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Characterization of Vanadia/Silica Mixed Gel Catalysts by Vibrational Spectroscopy

In a recent communication (*1*) the preparation and properties of a novel class of catalysts for the selective catalytic reduction (SCR) of nitric oxide have been reported. Highly dispersed vanadium oxide species in an amorphous silica matrix were obtained by the sol-gel process from mixtures of vanadia and silica hydrosols. Vanadia in the resulting catalysts exhibited high activity for SCR and was considerably more stable against thermal aggregation than vanadia layers immobilized on silica supports by alkoxide impregnation (*2*).

Here we would like to present structural information on the vanadia/silica mixed gel catalysts derived from Raman and FTIR spectroscopic investigations. Our results complement the previous characterization of these phases by electron microscopy, TPR, and electron spin resonance (*1*). Vibrational spectroscopy provides further support for the disordered character of the mixed gel catalysts and provides indications of the variation of local structure with vanadia content.

The samples investigated are identical with those characterized in Ref. (*1*). Vanadia and silica sols were prepared from vanadyl triisobutoxide and silicon tetraethoxide, respectively. These sols were diluted, mixed in appropriate amounts, dried, and calcined. Details of the preparation have been given in Ref. (*1*). The catalyst powders were pressed into self-supporting disks of 10 mm diameter and 1 mm thickness. For Raman spectroscopy an Argon ion laser (Spectra Physics, Model 2025-05) was used for excitation; typically 20 mW of power at 488 nm were focused onto a 10 × 0.1-mm line on the sample. The scattered light was dispersed in a double monochromator (SPEX, Model 14018) and detected using photon counting. Spectral resolution was set at 2 cm^{-1}; the total signal accumulation time was ~4 hr for a typical spectrum. FTIR reflectance spectra were recorded on a single beam instrument (Perkin–Elmer, Model 1710) equipped with diffuse reflectance optics.

Results of the Raman spectroscopic measurements are shown in Fig. 1. The spectrum of the amorphous silica is represented by the top trace. The middle traces correspond to vanadia contents of 1, 10, 20, and 50%, respectively. Bands will be discussed in comparison with the spectrum of crystalline V_2O_5, shown at the bottom of the figure.

The silica spectrum (top trace) is featureless and exhibits strong inelastic scattering due to the amorphous silica network. It is important to note that this sample has been prepared by the same procedure as the vanadia-containing catalysts. The resulting silica is completely amorphous, as has been shown by X-ray diffractometry (cf. Ref. (*1*), Fig. 2). Our spectrum is markedly different from the Raman spectra of commercial silica samples (as supplied, e.g., by Merck), for which well-structured spectra are obtained in the same integration time.

With a V_2O_5 content of 1% the low frequency region of the spectrum (below 300 cm^{-1}) is dominated by scattering from the amorphous silica. The vanadia gives rise to a shoulder at 260 cm^{-1}, a peak at 320 cm^{-1}, and two major broad features at 510 ± 5 and 695 ± 10 cm^{-1}.

When the vanadia content is increased to 10% the scattering from silica is strongly reduced, and the peak at 260 cm^{-1} is now clearly discernible. A hump at 350 cm^{-1}

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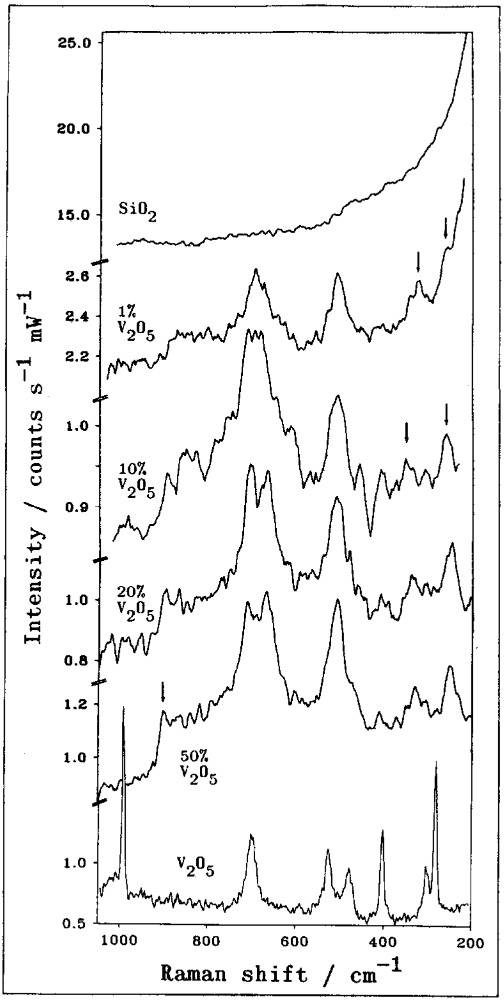

FIG. 1. Raman spectra of vanadia/silica mixed gel catalysts. From top to bottom, the traces represent the spectra from amorphous silica, from catalysts containing 1, 10, 20, and 50% vanadia, respectively, and from crystalline V_2O_5. The 488-nm line of an Ar^+ laser was used for excitation; details are given in the text.

hardly exceeds the noise. Again we find a peak at 510 cm^{-1}; the band at 695 ± 10 cm^{-1} is dominant in intensity, followed by a small maximum at 845 cm^{-1}. At 20% vanadia content the same qualitative features are observed, except that the main peak is clearly split into two components at 670 and 710 cm^{-1}. The highest frequency feature moves up in energy; with 50% vanadia content it is found at 890 cm^{-1}.

The spectrum of crystalline V_2O_5 (bottom trace of Fig. 1) has been assigned in the literature (*3*). Major bands are observed at 285, 305, 483, 530, 703, and 996 cm^{-1}. Only the 703-cm^{-1} band coincides directly with the main feature of the catalyst Raman spectra. The band at 510 ± 5 cm^{-1} observed with the catalysts is broad and centered in between the 483 and 530 cm^{-1} bands of V_2O_5.

Reflectance spectra of the catalysts are presented in Fig. 2. We have chosen to plot the quantity $-\log(R/R_0)$, where R is the diffusely reflected intensity, and R_0 is the reference intensity measured from a totally reflecting surface. Although it is more appropriate to characterize the "absorbance" of a powder sample by the Kubelka–Munk function, $f(R) = (1 - R/R_0)/[2(R/R_0)^2]$, we have found that small peaks are more clearly discernible in the logarithmic plot. This representation is permissible as peak intensities are not used for quantitative interpretation.

As mentioned above, the amorphous silica was prepared from $Si(OEt)_4$ by the same route as the mixed gel catalysts. The reflectance spectrum (top trace in Fig. 2) exhibits a sharp "absorption" edge at 500 cm^{-1}, as well as prominent peaks at 815, 1340, 1630, and 1870 cm^{-1}. The latter two peaks remain unchanged in frequency for all silica-containing samples (Fig. 2) and will not be discussed further.

The spectrum of the catalyst containing 1 wt% V_2O_5 does not exhibit perceptible changes, compared to the silica reference. With 10% V_2O_5, the 820-cm^{-1} peak appears upshifted 5 cm^{-1} from SiO_2, and the 1315-cm^{-1} band is downshifted by 25 cm^{-1}, compared to the top trace. This trend continues when increasing the vanadia content from 10 to 20% ($\Delta\tilde{\nu} = +7$ cm^{-1} for the 827-cm^{-1} peak, $\Delta\tilde{\nu} = -20$ cm^{-1} for the 1285-cm^{-1} band). For 20% vanadia we recognize the first unambiguous sign of a V_2O_5-related phase, i.e., the sharp band at 1025 cm^{-1}: This frequency corresponds to an IR-active vibration of V_2O_5 (*4*). In addition there is a broad maximum at 630 cm^{-1}.

Focusing on the corresponding four bands in the spectrum of the catalyst containing 50% vanadia we recognize that the first peak appears at 835 cm^{-1} ($\Delta\tilde{\nu} = +8$

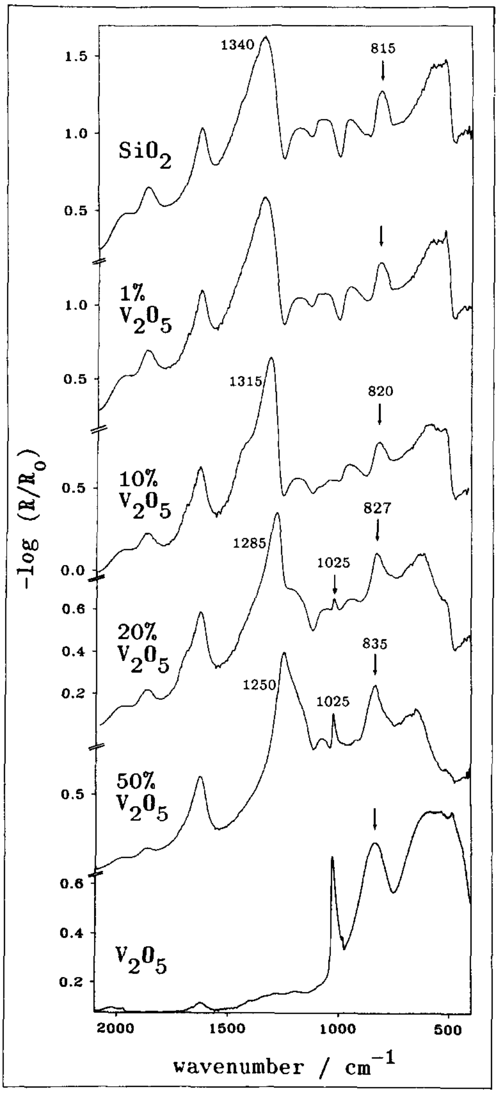

FIG. 2. FTIR reflectance spectra of amorphous silica, mixed gel catalysts, and crystalline V_2O_5 (in KBr dilution). The negative logarithm of the diffuse reflectance R is plotted as a function of wavenumber; R_0 is the reference intensity measured from a totally reflecting substrate. Peak positions (in cm^{-1}) are indicated for some of the bands discussed in the text.

cm^{-1}), at a position coincident with a maximum for V_2O_5 (bottom trace). The second band has reached a position of 1250 cm^{-1} ($\Delta\tilde{\nu} = -35$ cm^{-1}). There is a pronounced peak at 1025 cm^{-1}, and a broad band around 650 cm^{-1}.

The spectrum of crystalline V_2O_5 (measured in dilution with KBr) exhibits a broad maximum extending from 500 cm^{-1} to ~650 cm^{-1}, a band at 835 cm^{-1}, a peak at 1025 cm^{-1}, and two overtone bands around 2000 cm^{-1} that have been discussed by Busca and Lavalley (*4*).

To interpret the spectra presented above, three sources of data will be used: (i) Raman and infrared investigations of crystalline V_2O_5 (*3, 5*); (ii) studies of vanadates both in solution (*6, 7*) and in the solid state (*7, 8*); and (iii) Raman (*9–13*) and FTIR (*4, 13, 14*) investigations of V_2O_5 layers on oxidic supports deposited by a variety of techniques.

One striking difference between the catalyst Raman spectra and the spectrum of crystalline V_2O_5 is immediately evident from Fig. 1: The intensive 285 and 996-cm^{-1} bands of V_2O_5 are absent in the spectra of the mixed gel catalysts. These vibrations are assigned (*3, 5*) to deformational and stretching motions of terminal vanadyl (V=O) groups, which are a characteristic feature of the layered structure of crystalline V_2O_5 (*15*). In fact, there is an empirical correlation between the phenomenological V—O bond order and the frequency of the associated stretching motion (*6*). For isolated VO_4^{3-} units, where the bond order is 1.25, the stretching vibration is observed at 780 and 827 cm^{-1} (*6, 9*). In the $V_2O_7^{4-}$ ion (bond order 1.33) the corresponding band has a frequency of 877 cm^{-1}. For *meta*-vanadates $(VO_3^-)_n$, with a bond order of 1.5, the frequency increases to 945 cm^{-1}, and in crystalline V_2O_5 the stretching motion of the vanadyl group (bond order 2.0) is observed at 996 cm^{-1}. Inspection of all the data reproduced in Refs. (*5–8*) reveals that the above-mentioned vibration in the 800–1000 cm^{-1} range inevitably corresponds to the most intensive band of the spectrum. In contrast, all our catalysts apparently do not exhibit this vibration, as there are only weak signals above 800 cm^{-1}. From this observation we must conclude that the vanadium–oxygen "bond order" is less than the value found in VO_4^{3-}. The vanadium ions are surrounded by oxygen ions, all of which are in bridging positions in an amorphous oxidic network. Parenthetically we remark that this observation is consistent with the fact (*1*) that only part of the vanadium ions is accessible to reduction in temperature-programmed reduction experiments.

Let us examine whether the most intensive bands in the catalyst spectra, at 510 ± 5 cm^{-1} and ~700 cm^{-1}, support this conclusion. The signature (*9*) of monomeric VO_4^{3-}, i.e., a strong band at 827 cm^{-1} with a shoulder at 780 cm^{-1}, is not seen in our spectra. Vibrations around 500 cm^{-1} are observed (*6, 7*) for a variety of oligomeric and polymeric vanadate species, with both tetrahedral and octahedral coordination. A vibration at 700 cm^{-1} is seen only with octahedrally coordinated vanadium, such as in the decavanadate ion (*7*) which consists of face-connected VO_6 units. The bands corresponding to the terminal V=O groups, e.g., found at ~1000 cm^{-1} in decavanadates, are however not observed on our catalysts, as mentioned above.

A third fact relevant for the interpretation of our data is obtained from an analysis (*5*) of the oxide phonon spectrum of crystalline V_2O_5. The layers (*13*) of V_2O_5 contain oxygen atoms in bridging positions between three vanadium ions (designated OV_3), oxygen ions bridging between two vanadium centers (OV_2), as well as terminal oxygens. Analysis (*5*) shows that the OV_3 stretching vibrations give rise to two bands at 703 and 530 cm^{-1}. The two-connected bridging oxygens (OV_2) exhibit a deformational mode at 483 cm^{-1}.

Taken together these observations suggest that in the mixed gel catalysts no truly terminal vanadyl groups are present. The oxygen ligands are in bridging positions between two or three centers. With low vanadia contents it is reasonable to assume that V–O–Si bridges are involved. With increasing vanadia content there are more neighboring vanadium ions, and one approaches the binding situation of connected VO_6 octahedra, as found, e.g., in decavanadates.

It is interesting to correlate this interpretation with the results of EPR investigations of the mixed gel catalysts (*1*). For vanadia contents ≤10% an axial spectrum corresponding to well-dispersed vanadium ions has been found; at a vanadia content of 20% a spectrum corresponding to polymeric arrays of vanadyl species was detected.

Only a qualitative interpretation of the IR reflectance spectra can be given at present. Most remarkable is the continuous shift of two bands with increasing vanadia content. The 1340-cm^{-1} feature of amorphous silica shifts to 1250 cm^{-1} in the catalyst containing 50% V_2O_5. The 815-cm^{-1} band of silica shifts continuously to 835 cm^{-1}, which is the frequency also observed in the reflectance spectrum of diluted V_2O_5. This continuous tunability again implies that vanadia and silica coordination polyhedra are intimately mixed on a molecular scale. A similar behavior has recently been observed by us for silica/titania mixed oxide carriers. Quantitative analysis of the vibrational spectra of mixed oxide systems will be the subject of further work.

In the IR spectra of the catalysts containing 20 and 50% vanadia we do observe a sharp line at 1025 cm^{-1} which is indicative of crystalline vanadium oxide phases. This result is in agreement with high resolution electron microscopy studies (*1*): For a vanadia content of 50%, small domains consisting of microcrystalline V_3O_7 and/or V_6O_{13} phases have been detected. Inspection of the IR reflection data (Fig. 2) indicates that the amount of microcrystals is relatively small, which also explains why the corresponding peak is not detected in the Raman spectra of Fig. 1. The amount of V_3O_7 and V_6O_{13} phases estimated from temperature-programmed oxidation experiments (*1*), i.e. 20%, comprises reduced phases both in crystalline and in disordered states.

Highest specific catalytic activities for SCR of NO have been found for vanadia contents of 1 and 10% (*1*). For these systems the present study fully supports the structural model derived from other characterization techniques. Let us summarize the main conclusions derived from vibrational spectroscopy:

—The preparation of V_2O_5 catalysts by mixing of vanadia and silica hydrosols results in molecularly mixed oxides.

—The most intensive vibrations detected correspond to oxygen atoms in bridging positions between three or two centers (V^V and/or Si^{IV}, respectively). Frequencies closest to the observed ones are found in the sheets of crystalline V_2O_5 (in-plane skeletal motions) and in the face-connected octahedra of decavanadates.

—There are hardly any vibrations corresponding to vanadyl groups with double bonds, suggesting that all oxygen atoms are involved in bridging positions to neighboring centers of the amorphous network. Of course, some of these bridges will be relatively loose, such that the involved V—O bond has partial "double bond" character.

—In this context it is interesting to consider the highest frequency features of the Raman spectra. These are found at ~890 cm^{-1} for the catalysts containing 10, 20, or 50% vanadia. The gradual intensity increase of this feature visible in the spectra might be tied to the development of the $\mathrm{V}\underset{\cdots}{\overline{\quad}}\mathrm{O}$ bonds described above.

—Importantly, the most active catalysts containing 1 and 10% of vanadia do not exhibit the characteristic vanadyl (V=O) vibrations at all.

Inomata *et al.* (*16*) have suggested that the vanadyl (V=O) groups on V_2O_5 are important in the first step of SCR,

$$NO + NH_3 + V{=}O \rightarrow N_2 + H_2O + V{-}OH,$$

and that this reaction can be used for the determination of V=O groups at the surface of vanadium oxide-based catalysts (*17*). The present findings indicate that the role of V=O species in the mechanism of SCR postulated by Inomata *et al.* (*16*) needs revision, as has been pointed out very recently by Gasior *et al.* (*18*).

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