ESR Study of Monolayer Vanadium Oxide Catalysts Supported on Different Supports in Relation to Catalytic Oxidation of Methanol

by

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Summary. Vanadia monolayers deposited on various oxide supports (ZrO_2, Nb_2O_5, TiO_2, Al_2O_3 and SiO_2) have been investigated with the aid of electron spin resonance. The results show that the electronic structure of reduced vanadyl species generated during methanol chemisorption depends on the nature of the supporting matrix. This is shown by changes of the β^2 bonding coefficient calculated from the experimentally determined ESR parameters. It is demonstrated that the catalytic activity in methanol oxidation, expressed in terms of turnover frequency (TOF), can be correlated with the latter parameter and increases with the ionicity of the vanadyl in-plane π-bonding system.

Wachs *et al.* [1–3], in their extensive studies of surface structure and catalytic activity of vanadium oxide catalysts supported on ZrO_2, Nb_2O_5, TiO_2, Al_2O_3 and SiO_2, demonstrated that in the case of methanol oxidation, the catalytic activity normalized per vanadium atom (expressed in terms of the turnover frequency – TOF) varied by three orders of magnitude for different supports. On the other hand, the Raman and ^{51}V NMR spectra of these samples in a dehydrated state reveal that the structure of the surface vanadium oxide species is essentially identical for the first four supports, being a combination of isolated and polymerized VO_4 units possessing a terminal vanadyl bond, while only isolated surface VO_4 species with terminal $V{=}O$ groups exist on SiO_2. No correlation could be observed between the terminal $V{=}O$ bond strength calculated from Raman band position and the reactivity in the methanol oxidation reaction. In view of this, the authors suggested that the differences in catalytic performance were caused by the support influence via the V—O-support bond, the latter phenomenon being

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obviously too weak to affect the Raman spectra of the concerned species. In the present study we use ESR technique in order to get further insight into the nature of vanadium oxide species active in methanol oxidation. This method, owing to its sensitivity to the minor changes in the nearest coordination sphere of paramagnetic ions, is perfectly suited for this task and has been successfully employed in the past to characterize paramagnetic vanadium species in various matrices, such as oxides, zeolites, clay minerals, and, recently, mesoporous molecular sieves [4–12]. In an attempt to correlate the results of ESR analysis with the catalytic data the ESR investigation has been carried out on the samples used in the earlier described catalytic studies of methanol oxidation [1]. The reduced vanadium ions were generated by means of methanol chemisorption.

Experimental

Materials. Preparation of the samples was described earlier [1]. The vanadium oxide was deposited on different oxidic supports by the incipient wetness impregnation of vanadium triisopropoxide in methanol solution in a controlled environment (flowing nitrogen). After impregnation and thorough mixing, the oxide support and alkoxide solution were dried in a glove box for 16 h and subsequently heated to $120°$ C in flowing nitrogen. The final calcination was performed in oxygen at $450°$ C for vanadium oxide supported on ZrO_2 (39 m^2/g), Nb_2O_5 (55 m^2/g), and TiO_2 (55 m^2/g) and at $500°$ C for vanadium oxide supported on Al_2O_3 (180 m^2/g) and SiO_2 (300 m^2/g). Samples with vanadia content corresponding to a monolayer coverage were taken for ESR investigation.

Methanol chemisorption. Methanol chemisorption was carried out in ESR tubes attached to a vacuum line. Prior to adsorption the samples were subjected to 3 h outgassing at room temperature, at 10^{-5} Torr. Subsequently they were exposed to ca. 50 Torr of methanol vapour at 373 K for 30 min. The ESR spectra were recorded after freezing out the excess methanol in a liquid nitrogen trap.

Electron Spin Resonance. The ESR spectra were recorded at room temperature and at 77 K with an X-band SE/X (Technical University Wrocław) spectrometer. Diphenylpicrylhydrazyl (DPPH) was used as a *g*-factor reference. Evaluation of ESR parameters was done by comparison of experimental spectra with computer simulations. ESR simulation programs SIMAX and COMBI, kindly made available by Dr. Jose Conesa from Instituto de Catalisis y Petroleoquimica, CSIC, Madrid, Spain, were used for computations. Estimates of spin concentration were made by double integration of the ESR signals, using as a standard a sample of polycrystalline $VOSO_4$.

Results and Discussion

Already before contact with methanol all samples show ESR signals attributable to the presence of V(IV). The relative concentration of these sites ranges from < 0.1% for silica and alumina to ca. 0.5–1% for niobia, titania and zirconia. Exposure to methanol vapour enhances intensities of the spectra and results in a change of their lineshapes and parameters. After this treatment the relative concentration of V(IV) is ca. 0.5% for SiO_2 and Al_2O_3

and 6–9% for Nb_2O_5, TiO_2 and ZrO_2. In all cases (Figs. 1–5) a component with a characteristic eight-line hyperfine pattern due to the interaction of the unpaired electron with the ^{51}V nucleus ($I = 7/2$), typical of isolated vanadium centres can be seen, albeit with different relative intensity. Beside this signal, all spectra contain a broad, structureless component characteristic of reduced V ions situated in close proximity to each other. This signal is the dominant one for the vanadium oxide monolayer deposited on TiO_2, Nb_2O_5 and ZrO_2 supports. This is in the first place the consequence of higher contribution of polymeric species in these catalysts, but a possibility of a higher reducibility of surface polymers vs isolated units should also be taken into account. Table 1 shows the ESR parameters of the signals with

TABLE 1

ESR parameters of reduced V species generated by methanol chemisorption over supported monolayer vanadia catalysts

Sample	V wt. %	$g_\parallel$	$g_\perp$	$\|A_\parallel\|$ $\times 10^4$ cm^{-1}	$\|A_\perp\|$ $\times 10^4$ cm^{-1}	β_2	Signal contribution %
V_2O_5/SiO_2	3	1.933	1.977	174	67	0.785	28.5
		1.910	1.960	175	74	0.717	4.0
V_2O_5/Al_2O_3	17	1.930	1.976	173	63	0.806	43.0
V_2O_5/Nb_2O_5	7	1.924	1.976	180	67	0.823	4.0
		1.920	1.971	165	51	0.828	2.5
V_2O_5/TiO_2	6	1.923	1.976	176	63	0.821	4.0
		1.933	1.962	166	52	0.847	3.5
V_2O_5/ZrO_2	4	1.917	1.976	181	66	0.830	10.5
		1.924	1.958	172	57	0.846	4.0

resolved hyperfine structure and their relative contribution to the overall spectrum, determined from the computer simulation of the spectra. In the case of silica, niobia, titania, and zirconia supports, a reasonable fit could be obtained after assuming that the hyperfine structure was due to the presence of two types of isolated vanadium species. The calculated signals are marked in Figs. 1–5 with dashed lines.

The relative magnitudes of the g and A components of a V(IV) center depend on the symmetry of its coordination sphere and on the nature of the surrounding ligands [13–15]. Bearing in mind that in all samples the V centers can be surrounded only by the oxygen-donating ligands (be it oxide anion, hydroxyl group, methoxy species or water molecule), the experimentally observed values of $g_\parallel < g_\perp$ and $A_\parallel > A_\perp$ indicate the formation of a vanadyl bond in the vanadium species responsible for the ESR signals. The spectra were analysed following the reasoning presented earlier by many
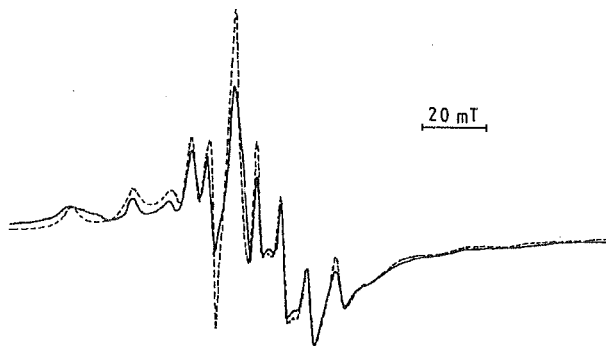
Fig. 1. ESR spectrum of a monolayer V_2O_5/SiO_2 catalyst, recorded at 77 K (solid line – experimental, dashed line – calculated)
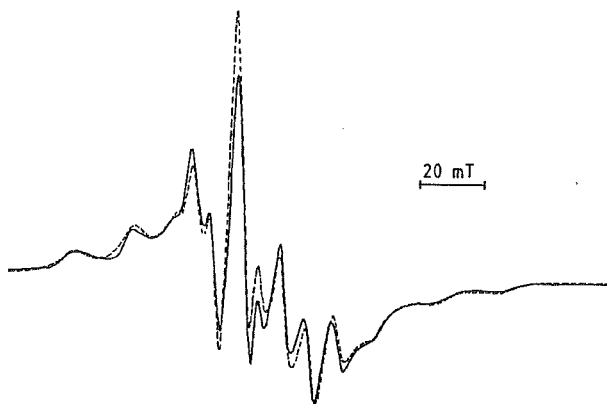

Fig. 2. ESR spectrum of a monolayer V_2O_5/Al_2O_3 catalyst, recorded at 77 K (solid line – experimental, dashed line – calculated)
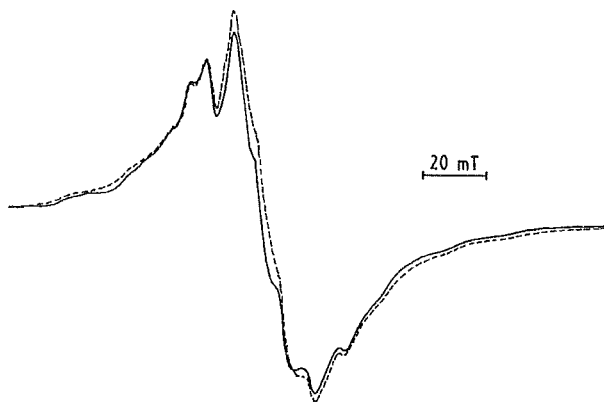

Fig. 3. ESR spectrum of a monolayer V_2O_5/Nb_2O_5 catalyst, recorded at 77 K (solid line – experimental, dashed line – calculated)
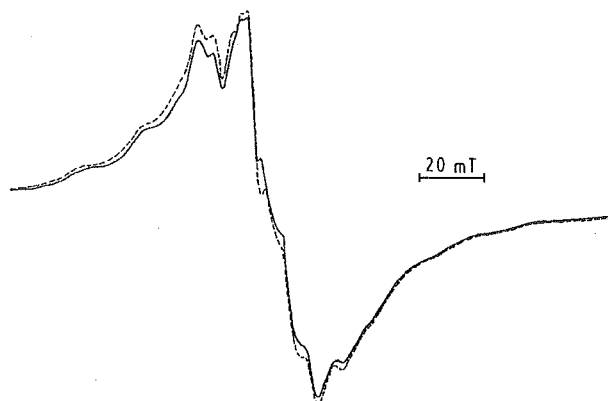
Fig. 4. ESR spectrum of a monolayer V_2O_5/TiO_2 catalyst, recorded at 77 K (solid line – experimental, dashed line – calculated)
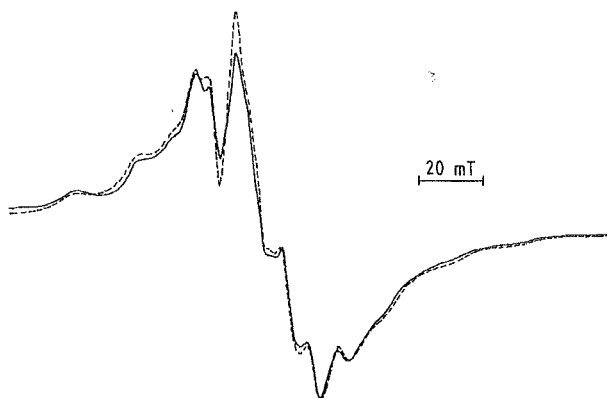

Fig. 5. ESR spectrum of a monolayer V_2O_5/ZrO_2 catalyst, recorded at 77 K (solid line – experimental, dashed line – calculated)

authors for vanadyl complexes [16–18], using an axial spin hamiltonian, assuming C_{4v} square-pyramidal symmetry of the ligand field surrounding the V(IV) and employing the LCAO-MO approach. The ground state for such complexes is a molecular orbital of b_2 symmetry and the corresponding wave function is

$$(1) \qquad |B_2\rangle = \beta_2|d_{xy}\rangle - \beta_2'|\varphi_{b2}\rangle$$

where $|\varphi_{b2}\rangle$ are ligand orbitals of b_2 symmetry, and β_2 and β_2' are the bonding coefficients. The squared MO coefficient $\beta_2{}^2$, which provides information about the degree of localization of the unpaired electron on the vanadium d_{xy} orbital, can be computed in terms of the empirical data according to

the following approximate relationship [17–19]:

$$(2) \qquad \beta_2{}^2 = 7/6\Delta g_{||} - 5/12\Delta g_\perp - 7/6(A_{||} - A_\perp)/P$$

where $\Delta g_{||} = g_{||} - g_e$, $\Delta g_\perp = g_\perp - g_e$, g_e being the free electron g value, and P is a term which takes into account the dipole-dipole interaction of the electron moment with the nuclear moment. In the present work the value of $P = 146 \times 10^{-4}$ cm^{-1} calculated by Morton and Preston [20] has been used. In vanadyl complexes the hyperfine interaction with the unpaired electron located on an orbital with mainly d_{xy} character results in negative values of $A_{||}$ and $A_\perp$ components. This has been taken into account when calculating $\beta_2{}^2$ from Eq. (2).

The calculated values of β_2, presented in Table 1, may serve as indication of the degree of electron delocalization within the in-plane π-bonding system of a V-O$_n$ polyhedron, i.e. on increasing β_2 the unpaired electron becomes more confined to the vanadium nucleus. It is interesting to correlate the electronic properties of V(IV) centres created upon interaction with methanol and represented by β_2, with the specific catalytic activity of V sites in methanol oxidation, expressed as turnover frequency (TOF), taken from reference [1]. Fig. 6a shows the relation between the two parameters, calculated for all resolved signals. Despite a significant scatter a trend may be seen correlating higher values of β_2 with lower TOFs. This trend is much more pronounced when mean weighted values of β_2 have been determined for the samples with two types of vanadyl species contributing to the hyperfine pattern, taking into account the statistical weight of each contribution (Fig. 6b). Even bearing in mind that the differences in β_2 are small, and the calculations only approximate, the trend indicating that the catalytic activity increases with the ionicity of the vanadyl in-plane π-bonding system seems to be significant.

According to the findings of Wachs *et al.* [1–3], essentially the same type of vanadium oxide structural units (characterized by the $\sim$ 1,030 cm^{-1} Raman band and the $\sim$-660 ppm peak in the solid state ^{51}V NMR spectra) exist on different dehydrated oxide supports. In view of this, the authors concluded that the significant differences in catalytic activity of the samples in methanol oxidation are associated with the nature of V—O-support bond, with oxide support acting as a ligand that influences the reactivity, rather than with the structural factor. According to the Raman data reported for vanadium oxide overlayers on alumina, titania and silica supports [21], interaction of alcohol vapour at moderate temperature with Al$_2$O$_3$ and TiO$_2$-supported samples does not affect the bonding between the vanadyls and the support, and consists in an increase of the coordination number around the vanadium centers, while in the case of SiO$_2$ partial alcoholisis reduces the extent of bonding between the vanadyl groups and silica surface. Thus,
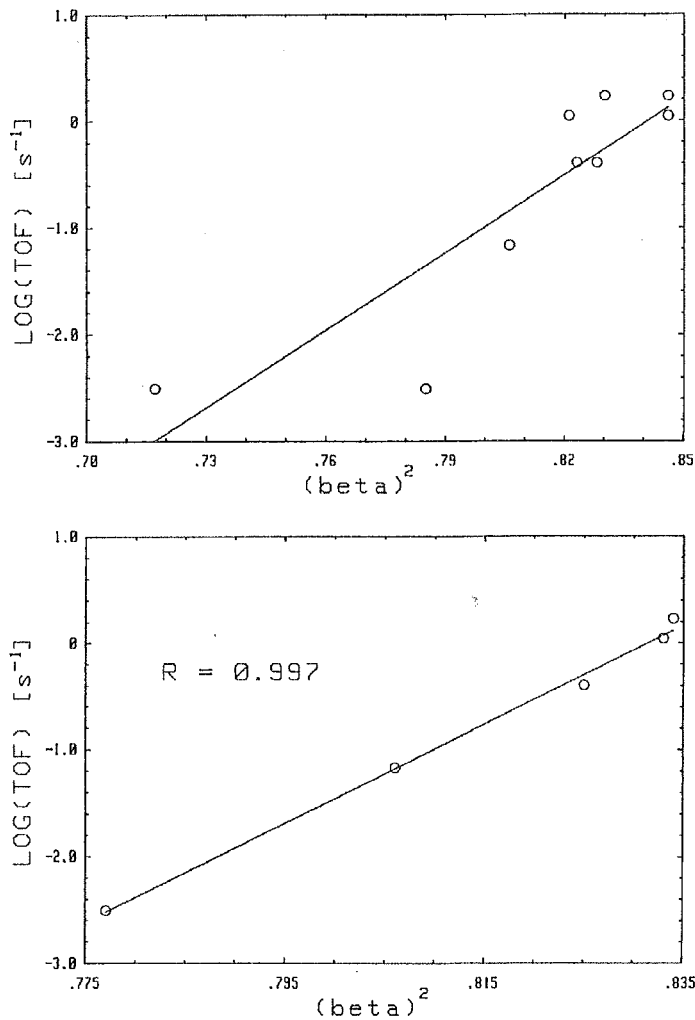
Fig. 6. Relationship between the methanol TOF and β_2 coefficient values for supported
monolayer vanadium oxide catalysts: a) all β_2 values, b) mean weighted β_2 values

one may visualise the reduced vanadium species generated by exposure to
methanol vapour as sharing at least part of the four in-plane oxygens with
the support. This allows one to rationalize the observed dependence of TOF
vs β_2 in terms of changes in the electronic structure of V centres induced
by the supporting oxides.

It is of course tempting to try to correlate the catalytic data with more
fundamental electronic properties of the supports such as their bulk elec-
tronegativity. We have adopted the approach proposed by Butler and Ginley
[22], based on bond length arguments, in which bulk electronegativity of a

compound is the geometric mean of the electronegativities of the constituent atoms

$$(3) \qquad\qquad \chi(M_xO_y) = [\chi^x(M)\chi^y(O)]^{1/x+y}$$

where the values of χ of the elements are determined following Mulliken's definition of electronegativity. In the latter the electronegativity of a neutral atom is the arithmetic mean of the atomic electron affinity and the first ionization energy and has an advantage of being based only on measurable physical parameters. Table 2 gathers all data required for calculation

TABLE 2

Ionization potentials IP [23], electron affinities EA [24] and Mulliken's electronegativities χ of elements constituting M_xO_y. $\chi(M_xO_y)$ – calculated bulk electronegativities of oxide supports

Element	IP [eV]	EA [eV]	χ	$\chi(M_xO_y)$
Si	8.15	0.29	4.22	6.22
Al	5.97	0.12	3.05	5.25
Nb	6.88	1.03	3.96	6.27
Ti	6.84	0.22	3.53	5.86
Zr	6.95	0.53	3.74	5.97
O	13.62	1.46	7.54	

of bulk electronegativity of all oxide supports while Fig. 7 shows the variation of TOF with the calculated values of $\chi(M_xO_y)$. It is evident that no
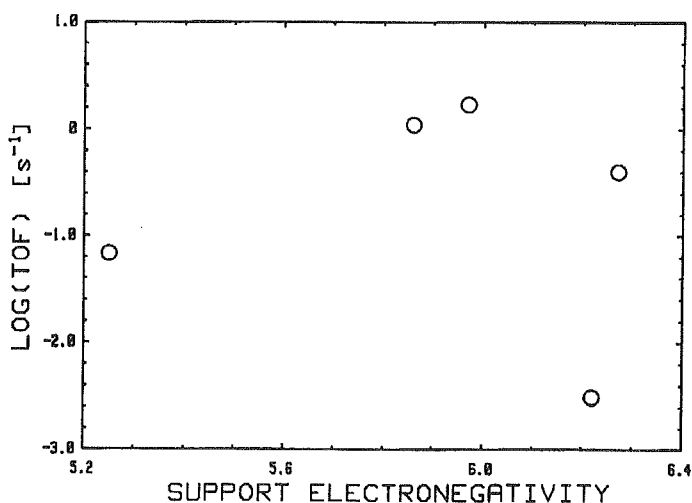

Fig. 7. Variation of the methanol TOF with bulk electronegativities of oxide supports

relationship exists beween the specific activity in methanol oxidation and the oxide support electronegativity. Scattered results indicate that beside the differences in the chemical nature of the supporting oxides other, finer factors, play an important role in determining the nature of V—O-support bond (e.g. local geometric demands imposed by the oxide surface).

Conclusions

Electronic structure of reduced vanadyl species generated during methanol chemisorption depends on the nature of the supporting matrix. This is shown by the changes of the β_2 bonding coefficient calculated from the experimentally determined ESR parameters and indicating the degree of in-plane π-covalency. It is demonstrated that the catalytic activity in methanol oxidation, expressed in terms of TOF, can be correlated with the latter parameter and increases with the ionicity of the in-plane π-bonding system.

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