On the effect of dopants and additives on the state of surface vanadyl centers of vanadia–titania catalysts

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The effect of dopants on the V=O stretching frequencies of vanadyls on low-V-loading vanadia–titania catalysts is shown. Alkali and alkali-earth metal cations decrease ν(V=O) while oxo-anions like sulphates, phosphates and arsenates increase it. Acid-type cations, like Al^{3+}, MoO^{4+} and WO^{4+} have a small effect. A relation with the effect of these dopants on the catalytic activity in the SCR of NO_x is proposed.

Keywords: Vanadia–titania; dopants; FT-IR spectroscopy; SCR of NO_x

Vanadia–titania mixed oxides are the basic components of the industrial catalysts for the selective oxidation of ortho-xylene to phthalic anhydride [1,2] and for the selective catalytic reduction (SCR) of NO_x by ammonia [3,4]. In both cases the anatase polymorphic form of TiO_2 is utilized as the support. However, the catalysts for selective oxidation contain vanadium oxide loadings sufficient [5,6] or even higher [7] than those needed to cover all the support surface with a theoretical geometric "monolayer" of V_2O_5. On the contrary, catalysts for SCR contain very small amounts of vanadium oxides, much lower than those needed to complete the "monolayer". Vanadium oxides are known to spread over the TiO_2-anatase surface [8] forming a relatively stable "discontinuous monolayer", formed by two different structures: (i) isolated vanadyl complexes, well characterized by IR and Raman spectroscopies [9–12], predominant at very low V loading; and (ii) polymeric species probably of the metavanadate type, formed at higher vanadium loadings [9–11]. In spite of the higher catalytic activity of the polymeric species, isolated vanadyls can be considered as the main responsible for the SCR reaction because of the low V loading of the industrial catalysts. In fact the activity of

SCR catalysts is sufficiently high also at low V loading and their composition is adjusted in order to avoid the parallel unwonted oxidation of SO_2 (present in waste gases) [4].

Additional components are added to vanadia–titania industrial catalysts, as activators or stabilizing agents, or are formed in reaction conditions. Catalysts for SCR contain molybdenum or tungsten oxides as well as silica [3,4] and can become sulphated as an effect of SO_2 present in waste gases. The present communication reports the results of an FT-IR study of the state of vanadyl centers on vanadia–titania catalysts doped with a third element. All samples are obtained by wet impregnation technique of soluble salts on TiO_2 P25 from Degussa (Hanau, Germany, 50 m^2/g). The loadings of supported phases are about 3% (w/w) for vanadium and 2% for the doping elements. The powder samples were pressed into self-supporting disks of appropriate thicknesses and evacuated in the IR cell at 623 K. The spectra have been recorded using a Nicolet 5ZDX Fourier transform instrument.

The spectra of pressed disks of the samples without dopants and with Cs and P, all after outgassing at 623 K, are reported in fig. 1. Isolated vanadyl centers are characterized in dry conditions by a single V=O stretching frequency evident as a sharp band in the same position both in IR and in Raman spectra [9–12], as well as by its first overtone well detectable in IR spectra [13]. The position of the V=O fundamental (when detectable) and of its first overtone in the different samples is reported in table 1. In the cases of samples containing silicon and phosphorus the

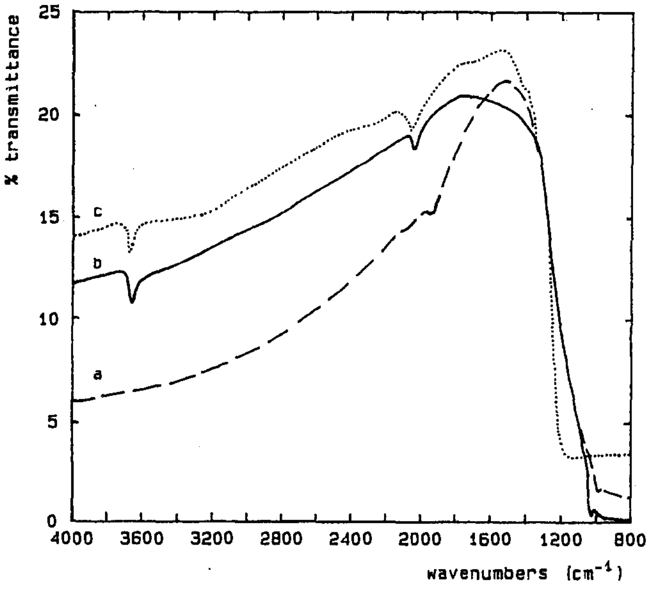

Fig. 1. FT-IR spectra of pressed disks of Cs-doped vanadia–titania (a), "pure" vanadia–titania (b) and P-doped vanadia–titania (c), after activation at 623 K. The spectra are slightly shifted to allow better inspection of the low-frequency region.

Table 1
Position of the V=O fundamental band and of its first overtone in 3% V_2O_5–TiO_2 samples doped with a third component

Additive element	V=O stretching frequencies (cm^{-1})		Other main absorptions (cm^{-1})
	fundamental	first overtone	
Cs	990	1952, 1934	
K	1013, 1002	2006, 1960	
Na	1020	2022	
Li	1030	2040	
Mg	1032	2042	
=	1035	2045	3650 (ν(VO–H))
W	1035	2045	1015 (ν(W=O)), 2020(2ν(W=O))
Mo	1035	2045	1000 (ν(Mo=O)), 1985 (2ν(Mo=O))
Si	masked	2045	3750 (ν(SiO–H)), 1200–1000 (ν(Si–O))
Al	1038	2048	
S	1038	2050	1370, 1200–1000 (ν(S–O))
As	1040	2052	3620 (ν(AsO–H))
P	masked	2056	3660 (ν(PO–H)), 1200–1000 (ν(P–O))

fundamental region is obscured by the Si–O and P–O stretching absorptions. The spectra can contain also additional absorptions in the transmission window 1000–4000 cm^{-1} (table 1) that are indicative of the state of the dopant. In particular, alkali, alkali-earth and Al cations only cause the disappearance of the VO–H stretching band evident as a weak band in pure vanadia–titania. Mo- and W-doped catalysts show typical absorptions of molybdenyl Mo=O [14] and wolframyl W=O [15] ions. S-, As- and P-containing powders show absorptions typical of sulphate (SO_4^{2-}), arsenates (AsO_4^{3-}) and phosphates (PO_4^{3-}) ions, respectively.

Relative to their effect on the V=O vibrations, the elements can be divided into three groups.

(i) The typical electropositive metal cations (alkali and alkali-earth metal cations) decrease strongly the V=O stretching frequency, the more so the smaller their electronegativity (or the smaller is the cation polarizing power). This behaviour can be explained taking into account the effect of the basicity of the ligands on the V=O bond order and stretching frequency in the case of vanadyl homogeneous complexes. It is in fact known that the V=O stretching frequency of these complexes decreases when strong basic ligands are present mainly in equatorial position [16]. We have confirmed by our IR experiments of adsorbed probe molecules that doping of TiO_2 [17] and of vanadia–titania with alkali cations causes the formation of new stronger basic sites. Vanadyl cations, that are Lewis acidic, probably are "attracted" by these new stronger basic sites and O=V–O–Ti bridges are substituted (at least in part) by O=V–O–M bridges (M = alkali or alkali-earth cation). As a result of the increased basicity of their ligands, coordinatively unsaturated vanadyl centers have their Lewis acidity weakened, as observed by using ammonia as a probe molecule.

(ii) At the other extreme, the typical non-metallic elements present as oxo-anions, like sulphates (SO_4^{2-}), arsenates (AsO_4^{3-}) and phosphates (PO_4^{3-}) tend to increase significantly the V=O stretching frequency. These anions are probably "attracted" by vanadyls for electrostatic reasons and can act as ligands for them. These anions are the conjugate bases of relatively strong acids: so, they are relatively weak bases. So, when they participate to the coordination sphere of vanadyl centers, V=O bond strength increases and V=O stretching frequency shifts up. As a result of the lowered basicity of their ligands, coordinatively unsaturated vanadyl centers have their Lewis acidity strengthened, as we observed by using ammonia as a probe molecule. Silicon, forming silicate anions, belongs to this group although its effect is the weakest.

(iii) The behaviour of elements that are present in a cationic form (Al^{3+}, MoO^{4+} and WO^{4+}) but whose oxides are acidic in nature, is intermediate. The character of these elements is roughly similar to that of vanadium, so their behavior is competitive with that of vanadyls (VO^{3+} and/or VO^{2+}) in the reaction with the basic sites of the TiO_2 support. They probably distribute over the support basic sites and "repel each other". Consequently they are far and do not influence strongly each other.

According to our previous mechanistic studies [18–20], coordinatively unsaturated vanadyl centers are the active sites in the SCR process. They coordinate the reducing agent ammonia and allow hydrogen abstraction giving an amide species (NH_2). Amide species react with NO giving water, nitrogen and a reduced vanadium center which is reoxidized by oxygen [18–20]. This mechanism is very similar to that proposed by Willey et al. [21] for iron-oxide based catalysts and found recently additional support by the work of Went et al. [11]. The activating or deactivating effect of the additional components can be in part related to their effect on the state of the vanadyl centers, discussed here. As for example, it is known that alkali and alkali-earth metal cations deactivate SCR catalysts [22,23]. In the case of alkali metals, the effect is stronger, the weaker is the element electronegativity. It seems reasonable to relate the inhibiting effect with the lowering of the Lewis acidity of the surface vanadyl centers, parallel to the weakening of the V=O bond order revealed by the shift down of the V=O stretching band. The lower the Lewis acidity, the weaker the adsorption of the reducing agent ammonia and, consequently, the weaker its perturbation upon adsorption. The first step in the reaction consequently slows down.

Conversely, cations that tend to increase the acidity are reported either to be weak inhibitors (as Al^{3+} [23]), or weak activators (as MoO_3 and WO_3 [3,4] that are deliberately added to SCR catalysts for stability reasons). The strong interaction of acidic oxo-anions with vanadyl centers, shown by their effect on the V=O stretching frequency, can justify an activating effect when they are present in small amounts (as it has been shown for sulphates [22,24]). However, when their amount is great they cause a blocking of the active sites and, consequently, a strong deactivation. This has been shown for sulphates and arsenates on V, Mo and W based catalysts [3,4,25].

In conclusion, the V=O stretching frequency and its first overtone on vanadia–titania-based catalysts are sensitive to the presence of dopants and additives and on their chemical nature. So, their position is a probe of the composition of SCR catalysts and could be informative in relation to their deactivation.

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