3$, and Al$_2$(WO$_4$)$_3$ Calculated as WO$_3$(wt%) in Samples Treated at 1223 K

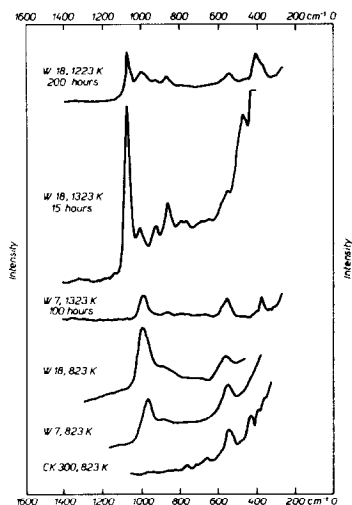| Time (hr)	CK 300 α-Al$_2$O$_3$	W3 WO$_3$	W3 α-Al$_2$O$_3$	W13 WO$_3$	W13 Al$_2$(WO$_4$)$_3$	W18 WO$_3$	W18 Al$_2$(WO$_4$)$_3$
100	5	3.4	—	11.8	—	17	12.7
200	6	3.3	—	10.9	1	15.5	13.3
400	10	3.3	4	9.2	1	14.3	13.8

FIG. 4. Raman spectra of γ-Al$_2$O$_3$, W7 and W18 samples.

1223 K which shows the presence of two species of W(VI): bulk Al$_2$(WO$_4$)$_3$ as indicated by the presence of the sharp band·at 1080 cm^{-1} and W(VI) dispersed onto ϑ-Al$_2$O$_3$ as indicated by the presence of the broad band at 980 cm^{-1}.

Electronic Spectroscopy

In Fig. 5 the electronic spectra of pure WO$_3$, W7 and W18 treated at 823 K, W7 and W18 calcined at 1323 K for 15 hr are shown. The electronic spectra of WO$_3$–γ-Al$_2$O$_3$ samples in the range 2–20% WO$_3$ dried at 383 K and treated at 823 K have been reported elsewhere (11); they are characterized by the presence of a band with the maximum centered at 250 mm and by a broadening of this band toward longer wavelengths with the increase of W(VI) content.

As previously mentioned a controversy exists on the coordination of W(VI) in the WO$_3$–γ-Al$_2$O$_3$ system (10, 11, 15). The absence of an additional maximum in the region of lower wave numbers and the chemical evidence obtained in the adsorption experiments suggest that the broadening of the band reflects the presence on the alumina surface of progressively distorted tetrahedral W(VI) species. This picture is consistent both with the heterogeneity and the quantity of the basic adsorption sites of γ-Al$_2$O$_3$ (16, 17) and with literature data which report the formation of aluminium tungstate species on the γ-Al$_2$O$_3$ surface (18), rather than with a change in coordination of W(VI) from tetrahedral to octahedral oxospecies.

After calcination at 1323 K all samples still exhibit the maximum at 250 nm.

Furthermore during the high temperature treatment the absorption band is modified little if any in the samples with lower W(VI) content while, in the samples in which the bulk aluminium tungstate is formed, the band shows a sharpening which would reflect the presence of less distorted tetrahedral W(VI) oxospecies (19).

Surface Area Measurements

In order to better stress the stabilizing effect of W(VI) on the alumina surface, the surface area is reported in Fig. 6 vs the initial content of WO$_3$ for samples calcined at 1323 K. It can be seen that there is an excellent agreement between X-ray diffraction patterns, Raman spectra, and surface area measurements. Thus samples which do not exhibit α-Al$_2$O$_3$ and bulk Al$_2$(WO$_4$)$_3$
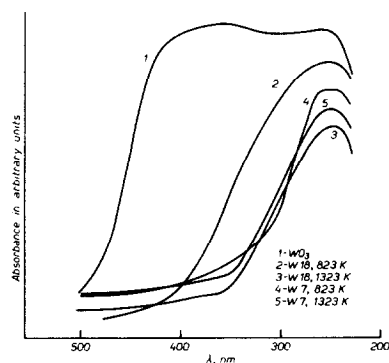

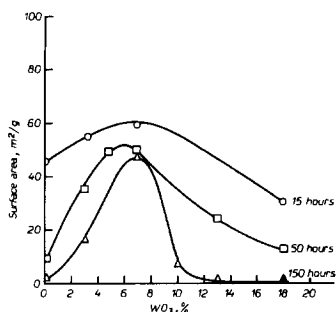FIG. 5. Electronic spectra of pure WO$_3$, W7 and W18 samples.

FIG. 6. Surface areas of the samples calcined at 1323 K.

exhibit a maximum of surface area too and W(VI) is still well dispersed as indicated by Raman spectroscopy. Furthermore the formation of α-Al_2O_3 or bulk $Al_2(WO_4)_3$ is matched by the sintering of alumina.

The technologically relevant observation concerning the stabilizing effect on the alumina surface of W(VI) added in an appropriate amount is reported elsewhere (20).

Discussion

The thermal desorption of W(VI) as a function of the degree of coverage makes evident the heterogeneity of the surface phase formed by the interaction of the basic sites of γ-Al_2O_3 and W(VI) oxoanions. In fact while the presence of a spectrum of basic sites (as well as acidic sites) on γ-Al_2O_3 is well established (7, 16, 17), the thermal desorption of W(VI) indicates that this heterogeneity gives rise to a spectrum of W–O–Al bond strengths. Thus on γ-Al_2O_3 there is a fraction of strong adsorption sites which give rise, by interaction with W(VI), to a surface phase stable at 1323 K.

This surface heterogeneity is in agreement with the slope of the adsorption isotherm of W(VI) from aqueous solutions onto γ-Al_2O_3 (11). It is relevant that the limiting amount of W(VI) which stabilizes the alumina surface corresponds quantita-

tively to the fraction of W(VI) that, in the WO_3-γ-Al_2O_3 system, is characterized by a low catalytic activity (13).

We cannot state at present if the fraction of W(VI) strongly interacting with alumina forms bonds of the type Al–OWO_2–OH or also Al–O–WO_2–OAl; i.e., besides differences in bond strength, there are on the alumina surface differences in number of bonds.

We recall now that the WO_3-γ-Al_2O_3 samples were prepared by a procedure which can be considered an ionic exchange process. This procedure favors the incorporation of W(VI) as isolated oxoanions interacting with the basic sites of γ-Al_2O_3.

The Raman spectra of chemisorbed W(VI) in samples treated at 823 K give further consistency to this picture.

Thus the crystallization of the $Al_2(WO_4)_3$ at high temperature cannot be described merely as a clustering of $Al_2(WO_4)_3$ microcrystallites (not revealed by X-ray diffraction patterns) preexisting in samples calcined at 823 K, nor as a product of interaction of microcrystallites of WO_3 with alumina.

Spectroscopic evidence suggests that the process could be more adequately pictured as a precipitation of bulk aluminium tungstate from a "surface" (bidimensional) solution of aluminium tungstate-like species.

This idealized description, similar to the models proposed in zeolite systems (21), is not in contrast with the electronic spectra of the dispersed and crystallized W(VI) species. In fact, in the crystallization process which takes place in sample W18, no change in the position of the maximum of the absorption band in the UV region is observed.

This suggests that little change takes place in the first coordination sphere of W(VI) oxoanions during the transition (i.e., change in the degree of distortion more likely than coordination number).

The influence of the thermal desorption

of W(VI) which occurs simultaneously with the crystallization must be also considered.

The transition $\gamma \rightarrow \vartheta$ alumina is observed in all samples irrespective of WO_3 content and independently of the formation of $Al_2(WO_4)_3$. The inhibiting effect of some additives on the $\vartheta \rightarrow \alpha$ transition and the stabilizing effect of the surface area are well known (20, 22, 23).

These additives, which are used to increase the thermal stability of the alumina surface, are anionic or cationic and most of them are incorporated in the surface by impregnation. However, because of the surface heterogeneity of alumina, the mechanism of their inhibiting action has not been elucidated yet.

While our results would suggest that on γ-Al_2O_3 there are a number of strong basic sites which may both react with W(VI) oxoanions and be responsible for the nucleation of α-Al_2O_3, our picture does not account for the stabilizing effect of cations such as Ba^{2+} (24). In fact we observed an increase in the thermal stability of the surface in some aluminas containing $Ba(OH)_2$ (25). Thus there is experimental evidence which suggests that strong acid and basic sites play an important role in the nucleation of α-Al_2O_3; these results can be rationalized if the existence of acid–base sites closely adjacent or conjugated is hypothesized. This picture brings to mind the suggestion of Peri (26) concerning the existence on the alumina surface of strained Al–O–Al groups responsible for the catalytic activity of alumina. The presence of conjugated acid–basic sites on γ-Al_2O_3 has been already advanced (27). These Al–O–Al strained groups have the character of conjugated acid–basic Lewis sites which are converted to Brönsted sites by hydration. It is quite conceivable that these sites, due to their strains, are also the sites of nucleation of α-Al_2O_3. For this reason these strains can be reduced and the sites can be stabilized by

chemisorption of appropriate anions and cations and therefore the formation of α phase can be inhibited.

At present we consider this picture merely as a working hypothesis for further studies. The surface of γ-aluminas is heterogeneous and still ill-defined.

It must be stressed that the surface structure of the transition aluminas and the kinetics of the transition to α-phase are strongly dependent on the preparation variables and on the presence of impurities, so that it must be expected that different batches of γ-aluminas will give different stabilization effects by the incorporation of W(VI).

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