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# On the Consistency of Data Obtained from Different Techniques Concerning the Surface Structure of Vanadia–Titania Catalysts: Reply to the Comment of Israel E. Wachs

In a recent paper Eckert and Wachs (*1*) presented $^{51}$V NMR data on vanadia–titania catalysts that are discussed in terms of the structure of the surface vanadium oxide centers. This paper appeared almost simultaneously with a note published in this journal (*2*), reporting FTIR and laser Raman data on the same topic. According to Wachs' comment (*3*) our interpretation does not agree completely with his own.

The data presented by Eckert and Wachs (*1*) show a "spectacular" perturbation of the $^{51}$V NMR line due to a change in the coordination state of the main vanadium centers on vanadia–titania with low V loadings upon dehydration: the overall coordination of V is lowered from a sixfold to a fourfold one. In our opinion, this agrees perfectly with our IR and Raman data (*2*). It has in fact been shown that the absorption bands associated with V=O stretching vibrations shift markedly upon adsorption and desorption of water, due to a change in the overall coordination of vanadium. Our statement that the above vibrational bands arise from the same species in two different forms (one coordinatively unsaturated on dry samples and one coordinatively saturated on wet samples) is equivalent to Wachs' opinion that they arise from two species having different coordinations. In fact, one species is formed at the expense of the other due to water adsorption/desorption. On the other hand, as noted by Haber *et al.* (*4*) and by Eckert and Wachs (*1*), the coordination of vanadium in oxides is defined somewhat arbitrarily; e.g., on $V_2O_5$ it can be described alternatively as distorted octahedral or square pyramidal. With this in mind our definitions of the dehydrated species as "coordinatively unsaturated" and of the hydrated species as "coordinatively saturated" are perhaps more satisfactory than those given by Eckert and Wachs (*1*), namely, "distorted tetrahedral" (or fourfold coordinated) and "distorted octahedral" (or sixfold coordinated).

In any case the essential information that such species consist of "monooxo" vanadyls arises from vibrational spectroscopies and, in particular, from the following evidence: (i) the high value of the $\nu_{V=O}$ frequencies; (ii) the coincidence of the $\nu_{V=O}$ frequency measured by IR and Raman; (iii) the lack of complexity of the IR first overtone of this mode. Along these lines we would like to stress the usefulness of combining IR and Raman measurements, not only for purposes of mutual confirmation. In fact, the use of Raman spectroscopy alone on wet samples does not allow one to distinguish the $\nu_{V=O}$ vibrations of hydrated vanadyls and bulk vanadia, both falling near 995 cm$^{-1}$ (*2*). On the other hand, IR spectroscopy allows the discrimination between these two species, because the more intense $\nu_{V=O}$ IR band of $V_2O_5$ occurs near 1020 cm$^{-1}$.

FTIR data provided the additional relevant information that coordinatively unsaturated surface vanadyls can act as Lewis acid sites. In fact a shift of the first overtone band of the $\nu_{V=O}$ mode which roughly depends on the strength of the adsorbed base (*5*) is observed upon adsorption of several basic molecules. Accordingly coordinatively unsaturated vanadyls were suggested to adsorb and activate hydrocarbons in selective oxidation reactions (*6–8*) and

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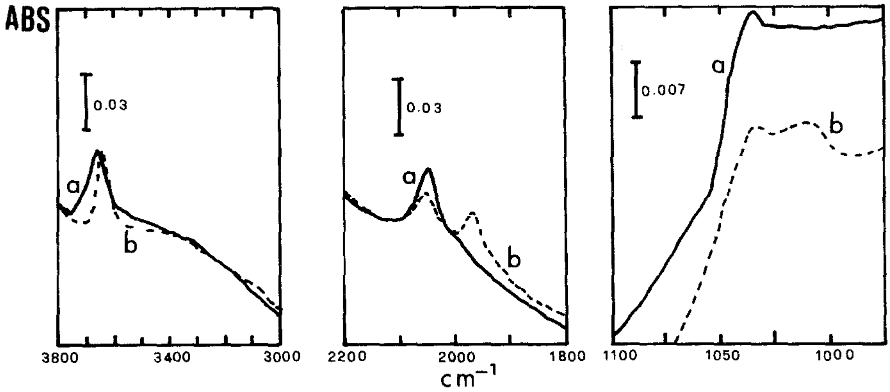

FIG. 1. FTIR spectra of vanadia–titania (a) and of partially $^{16}O/^{18}O$-exchanged vanadia–titania (b) outgassed at 623 K.

adsorb and activate ammonia in the selective catalytic reduction of $NO_x$ (*9*).

An additional proof of the monooxo structure of these species is obtained from the $^{16}O/^{18}O$ exchange experiments recently carried out in our laboratories, following the method used by Saur *et al.* (*10*) (Fig. 1). A partially $^{18}O$-exchanged vanadia–titania dehydrated surface shows the presence of split IR vanadyl absorptions both in the fundamental and in the first overtone regions. The bands at 1035 cm$^{-1}$ ($\nu_{V=^{16}O}$ fundamental) and 2045 cm$^{-1}$ (first overtone) are observed together with new bands near 1000 cm$^{-1}$ ($\nu_{V=^{18}O}$ fundamental) and at 1965 cm$^{-1}$ (first overtone). The experimental isotopic shifts compare well with the theoretical ones ($\nu_{V=^{16}O}/\nu_{V=^{18}O} = 1.04$). If these bands were due to coupled vanadyls (as in the case of dioxo species), three bands instead of two would be expected on a partially exchanged surface both in the fundamental and in the first overtone regions, due to $^{16}O{=}V{=}^{16}O$, $^{16}O{=}V{=}^{18}O$, and $^{18}O{=}V{=}^{18}O$ species. It is interesting to remark that in a partially exchanged surface the $\nu_{OH}$ bands (assigned previously to surface VOH groups) also undergo a shift from 3650 to 3637 cm$^{-1}$. Again, the experimental isotopic shift agrees with the theoretical one ($\nu_{^{16}OH}/\nu_{^{18}OH} = 1.003$).

Finally, the interpretation of the $^{51}V$ NMR (*3*) data also supports our statement that the lower frequency vibrational bands (940–920 cm$^{-1}$) can be due to tetrahedral vanadate species.

FTIR, laser Raman and solid-state NMR data reported in the literature further support the conclusion that "the dehydration products of low-surface-coverage vanadium oxide on $TiO_2$ (anatase) and on alumina are essentially identical" (*1*). In fact coordinatively unsaturated monooxo vanadyls have been observed on the surfaces of vanadia–alumina as well (*11, 12*) although the V=O stretching frequency is slightly higher (*11*). We have shown that similar centers exist also on the surface of bulk vanadia (*11*) and are probably located on the (100), (001), and (101) planes. They are not expected to be present on the (010) basal planes of the layered $V_2O_5$ structure. This agrees with the data of Haber and coworkers (*13*), indicating that the above planes are responsible for the activity of pure vanadia in the selective catalytic reduction of $NO_x$.

In conclusion we think that the data of Wachs and Eckert (*1, 3*) and their interpretation, as well as the previous laser Raman and $^{51}V$ NMR data of Le Coustumer *et al.* concerning the related system vanadia–alumina (12), agree with our data and altogether allow a good characterization of the active sites of vanadia-based catalysts.

However, we note that all experimental techniques have limitations, and that several other problems related to vanadia-based catalysts still need further clarification. We refer, for example to the nature of reduced V(IV) sites. A large number of V(IV) centers are detected on vanadia–titania by UV-Vis-DR spectroscopy and by chemical analysis (*14–17*), both after catalytic reactions and after calcination or degassing. ESR spectroscopy indicated that these sites consist of vanadyls and are sensitive to the adsorption/desorption of water (*14, 18*). Vibrational techniques are sensitive both to V(IV) and V(V) species but they do not easily discriminate between them. On the other hand V(IV) species (*19*) are not taken into account in the discussion of $^{51}$V NMR data of vanadia–titania (*1, 3*). Another topic not yet completely clarified is the apparent poor consistency of the data discussed in the present note with those obtained by EXAFS (*4, 20*).

It seems therefore that further experimental work and other techniques could be useful to improve and complete the picture of the surface structure of titania- and alumina-supported vanadia catalysts.

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