The electronic structure of oxide-supported tungsten oxide catalysts as studied by UV spectroscopy

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The UV spectra of tungsten oxide catalysts supported on alumina, titania and zirconia, and on titania–alumina and titania–zirconia mixed oxides are reported and discussed. Evidence is provided for the different electronic structure of supports and catalysts, which could affect the behavior of the tungsten oxide centres in the different cases. On alumina, tungsten oxide centres are “isolated” by the insulating support, while on titania-based materials they are likely in electronic contact with each other and with Ti centres through the support conduction band. In the case of WO_3–ZrO_2, the 5d levels of tungsten ions fall just below of the lower energy limit of the support conduction band.

Keywords: tungsten oxides, UV-vis spectra, electronic structure, HDS catalysts, SCR catalysts, oxidation catalysts, titania, alumina, zirconia, titania–alumina, titania–zirconia

1. Introduction

Oxide-supported metal oxides represent a relevant family of solid catalysts [1]. In particular, materials belonging to this system are used for the selective catalytic reduction (SCR) of NOx by ammonia (V_2O_5–WO_3 or V_2O_5–MoO_3 supported on TiO_2 anatase [2]), for the selective oxidation of some alkyl aromatics such as *ortho*-xylene to phthalic anhydride (vanadia–titania [3]), and in acid catalysis (supported tungsten oxide [4]). Additionally, tungsten and/or molybdenum supported oxides are used as precursors of the corresponding supported sulfides, used in hydrotreatment (HDS) catalysis [5,6], and of reduced catalysts for olefin methathesis [7]. To improve the performance of these catalytic systems, different oxide carriers have been investigated or used. The most popular carriers are alumina and titania, in the form of anatase. The former support is reported to allow good catalyst performance with good mechanical properties. However, titania anatase seems to give rise frequently to more active catalysts than those supported on alumina, both in the case of HDS sulfide catalysts [8,9], and in the case of oxidation catalysts [10], although with worst mechanical properties. Recently, zirconia has also been proposed as a promising support for HDS [11], for SCR [12] and for acid catalysis [13]. Mixtures of these three oxides have also been catalytically tested in some reactions [8,9]. The characterisation of these materials has been largely based on vibrational spectroscopies such as IR [14] and Raman [15]. In particular, the role of different supports on the dispersion of the active phases, and on the acid–basic properties of catalysts has been largely discussed in the scientific literature. Moreover, some authors [16] have pointed out that the electronic properties of the supports are important and can also be involved, particularly in redox reactions carried out on oxide-supported oxides (or sulfides), such as in selective oxidation and hydrotreating [17]. Clearly, the study of the electronic properties of these support materials is of importance to catalysis. Among the catalyst characterisation techniques, ESR spectroscopy [18] and electric conductivity measurements [19] found some application for these systems. UV-visible spectroscopy has been mainly applied to determine the coordination state of the supported phases [20,21].

In the present study we analyse and compare the UV-vis spectra of tungsten-oxide-based catalysts, supported on different carriers, in order to obtain information on the electronic properties of supports and catalysts and on possible electronic interactions between the different supports and the supported tungsten oxide phase.

2. Experimental

The different support samples, ZrO_2, Al_2O_3, TiO_2, TiO_2–Al_2O_3 and TiO_2–ZrO_2, have been prepared starting from $Zr(NO_3)_4$ (MEL Chemicals, solution 40%), $Al[OCH(CH_3)_2]_3$ and $Ti[OCH(CH_3)_2]_4$ (both from Aldrich, 97%). For the Al-containing solids, $Al[OCH(CH_3)_2]_3$ was dissolved in n-propanol. The reagents were mixed carefully prior to hydrolysis with water. The precipitates were dried at 393 K for 12 h, and nitrates and residual organic compounds were calcined at 723 K for 4 h [22]. The preparation of the tungsten-based catalysts was accomplished by impregnating the supports with an aqueous solution of am-

Table 1
Composition and surface areas of the samples under study.

Sample	WO_3 (% w/w)	Surface area (m^2/g)
TiO_2 (anatase)	0	94
ZrO_2 (monocl. + tetr.)	0	94
Al_2O_3 (γ-)	0	210
TiO_2–ZrO_2 (amorphous)	0	203
TiO_2–Al_2O_3 (amorphous)	0	220
WO_3/TiO_2	10	92
WO_3/ZrO_2	10	85
WO_3/Al_2O_3	10	205
WO_3/TiO_2–ZrO_2	10	182
WO_3/TiO_2–Al_2O_3	10	182

monium metatungstate ($(NH_4)_6H_2W_{12}O_{40}$) in the appropriate concentration to yield the composition values given in table 1. The catalyst precursors were dried and calcined under the same conditions as the supports.

The BET surface areas of the samples were measured by nitrogen physisorption using a Micromeritics ASAP 2000 apparatus. The UV-vis diffuse reflectance spectra were obtained at room temperature in a Cary 5E UV-vis-NIR spectrometer using polytetrafluoroethylene as a reference. Some spectra were also acquired under vacuum (dehydrated conditions), using a special quartz cell which allowed heating of the sample wafer, connected to a vacuum line, using a Jasco V570 instrument.

3. Results

The tungsten content and the surface area of the samples under study are reported in table 1. The incorporation of WO_3 to the supports causes a minor decrease in the surface area of the pure supports and from 10–20% in the mixed oxides.

Figure 1 presents the diffuse reflectance UV-visible spectra of the samples under study recorded in air. Regarding the support samples, it is observed that titania anatase shows an absorption edge with an onset near 450 nm and an inflection point near 370 nm. An absorption plateau is also found in the region between 330 and 230 nm. The edge is due to the $O^{2-} \rightarrow Ti^{4+}$ charge transfer transitions corresponding to the excitation of electrons from the valence band (having the O 2p character) to the conduction band (having the Ti 3d character) [23,24]. The position of this absorption and the corresponding energy gap ($E_g \rightarrow 3$ eV) characterises stoichiometric TiO_2 anatase as an intrinsic semiconductor [25].

The pure zirconia sample presents a clear absorption edge, but located at much lower wavelength than the one found for titania. For our zirconia sample, which is actually a mixture of the tetragonal and monoclinic phases, we find the inflection point of the absorption edge near 240 nm, although an absorption tail can also be observed in the 400–250 nm region. This tail, associated to impurity absorptions, makes finding the exact position of the edge onset difficult. The main edge is likely due to $O^{2-} \rightarrow Zr^{4+}$ charge transfer transitions, corresponding to the excitation of electrons from the valence band (having O 2p character) to the conduction band (having Zr 4d character). The edge position agrees well with literature data, reporting an E_g value for zirconia of near 5 eV [13], showing that zirconia is almost an insulating material.

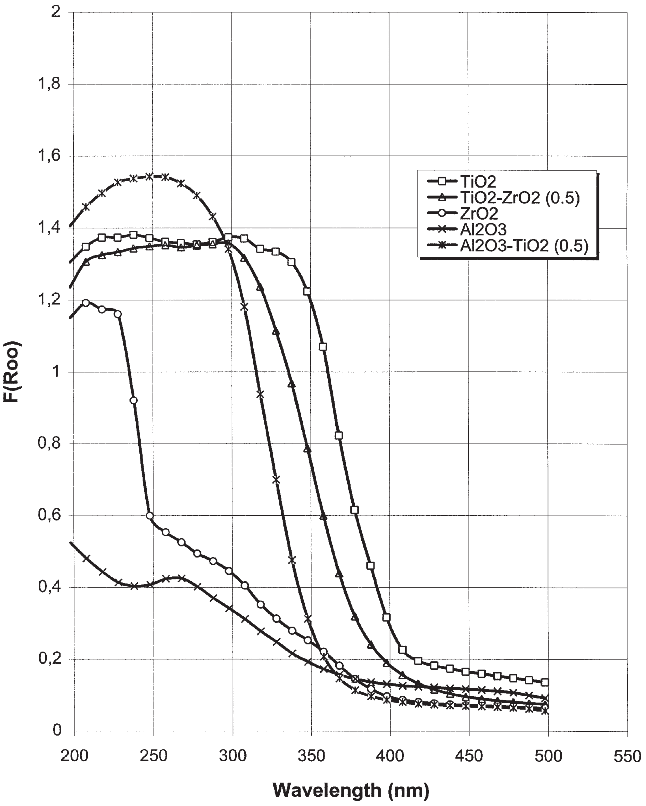
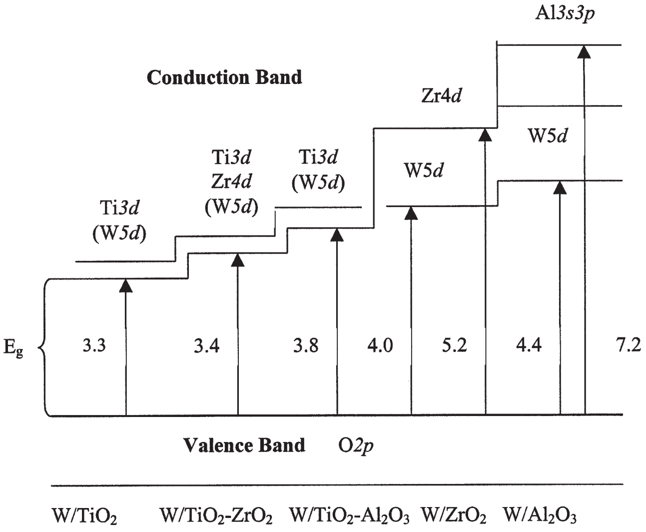


Figure 1. UV-vis DRS spectra for the support samples.



Scheme 1. Electronic structures of oxide-supported tungsten oxides (E_g = energy band gap (eV)).

In the case of the alumina sample, no strong absorption is observed in our available spectra region ($\lambda > 200$ nm), although a weak peak, also associated to impurity absorp-

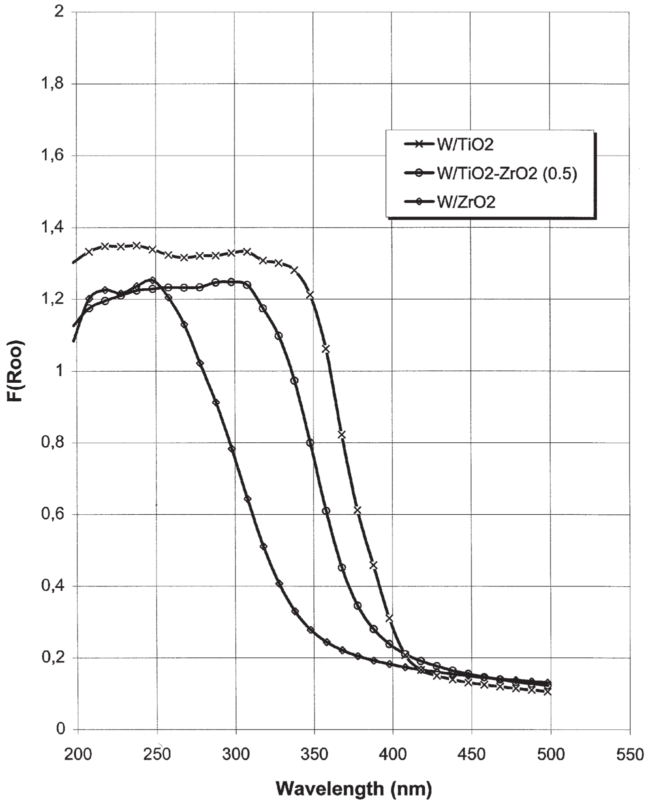


Figure 2. UV-vis DRS spectra for tungsten-based catalysts supported on titania, zirconia and titania–zirconia supports.

tions, can be found centred near 265 nm. These observations are well in line with the strongly insulating character of alumina polymorphs, including γ-Al_2O_3, which is reported to have an E_g as high as 7.2 eV [26].

With respect to the mixed oxide supports containing titania (TiO_2–ZrO_2 and TiO_2–Al_2O_3), they show a strong absorption with an edge which is located at only slightly higher energies than that of titania. The inflection points can be observed near 355 nm for titania–zirconia and near 325 nm for titania–alumina. This means that the dilution of titania with more insulating oxides increases the energy gap due to a mixing of the character of the conduction bands.

The incorporation of tungsten oxide to the titania, titania–zirconia and titania–alumina supports (figures 2 and 3) does not modify at all the position of the absorptions of the corresponding supports. This means that the empty orbitals of hexavalent tungsten (W 5d) lie into the Ti 3d conduction band so that the $O^{2-} \rightarrow W^{6+}$ charge transfer transitions are likely mixed with the $O^{2-} \rightarrow Ti^{4+}$ charge transfer transitions in the three cases. In contrast, the zirconia UV spectrum is strongly modified by the tungsten supported oxide species. In fact, in this case, an additional absorption, with an onset near 400 nm and an inflection point near 300 nm, is clearly observed at the lower energy side of the zirconia edge. Moreover, the limit of this absorption is less sharp than that found in the cases cited above, suggesting that this absorption, rather than being due to a band-to-band transition, can be associated to a broad level-to-level transition.

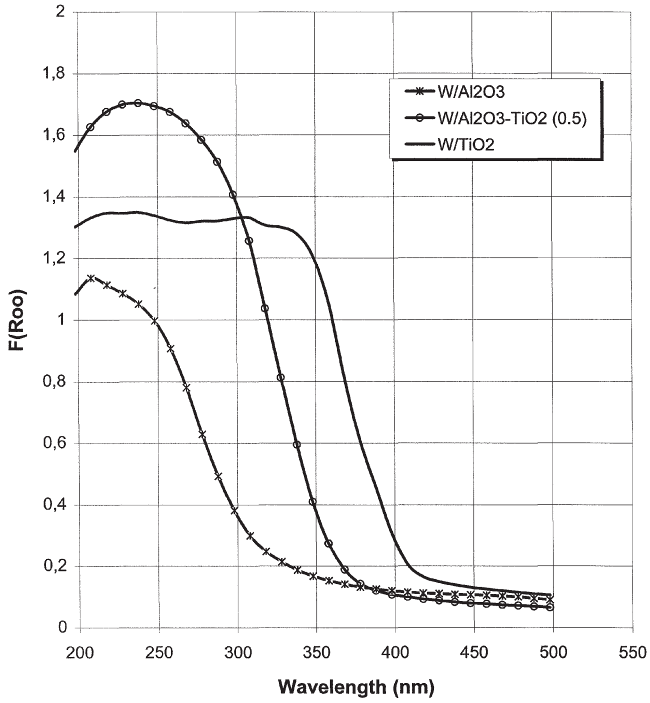


Figure 3. UV-vis DRS spectra for tungsten-based catalysts supported on alumina, titania and alumina–titania supports.

The UV spectrum of alumina is also strongly modified when tungsten oxide is supported on it. In fact, a strong absorption with a main maximum near 215 nm, and a pronounced shoulder near 250 nm, which is not present in the spectrum of the pure alumina sample, is found for WO_3/Al_2O_3. This band is certainly associated to $O^{2-} \rightarrow W^{6+}$ charge transfer transitions involving surface tungsten oxide species. Interestingly, this absorption is located at definitely lower energies with respect to the corresponding absorption observed for bulk WO_3 [27,28], corresponding to the transition of electrons from the O 2p valence band to the W 5d conduction band of WO_3. This shows definitely that the electronic state of tungsten oxide monolayers on alumina is different from that of bulk tungsten oxide, in agreement with previously reported IR and Raman spectra that showed the predominant wolframylic nature of these species (with one very short W=O bond [15,29,30]), in contrast with the more symmetric octahedral coordination of tungsten in the bulk of tungsten oxide polymorphs, with no short W=O bonds.

To have an indication of the possible effect of surface hydration/dehydration on the UV spectra of the samples, we have also recorded the spectra under outgassing at increasing temperatures, as shown in figure 4 for WO_3/Al_2O_3. It is evident that only slight changes are found in the position of the $O^{2-} \rightarrow W^{6+}$ charge transfer transitions, associated to the conversion of the tungsten oxide centres from hydrated to dehydrated forms. The same is observed for WO_3/ZrO_2 (not shown). In contrast, in the case of WO_3 supported on TiO_2-containing supports, we observe (upon

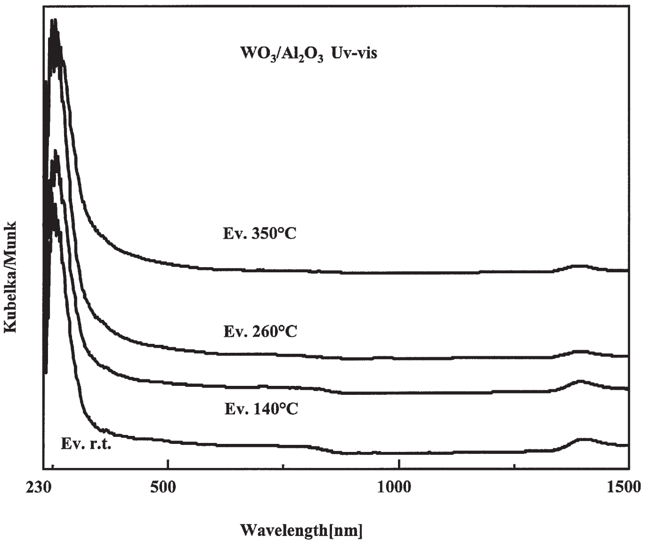


Figure 4. UV-vis DRS spectra for WO_3/Al_2O_3 after outgassing at increasing temperatures.

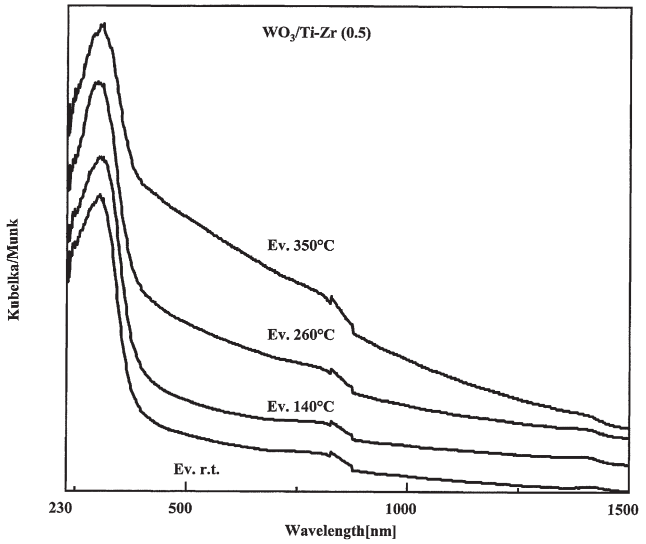


Figure 5. UV-vis DRS spectra for $WO_3/ZrO_2–TiO_2$ after outgassing at increasing temperatures.

outgassing at higher temperatures) a progressive increase of the absorption baseline in the region above the edge, i.e., below the energy of the gap. This is shown in figure 5 for the $WO_3/ZrO_2–TiO_2$ sample. This behavior is typically observed for pure titania too [31] and for other titania-supported or titania-containing catalysts, and is due to a partial reduction of the titania bulk. It is, in fact, well known 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 [32]. So, electrons lying in the conduction band or in donor levels are responsible for low energy absorption. On the other hand, no shift is observed for the edge due to the $O^{2-} \rightarrow Ti^{4+}$ charge transfer transitions upon outgassing WO_3 samples on titania-containing supports.

4. Discussion

The above-discussed data show that the three pure supports, titania, zirconia and alumina, differ very much with respect to their electronic properties. The value of the energy gap for TiO_2 characterises it as a semiconductor, while zirconia and, even more, alumina are insulating materials. This is, in fact, well known, but the important issue is that this electric property of the support is certainly related to the catalytic properties of the supported WO_3-based catalysts, especially for reactions that have a redox character. From the point of view of the electronic properties, titania-containing mixed oxides ($TiO_2–ZrO_2$ and $TiO_2–Al_2O_3$), with 50 mol% titania, resemble more titania than zirconia or alumina. Dilution of titania with zirconia and, more, with alumina causes a shift of the energy gap to higher energies, so showing a detectable perturbation of the electronic properties of titania.

The data also show that the electronic nature of the support can also have an effect on the electronic properties of the supported species. We find that the addition of tungsten oxide to the surface of titania and titania-based mixed oxides does not shift the absorption edge. This has been interpreted as an evidence of the location of the W 5d levels within the conduction band of the overall solid. In line with this interpretation, previously published data show that slight reduction of WO_3/TiO_2 gives rise to a reduction of the overall solid, where localised electrons, giving rise to W^{5+} or Ti^{3+} centers, were not found by ESR spectroscopy [16,18], but only free electrons in the conduction band are found. This fully agrees with the present results on samples outgassed at high temperature.

The above UV data show, instead, that the $O^{2-} \rightarrow W^{6+}$ charge transfer transitions fall at lower energies with respect to the lower limit of the absorption edge of ZrO_2 for $WO_3–ZrO_2$. However, in this case, working at temperatures higher than room temperature, the available energy is likely sufficient to allow promotion of electrons from the W 5d levels, located into the gap, to the conduction band of the overall solid.

This behavior is not expected in the case of $WO_3–Al_2O_3$, where the W 5d levels are located at much lower energies than the lower limit of the alumina conduction band, and, even at reasonable high temperatures, electrons can hardly occupy the conduction band. In this case, reduction of the catalyst should certainly give rise to reduced W centres electronically isolated from one another (at moderate temperature), due to the insulating character of the alumina support.

According to data previously published by us [33], changes in the structural properties induced by variations of the W loading, below the monolayer capacity, alter the position of the absorption band of W-oxide species only slightly in the case of WO_3/Al_2O_3. This clearly supports the interpretation of the above observations, at least at the W loading used here.

The analysis of the DRS-UV-vis spectra of some of the above samples, obtained under vacuum after heat treatment (dehydrated conditions), and which should be closer to the behavior observed under reaction conditions, is also well in line with the observations made at room temperature (ambient conditions). It is evident that the dehydration of the surface only causes small changes in the position of the absorptions due to $O^{2-} \rightarrow W^{6+}$ charge transfer transitions (when they are detectable, i.e., for WO_3/Al_2O_3 and WO_3/ZrO_2) and do not change the relations between the energy of these transitions and energy of the gaps of the supports and catalysts.

On the other hand, the UV-vis-NIR spectra of the titania-containing samples definitely demonstrate that they are easily reducible by simple outgassing at higher temperatures, in contrast to materials based on zirconia and alumina. The color change of the Ti-containing samples, under evacuation and heating, indicates the presence of reduced Ti species, responsible for the increased absorption.

These differences in supports and catalysts, evidenced by the UV spectra described here, allow one to propose that the electronic properties of the oxide support should greatly influence the redox properties of oxide-on-oxide catalysts, and, reasonably, also of reduced oxide-supported and sulfided catalysts. Electronic interactions between support and metal oxide active phase can explain, in part, the greater reducibility and the better activity of some catalysts supported on pure titania anatase, titania-containing Al and Zr mixed oxides and, to a lesser extent, on zirconia, with respect to those supported on alumina, as found for SCR process, oxidation catalysis and hydrotreating sulfided catalysts.

5. Conclusions

The analysis of the UV spectra of tungsten oxide catalysts supported on titania, zirconia, alumina, titania–zirconia and titania–alumina allows one to propose that the better properties of catalysts based on titania are associated to the ability of titania to put into electronic contact the surface tungsten oxide centers, located in different parts of the support, through their own conduction band. These UV spectra also evidence a great difference of the electronic state of tungsten oxide partial monolayers on alumina and zirconia, with respect to bulk tungsten oxide.

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