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Effect of Sodium on the Reducibility of V(V) Ions during Propene Adsorption on V_2O_5/TiO_2 Catalysts

The adsorption of propene at 300 and 343 K on Na-containing and Na-free vanadia–titania catalysts was studied by volumetric methods, and the state of the solid was also checked by XPS and visible–ultraviolet (diffuse reflectance) techniques. Na–V compounds were detected when fairly large amounts of sodium and vanadium are present, and, under these conditions, propene is only adsorbed physically, while vanadium species are stable. On the contrary, when sodium is not present partial reduction of the vanadium species takes place and larger amounts of propene are adsorbed continuously. These results have been related to the ability of these solids to oxidize propene to acrolein. © 1988 Academic Press, Inc.

Vanadium oxide-containing catalysts, widely used in oxidation reactions (*1*), show a noticeable change in their catalytic activities and selectivities when doped with alkaline metals, phosphorus oxides, sulfates, etc., that are added to industrial catalysts to reinforce their mechanical strength, or that appear in the composition of the catalyst as casual contaminants. Although the ultimate role played by these promoting substances in the properties of such catalysts is still a matter of controversy, it is generally assumed that one of their main effects is on the surface acidity of the catalyst, thus favoring reactions (modifying selectivity), or on the way that reagents/products are adsorbed/desorbed (thus affecting activity). Baiker and co-workers (*2*) have reported an increased production of formaldehyde by oxidation of methanol on vanadia when K_2SO_4 is added to the catalyst and have related this effect to an easier reduction of the vanadium cations. Wainwright and co-workers (*3*) have related the modification found in the structure of silica-supported vanadia catalysts following the addition of alkaline metal sulfates to their activity in CO and benzene oxidation; the formation of surface sulfates and pyrosulfates seems to be of paramount importance to the catalytic behavior observed. In previous papers (*4*, *5*) we described the preparation of several vanadia–titania catalysts used to oxidize propene to acrolein; according to the synthesis method used, in some cases sodium was incorporated, leading to the formation of Na–V compounds that modify the activity and selectivity of the reaction. Moreover, the method used to obtain these catalysts leads to well-dispersed vanadium species, as already shown by other authors (*6*, *7*). In the present paper, a study was conducted on the way that the adsorption of propene affects the properties of the catalyst. We found that following adsorption of propene a partial reduction of V^{5+} ions takes place only in the absence of such Na–V compounds.

Three series of catalysts were prepared, as described elsewhere (*4*, *5*). Briefly, the support (TiO_2 P-25, Degussa, Frankfurt) was submitted to calcination in air for 5 h at 773 K to remove surface organic impurities and then used to obtain samples N1, A1, and C1 (see naming of samples in Table 1). For samples, N2, A2, and C2 the support was previously conditioned (outgassing at 670 K for 2 h at 10^{-4} N m^{-2} followed by impregnation in He with an aqueous solution of NaOH, pH 8.5, 1 M NaCl) to increase the surface concentration of basic OH groups (*5*, *8*); this conditioning treatment led to the simultaneous incorporation of appreciable amounts of sodium onto the samples. The samples were characterized by conventional physicochemical methods;

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the results have been published elsewhere (*4*) and are summarized in Table 1. Adsorption of propene was studied at 300 and 343 K in a conventional volumetric high-vacuum system (*5*); prior to adsorption, samples (ca. 0.2 g) were calcined *in situ* at 773 K for 1 h in air and outgassed at 473 K for 2 h; in *all* cases an initial propene (from SCO, 99.95%) pressure of 10 mbar was used (1 mbar = 100 N m^{-2}). The electronic spectra of the samples were recorded in a Shimadzu UV-240 spectrophotometer provided with a diffuse reflectance accessory using MgO or parent TiO_2 as reference, with a slit width of 5 nm; a custom-built quartz cell was used to record the spectra in the absence of air and under controlled conditions. X-ray photoelectron spectra (XPS) were recorded on a Leybold Heraeus LHS-10 apparatus provided with a pretreatment chamber, an EA10 photoelectron analyzer, and a data acquisition and processing station (Hewlett–Packard 2113-E); the $K\alpha$ radiation of Mg (1253 eV) was used. Adsorption of propene was studied under-experimental conditions as close as possible to those used in the conventional high-vacuum system or during catalytic runs for the oxidation of propene on these samples.

TABLE 1

Chemical Analysis, XRD Data, and Specific Surface Area Values of the Samples[a]

Sample	% V	% Na	% Anatase	S_{BET}	Precursor salt
TiO_2	—	—	55	49.3	
N1	1.09	—	55	45.5	NH_4VO_3 (*4b*)
N2	2.16	2.2	55	44.6	NH_4VO_3 (*4b*)
A1	4.4	—	55	38.5	$VO(acac)_2$ (*4b*)
A2	5.0	4.5	32	20.6	$VO(acac)_2$ (*4b*)
C1	1.4	—	55	45.2	$VOCl_3$ (*4a*)
C2	3.3	4.3	40	28.6	$VOCl_3$ (*4a*)
V_2O_5	n.m.	n.m.	—	4.4	NH_4VO_3 (*4a*)

[a] n.m. = not measured; S_{BET} in $m^2\ g^{-1}$; V and Na contents by weight.

Previous X-ray diffraction (XRD) studies have shown that Na-free samples (N1, A1, and C1) and sample N2 (with a fairly low Na content) show only diffraction peaks due to the support (anatase and rutile), thus indicating a large dispersion of the vanadium species on the support surface. However, samples A2 and C2, where appreciable amounts of sodium exist, also show diffraction peaks that have been ascribed (*4*) to the presence of Na–V compounds such as $Na_xV_2O_5$ bronzes. It should be noted that some sort of relationship must exist between the chemical composition of the solid (V and Na), its S_{BET} specific surface area, and its anatase content: initially, the noticeable decrease in the S_{BET} value for sample A2 may have been due to the rutilization occurring in this sample (its anatase content was 32%, whereas in the unloaded parent titania it was 55%). However, this decrease in the S_{BET} of the sample was also observed for sample C2 (S_{BET} = 28.6 $m^2\ g^{-1}$), where the anatase content was only 5% lower than in the original support. Accordingly, the decrease in S_{BET} cannot be due only to rutilization. On the other hand, samples A2 and C2 (those showing the largest decrease in S_{BET}) also exhibit the largest contents in *both* vanadium and sodium and are the only ones whose XRD diagrams show peaks due to Na–V compounds. Similar behavior was observed with sample A1 (with a large vanadium content, but without sodium), which had the same anatase content as the original support, but showed a slight decrease in the S_{BET}. It may therefore be concluded that the formation of Na–V compounds requires the simultaneous presence of fairly large amounts of both vanadium and sodium. The presence of such species decreases the specific surface area of the samples, which cannot unequivocally be ascribed to rutilization (this occurs in sample A2, but not in sample C2). By contrast, with a large vanadium content, but without sodium (sample A1), such Na–V compounds are not formed, rutilization is not observed, and only a small decrease in the specific surface area is observed. In this case, where no peak due to V-containing species is recorded by XRD, it seems that the large dispersion of vanadium ions on the surface of the support simply favors sintering of the particles, as previously found with samples similar to those used in the present work (9).

The pressure–time curves for the adsorption of propene at 300 and 343 K on the samples calcined *in situ* at 773 K for 1 h in air and outgassed at 473 K for 2 h were recorded. In all cases the curves are fairly similar, regardless of the adsorption temperature used (300 or 343 K), although the amount of propene adsorbed changed considerably from one sample to another. After pressure depletion due to expansion, all curves showed a sharp initial decrease, followed by a slow adsorption characteristic of each sample. When the amount of gas adsorbed during the first step (i.e., at the very beginning of the adsorption process, before the curve deviates from verticality) was measured, the amount of gas adsorbed was observed to decrease as adsorption temperature increased, suggesting that such a process corresponds to simple physical adsorption of propene on the samples. After this first step, both the support and samples A2 and C2 (those containing Na–V compounds) show a flat curve, indicating that further adsorption does not take place, although in the case of the bare support the flatness of the curve is observed only after 15–25 min. By contrast, bulk vanadia and all other vanadia–titania samples show a slow adsorption that is not completed even after 1 h. This second adsorption step must correspond to a chemical adsorption process, since the amount of gas adsorbed increases with adsorption temperature. The total amount of gas adsorbed (after 60 min) on sample N1 was larger at 300 K than at 343 K, although this may have been due to the very large physical adsorption capacity shown by this sample. A summary of total adsorption capacities (molecules nm^{-2}) for all eight samples is shown in Table 2.

TABLE 2

Chemical Adsorption Capacities of Propene on the Samples[a]

Sample	At 300 K	At 343 K
TiO_2	1.20	0.40
N1	0.68	0.49
N2	0.42	0.45
A1	0.56	0.59
A2	0.20	0.10
C1	0.53	0.69
C2	0.25	0.07

[a] Sample treatment: oxidation in air at 773 K and outgassing 2 h at 473 K. Adsorption capacities in molecules nm^{-2}. Chemical adsorption corresponds to the amount of propene adsorbed after deviation from verticality in the pressure–time curves.

Throughout the adsorption experiments, the samples whose XRD diagrams did not show Na–V peaks (N1, N2, A1, and C1) changed remarkably in color from yellow to grayish brown. To check the origin of this color change, the visible–ultraviolet spectra (diffuse reflectance) of these samples were recorded; the samples were outgassed *in situ* at 473 K for 2 h at 10^{-4} N m^{-2} and then placed in contact with propene for 60 min. When temperature was kept between 300 and 350 K, the samples darkened and only a broad, weak, and ill-defined absorption centered at ca. 700 nm was recorded. However, on heating at ca. 600–650 K [the temperature range generally used to oxidize propene to acrolein on vanadia-containing catalysts (*10*)], the sample turned gray and absorption around 700 nm increased. In addition, an intense band between 200 and 400 nm, due to an $O^{2-} \rightarrow Ti^{4+}$ charge-transfer process (*11*) and readily detected when heating below 350 K, decreased in intensity when the system was heated at 600–650 K. These findings indicate that besides a partial reduction of V^{5+} species, heating in the presence of propene at high temperatures leads to reduction of the support, thus decreasing absorption at 200–400 nm; the band at ca. 700 nm can be tentatively ascribed to V^{4+} species in an environment of octahedral oxide ions or even to overlapping bands that are due to lower oxidation states of vanadium.

To check the reducibility of the vanadium species in the samples their X-ray photoelectron spectra were recorded. After background subtraction and smoothing computing, the $V(2p_{1/2})$ and $V(2p_{3/2})$ peaks were recorded at 524.4 and 516.8 eV for sample A1 outgassed at 623 K; following treatment in propene (8 mbar) at the same temperature for 30 min in the X-ray photoelectron spectrometer chamber, signals were recorded at 523.4 and 515.7 eV, respectively; the $V(2p_{3/2})$ signal was found to be appreciably wider, indicating partial reduction of the V^{5+} species. After the same treatment the Ti $(2p_{3/2})$ signal close to 460 eV showed a certain asymmetry on its low-binding-energy-side, suggesting that partial reduction of Ti^{4+} to Ti^{3+} had also taken place. Wachs *et al.* (*6, 7*) have reported an XPS signal at 517 eV due to V^{5+} ions $(2p_{3/2})$, shifting to 515.6 eV on reduction with H_2 at ca. 720 K. This has been ascribed to V^{3+} species.

However, the samples containing Na–V species (A2 and C2) did not change their color after treatment with propene at 300 or at 343 K and no chemical adsorption was observed after the fast initial physical adsorption following depletion of propene pressure after expansion. The corresponding XPS for sample A2 did not show any shift in the position of the $V(2p_{1/2})$ and $V(2p_{3/2})$ signals, the latter being recorded at 517.2 eV and the former being too close to the $O(1s)$ signal to be resolved unequivocally. Accordingly, propene treatment does not lead to a reduction of vanadium species, at least as easily as in the case of samples without Na–V compounds.

Kinetic analysis of the data corresponding to chemical adsorption was performed assuming first-order, diffusion, or polymerization processes. In no case was a good fit achieved, indicating that such adsorption does not follow a single-mechanism process.

The present findings may account for the behavior followed by these and other samples during the catalytic oxidation of propene (*4c, 5*). Whereas samples without Na–V compounds show higher activities (i.e., a more pronounced conversion of propene to oxidation products, such as CO and CO_2), the presence of such Na–V compounds leads to a more selective formation of acrolein. Taking into account that propene oxidation may take place via the intermediate reduction of V^{5+} centers to V^{4+} (*12*) and, as shown in this paper, formation of Na–V compounds cancels such a reduction, it may be concluded that the oxidation of propene to acrolein on vanadia–titania catalysts does not necessarily occur through a transient reduction of lattice vanadium species. This conclusion is similar to that drawn by Wainwright and co-workers (*3*) to the effect that lattice oxide ions participate in CO oxidation, but that the oxidation of hydrocarbons (benzene) is due to adsorbed oxygen.

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REFERENCES

1. Gellings, P. J., *in* "Catalysis" (G. C. Bond and G. Webb, Eds.), Specialist Periodical Reports, Vol. 7, p. 105. Royal Soc. Chem., London, 1985.
2. Monti, D., Reller, A., and Baiker, A., *J. Catal.* **93,** 360 (1985).
3. Vorlow, S., Wainwright, M. S., and Trimm, D. L., *Appl. Catal.* **17,** 103 (1985); **17,** 87 (1985).
4. (*a*) Martín, C., and Rives, V., *Adsorption Sci. Technol.* **2,** 241 (1985); (*b*) *J. Coll. Interface Sci.* **120,** 469 (1987); (*c*) *J. Mol. Catal.*, in press.
5. Martín, C., Ph.D. thesis, University of Salamanca, 1987.
6. Wachs, I. E., Saleh, R. Y., Chan, S. S., and Chersich, C. C., *Appl. Catal.* **15,** 339 (1985).
7. Saleh, R. Y., Wachs, I. E., Chan, S. S., and Chersich, C. C., *J. Catal.* **98,** 102 (1986).
8. Munuera, G., González-Elipe, A. R., Rives-Arnau, V., Navio, A., Malet, P., Soria, J., Conesa, J., and Sanz, J., *in* "Adsorption and Catalysis on Oxide Surfaces" (M. Che and G. C. Bond, Eds.), p. 113. Elsevier, Amsterdam, 1985.
9. del Arco, M., Holgado, M. J., Martín, C., and Rives, V., *J. Catal.* **99,** 19 (1986).

10. (*a*) Portefaix, J. L., Figueras, F., Forissier, M., and Foujols, D., *Bull. Soc. Chim. Fr.*, 33 (1984); (*b*) Ono, T., Nakagawa, Y., and Kubokawa, Y., *Bull. Chem. Soc. Japan* **57,** 1205 (1984).
11. Borgarello, E., Kiwi, J., Grätzell, M., Pellizzetti, E., and Visca, M., *J. Amer. Chem. Soc.* **104,** 2996 (1982).
12. Mars, P., and van Krevelen, D. W., *Chem. Eng. Sci.* (*Suppl.*) **3,** 41 (1954).

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