Photoluminescence of supported vanadia catalysts: linear correlation between the vanadyl emission wavelength and the isoelectric point of the oxide support

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Photoluminescence spectra of vanadium oxide supported on SiO_2, TiO_2, Al_2O_3, K-doped Al_2O_3, ZnO and MgO were recorded. All the vanadium-containing solids exhibit room-temperature luminescence in the 550–700 nm region upon excitation from 250 to 400 nm. Significant spectral shifts of the emission maximum wavelength ($_{\mathrm{phos}}$) depending on the acid/basic nature of the support have been observed. In this way, the higher the isoelectric point (or zero point charge, pzc) of the oxide support, the higher is the $_{\mathrm{phos}}$ of the supported vanadia catalysts. The linear relationship between these two properties clearly proves that the characteristics of the oxide support has a direct influence on the phosphorescence, and hence on the electronic states, of the vanadyl group. Kinetic analysis of the luminescence decay of supported catalysts has also been determined.

Keywords: photoluminescence, supported vanadium oxide catalysts, selective oxidation and oxidative dehydrogenation of alkanes and olefins

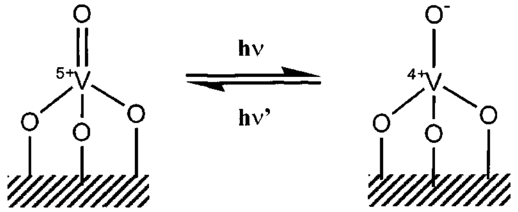
1. Introduction

Vanadium oxides anchored on oxide supports are among the most important heterogeneous catalysts for both the selective vapor-phase oxidation of alkylaromatic hydrocarbons, aliphatic alcohols, alkenes and alkanes and the selective reduction of NO_x [1–4]. Several physico-chemical techniques have been used to characterise these catalysts, however, many of these show both bulk and surface of catalyst.

Photoluminescence is one of the most sensitive and selective spectroscopic techniques to detect and report on the chemical environment of the emitting groups. In recent years, there has been a renewed interest in the application of luminescence to study the active sites in solid catalysts [5]. This interest stems from the fact that in many cases the active sites in heterogeneous catalysis only account for a minute amount of the bulk material that can be below the detection threshold of other common spectroscopic tools, particularly solid-state NMR, IR and Raman spectroscopies. The vanadyl group is a well-known photoluminescent group, in which the emission derives from the triplet V^{4+}–O excited state generated from $V^{5+}=O$ through a light-induced internal charge transfer in the vanadyl group from oxygen as donor to V^{5+} as acceptor (scheme 1) [5]. Photoluminescence emission spectra of a series of supported vanadia catalyst [5–9] and V-containing zeolites [10,11] have been reported in the last years. However, a correlation between photoluminescence spectra and a physico-chemical parameter of the support has not yet been reported.

It is well known in this type of catalysts that the nature of the metal oxide support plays an important role modulating both the nature of V species and the catalytic behaviour for oxidation reactions. This fact could be rationalised by considering the variations in the electron density of the vanadyl V=O double bond caused by the inductive effect through the three single O–V bonds anchoring the *tripodal* vanadyl group to the inorganic support. The assessment of the influence of the support on the vanadyl double bond is crucial in order to have a tool to predict the catalytic performance of particular vanadium-containing material as catalyst. In this way, it is known that oxydehydrogenation is selectively carried out on tetrahedral V^{5+} species while the O-insertion reactions occur on V^{5+} with a higher coordination [1,2].

In this paper we present a photoluminescence study of supported vanadium oxide catalysts. Different V contents have been incorporated on the metal oxide supports in order to obtain isolated tetrahedral V^{5+} species. We have found that there is a consistent shift in the emission max-



Scheme 1. The triplet V^{4+}–O excited state generated from $V^{5+}=O$ ground state through a light-induced internal charge transfer in the vanadyl group.

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Table 1
Physico-chemical characteristics including the wavelength of the emission ($_{\text{phos}}$) and excitation ($_{\text{ex}}$) spectra of metal-oxide-supported vanadia samples.

Catalyst	Pzc of suppport[a]	S_{BET}	V content[b] (wt%)	Nature of V species[c]	$_{\text{ex}}$ (nm)	$_{\text{phos}}$ (nm)
$0.8V/SiO_2$	1:5	181	0:8	O_3 V=O	375	515
$4V/SiO_2$	1:5	181	3:7	O_3 V=O, V_2O_5	375	515
$3V/TiO_2$	6:0	48	3:1	$O_2=V(=O)_2$, VO_4	350	540
$2V/Al_2O_3$	7:0	172	2:2	VO_4, $(VO_3)_n$	295	545
$2V/(Al_2O_3$ + K)	8:0[d]	170	2:2	VO_4, $(VO_3)_n$	295	545
2V/ZnO	8:4	45	1:9	VO_4, $Zn_3V_2O_8$	280	575
28V/(HTH)[e]	10:7[d]	166	27:6	$Mg_3V_2O_8$, $Mg_2V_2O_7$	270	585
9V/MgO	12:0	142	8:9	VO_4	278	613
20V/MgO	12:0	136	20:0	VO_4, $Mg_3V_2O_8$	278	613

[a] Pzc, point of zero charge in pH units, were obtained from [1].

[b] V content in wt% of V_2O_5.

[c] Determined by ^{51}V-NMR spectroscopy.

[d] Pzc, point of zero charge in pH units, were calculated from the chemical composition as suggested in [15].

[e] HTH, heat-treated Mg–Al–O hydrotalcite.

imum wavelength (λ_{phos}) that correlates linearly with the acid–base character (isoelectric point) of the oxide support. This constitutes an additional spectroscopic experimental evidence of the influence of the support on the vanadyl group, giving a base to rationalise a simple surface property of the support with the catalytic performance of these materials in catalysis.

2. Experimental

Supported vanadium oxide catalysts were prepared by impregnation of the metal oxide support with an aqueous vanadyl oxalate solution, according to the preparation procedure reported previously [12–16]. Then, the solids were filtered and dried at 80 C for 16 h. In all cases, the samples were calcined at 600 C for 4 h. The chemical composition and characteristics of the catalysts are presented in table 1.

Al_2O_3 (Gidler T126), SiO_2 (Aerosil-2000), TiO_2 (Degussa), and prepared K-doped Al_2O_3, MgO, ZnO and calcined Mg–Al hydrotalcite were used as metal oxide supports. K-doped Al_2O_3 was prepared by impregnation of Al_2O_3 with a potassium carbonate aqueous solution. Heat-treated Mg–Al hydrotalcite (Mg/Al ratio of 3) has also been used as a support and it has been named as HTH. The preparation procedure and characteristics of this material were described previously [15].

Photoluminescence spectra were recorded in an Edinburg FS-900 CDT spectrophotometer. The solids were placed on a septum-capp quartz cavette and N_2 purged for at least 15 min before measurements. Emission lifetimes were determined in the same way as before using the Edinburg FL-900 NS instrument and pulsed hydrogen lamp [17].

3. Results and discussion

The list of vanadium-containing solids that have been subject to the present study as well as their main analytical and physicochemical parameters are contained in table 1. The selection of these metal oxide supports has been made with the objective to cover the widest range of surface acidity and basicity. Characterisation of these V-containing solids as catalysts has previously been reported [12–16].

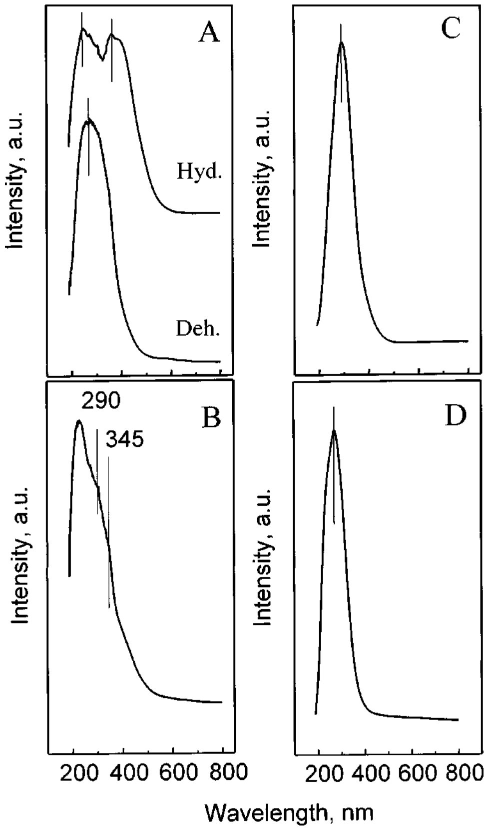


Figure 1. Diffuse reflectance UV-vis spectra of selected supported vanadia catalysts: (A) hydrated and dehydrated $0.8V/SiO_2$, (B) $3V/TiO_2$, (C) $2V/Al_2O_3$ and (D) 20V/MgO.

DR spectra of supported vanadia catalysts are shown in figure 1. Some differences were observed between hy-

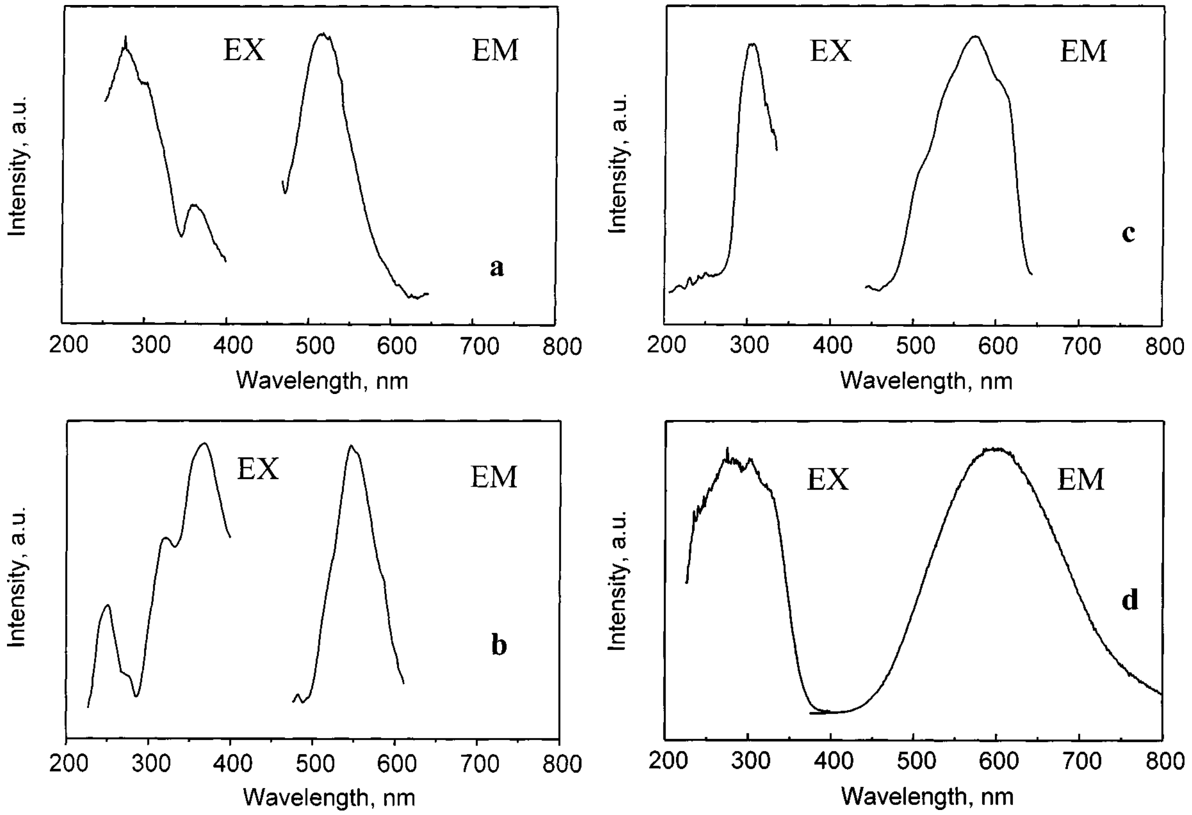


Figure 2. Emission (EM) and excitation (EX) spectra recorded at room temperature of vanadyl group anchored on metal oxide: (a) hydrated $0.8V/SiO_2$, (b) $3V/TiO_2$, (c) $2V/Al_2O_3$ and (d) 20V/MgO.

drated and dehydrated V/SiO_2 samples as a consequence of the presence of water (figure 1(A)). The appearance of a broad band at 270 nm in addition to a band at 345 nm in the dehydrated samples indicates the presence of both isolated and polymeric V^{5+} species, respectively. In addition to these, V_2O_5 crystallites were also observed at high V loading ($4V/SiO_2$).

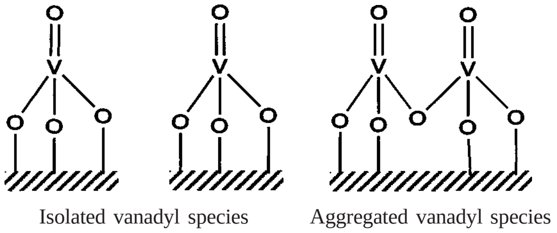
A higher dispersion of vanadium has been observed on TiO_2 (figure 1(B)) and Al_2O_3 (figure 1(C)). However, and in addition to isolated VO_4 tetrahedron (band at 290 nm), isolated O=V=O (band at 345 nm) (figure 1(B)) and polymeric tetrahedral $-(VO_3)_n-$ (band at 310 nm) (figure 1(C)), were also observed.

In the case of V/MgO (figure 1(D)) and V/ZnO (spectrum not shown) samples, isolated tetrahedral V^{5+} species (band at 270 nm) were mainly observed by DR spectroscopy. In both cases, amorphous and crystalline ($Mg_3V_2O_8$ and $Zn_3V_2O_8$, respectively) materials have also been observed by ^{51}V NMR and Raman spectroscopies, although the crystallinities of these phases increase with the V loading. On the other hand, both $Mg_3V_2O_8$ and α-$Mg_2V_2O_7$ crystalline phases have been observed in the V/HTH sample by XRD and Raman spectroscopy while the DR spectrum presents a high-intensity charge transfer band in the 250–350 nm region [15].

These DR results are in agreement with earlier studies in which the lower the acid character of metal oxide support, the lower both the coordination and the agglomeration of V atoms is [1–4,12–16,18].

As expected, all the vanadium-containing solids exhibit room-temperature luminescence in the 550–700 nm region upon excitation from 250 to 400 nm. Blank controls of the supports before anchoring the vanadium showed that the inorganic oxide does not have detectable emission under our experimental conditions. It is known that vanadyl phosphorescence is characterised by a fine structure reflecting the V=O vibrational states. However, this fine structure is generally observed only at low temperatures and disappears when the luminescence is recorded at room temperature. In our case, the emission was in all cases structureless, except for vanadium anchored on VO_x/TiO_2, where some vibrational features are still observed. Some representative emission spectra are included in figure 2. The excitation spectra agree reasonably well with the ground-state diffuse reflectance UV-vis absorption spectra of the samples (figure 1) indicating that the chromophores observed in the absorption spectrum are also responsible for the emission.

It is worth noting that the amount of vanadium in V/SiO_2 or V/MgO modifies only the intensity of the emission band but not its position which only depends on the nature of the oxide support. In fact, at low surface coverages, an increase in the V content on the support produces initially a relative increase in the luminescence intensity, while a significant decrease of the emission intensity is observed as the V loading increases. This effect can be easily rationalised



Scheme 2. Formation of polyvanadate aggregates from isolated VO_4 vanadyl groups for increasing surface coverages.

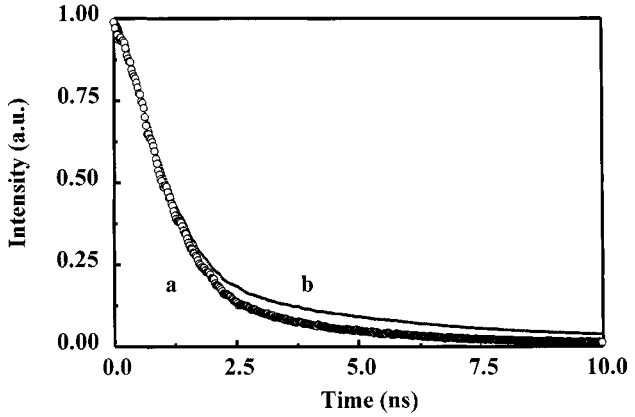


Figure 3. Emission decays monitored at room temperature after N_2 purging of vanadyl species in different surfaces: (a) 2V/ZnO and (b) 20V/MgO.

for V/SiO_2 materials as a reflection of an increasing formation of di-, tri- and polyvanadium aggregates anchored on the support surface at the expense of isolated single vanadyl groups which would be the most intensely emitting fluorophores (scheme 2). In the case of MgO-supported vanadia catalysts, $Mg_3V_2O_8$ crystals are observed at high V loading, modifying the number of single vanadyl groups.

On the other hand, the hydration degree of V/SiO_2 samples modifies only the intensity of the emission band but not its position. As concluded from the DR spectra (figure 1(A)) the number of isolated vanadyl groups depends on the hydration degree of these samples.

We attempted a kinetic analysis of the luminescence decay. Thus, the time emission profile was followed up to the longest limit of our setup (<100 μs). However, no significant decay of the emission intensity could be monitored on this time scale except for the vanadyl supported on magnesia and zinc oxide. These kinetic measurements agree well with the literature data on vanadyl emission lifetimes, which typically expand to several milliseconds. In contrast, the emission decay of vanadium anchored on MgO or ZnO was remarkably shorter compared to the rest of the samples, reflecting the particular characteristics of the vanadyl group on these basic supports (figure 3). The curve fittings of the phosphorescence time profile to single monoexponential decays were reasonably good, giving lifetimes of ca. 20 μs, that is about two orders of magnitude shorter than the normal values.

What is noteworthy in the luminescence spectra is the significant spectral shift of λ_{phos} depending on the acid/basic nature of the support. These shifts are a reflection of the influence of the support on the electron density of the vanadyl group. The actual λ_{phos} values are collected in table 1. In an attempt to correlate these variations with a characteristic property of the support surface, figure 4 shows the plot of the λ_{phos} vs. the isoelectric point or zero point of charge (pzc) of the oxide support. In this case, the pzc of the oxide support can be considered as a parameter related with the acid–base character of the surface oxide support [1,3,19]. The linear relationship between these two properties clearly proves that the acid–base character of the oxide support has a direct influence on the phosphorescence, and hence on the molecular orbitals, of the vanadyl group.

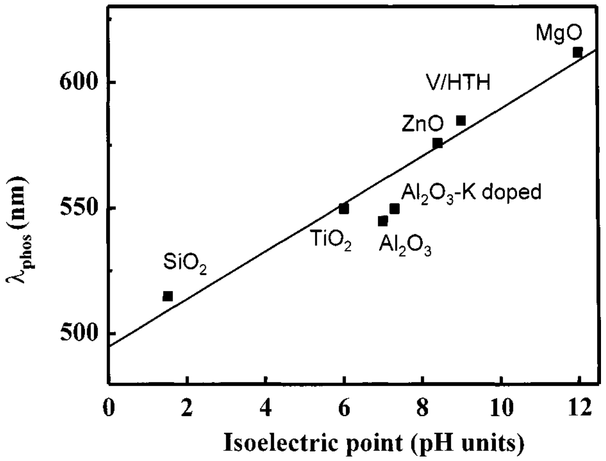


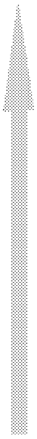
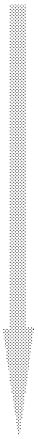
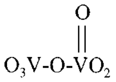
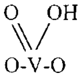
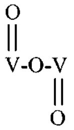
Figure 4. Variation of the the emission maximum wavelength ($_{phos}$) with the isoelectric point or pcz of the oxide support in supported vanadia catalysts.

The relevance of our finding in catalysis is clearly exemplified in table 2. This table indicates the variation of the catalytic behaviour of V-containing solids with the nature of V species. The selectivity to oxygenated products during the selective oxidation of hydrocarbons, which has previously been related to the presence of a V=O double bond in which V shows an octahedral coordination [1,20], decreases but the selectivity to the alkane oxydehydrogenation increases as λ_{phos} of the sample increases. What we propose is that a simple photoluminescence measurement can help to predict the catalytic properties of V^{5+}-containing solids.

It is clear that the V loading also influences the catalytic behaviour and, in the case of V/SiO_2 catalysts, we can have selective catalysts to oxydehydrogenation (low V loading) or O insertion (high V loading) reactions. However, the variation of the intensity of photoluminescence spectra as it is observed in both SiO_2- and MgO-supported vanadia catalysts can also show the dispersion of tetrahedral V^{5+} species, which is higher on V/MgO samples.

The nature of the support has also influence on the vibrational structure of the emission band. Even though the fine structure is better resolved at much lower temperatures, we have still been able to observe room temperature vibrational

Table 2
Nature of active V^{5+} species in selective oxidation reactions.

Catalyst[a]	V species	Selective oxidation reaction[b]	H-abstraction selectivity[c]	Oxygen insertion power[d]
$Mg_3V_2O_8$		C_3H_8 to C_3H_6		
V/MgO	Isolated VO_4			
V/SiO_2-L		C_4H_{10} to C_4H_8		
V/Al_2O_3-L	Polymeric $-(VO_3)_n-$	C_3H_8 to C_3H_6		
$Mg_2V_2O_2$	 $O_3V{-}O{-}\overset{\overset{O}{\Vert}}{V}O_2$	C_3H_8 to C_3H_6 C_3H_6 to acrolein		
V/TiO_2		*o*-xylene to PA Butadiene to MA		
V_2O_5	 $\overset{\overset{O}{\Vert}}{V}{-}O{-}\underset{\underset{O}{\Vert}}{V}$	*o*-xylene to PA		
V/SiO_2-H				
V/Al_2O_3-H		Butadiene to MA		

[a] L and H correspond to low and high V loading, respectively.
[b] PA = phthalic anhydride, MA = maleic anhydride.
[c] H-abstraction selectivity, i.e., oxidative dehydrogenation of short chain alkanes.
[d] Partial oxidation (O-insertion) of hydrocarbons.

structure for V/SiO_2 with a transition energy corresponding to 1030 cm^{-1} in agreement with the IR and Raman vibration wavenumber of V=O. In other supports, particularly V/MgO samples, the room temperature fine structure is lost.

In conclusion, we have shown that there is an influence of the nature of the support surface on a specific property of the vanadyl group. Given the high sensitivity of the photoluminescence measurements, our study can open the way to apply photoluminescence to gain insight on the population and distribution of vanadyl groups anchored on metal oxide supports and/or vanadyl groups in different environment aimed to anticipate the catalytic activity of these solids. Mixed metal oxide supports have recently been proposed to improve the performance of supported vanadia catalysts. Measurements of photoluminescence of the vanadyl group on mixed oxide of different proportions can be used as a simple tool to predict the influence of the support composition in supported catalysts on their catalytic performance.

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