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RESEARCH NOTE

Coordination Symmetry and Reduction Features of V Ions in V_2O_5/SiO_2 Catalysts: Relevance to the Partial Oxidation of Light Alkanes

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The catalytic properties of supported V_2O_5 catalysts are strongly affected by the catalyst composition (i.e., oxide loading and nature of the support) since the metal oxide–support interaction controls both the reducibility and the dispersion of the active phase (1, 2). In particular, the higher activity and selectivity of supported V_2O_5 catalysts in the partial oxidation of hydrocarbons with respect to the bulk V_2O_5 system arises from the formation of easily reducible "surface oxide species" ensuring an easier occurrence of the redox cycle under reaction conditions (3). In this connection, in our previous studies dealing with the reactivity of V_2O_5/SiO_2 catalysts in the partial oxidation of methane (POM) we pointed out that the high performance of low- to medium-loaded (2–5 wt.%) catalysts arises from their capability to stabilise "surface-reduced sites" able to activate gas-phase oxygen (4, 5). By contrast, highly (>10 wt.%) loaded V_2O_5/SiO_2 systems, in spite of the high density of reduced sites, exhibit a poor catalytic performance in POM (5). We argued that the difference in reactivity of low-, medium-, and highly loaded V_2O_5/SiO_2 catalysts in POM lay in a different interaction mode with molecular oxygen linked with the formation of different "surface structures" (5, 6).

This article is aimed to address the reduction features of the "surface structures" in differently loaded V_2O_5/SiO_2 catalysts in regard to their relevance to the partial oxidation of light alkanes.

Two silica-supported V_2O_5 (5.3 wt.% V_2O_5/SiO_2, VPS 5, and 20.8 wt.% V_2O_5/SiO_2, VPS 20) catalysts were prepared by incipient wetness impregnation of a "precipitated" silica (Si 4-5P Grade, Akzo product; BET S.A., 400 $m^2\ g^{-1}$) with a basic aqueous solution (pH $\approx$ 11) of ammonium metavanadate. After impregnation the catalyst samples were dried at 110°C for 24 h and then calcined in air at 600°C for 16 h.

H_2-temperature programmed reduction (H_2-TPR) measurements of the V_2O_5/SiO_2 catalysts in the range 200–1100°C were performed in a conventional flow apparatus using a linear quartz gradientless microreactor (i.d., 4 mm; *l*, 200 mm), a 6% H_2/Ar mixture flowing at 60 $cm^3_{stp}\ min^{-1}$, and a heating rate of 20°C min^{-1}. The sample weight was set between 0.03 and 0.1 g and the TCD response was quantitatively calibrated by monitoring the reduction of known amounts of CuO, NiO, and SnO_2 oxides. Under such experimental conditions, TPR is reliable and accurate both in peak position (±5°C) and in hydrogen consumption (±5%).

CO-temperature programmed reduction (CO-TPR) measurements in the range 200–1100°C were performed in the above apparatus using a 10.1% CO/He mixture flowing at 30 $cm^3_{stp}\ min^{-1}$ and a heating rate of 20°C min^{-1}. CO_2 formation was followed by a Thermolab (Fisons Instruments) quadrupole mass spectrometer connected on line to the microreactor by a heated ($\approx$180°C) inlet capillary system (transit time <0.5 s) and operating with an ionisation potential of −70 V and a voltage of the SEM amplifier of 2 kV.

Photoluminescence spectra of the V_2O_5/SiO_2 samples, calcined in O_2 at 600°C, were obtained by a Spex-Fluorolog FL 212 spectrometer with a double monochromator.

The H_2-TPR and CO-TPR patterns of the VPS 5 and VPS 20 catalysts in the range 200–1000°C are shown in Figs. 1A and 1B, respectively. The H_2-TPR profile of the low-loaded VPS 5 catalyst (Fig. 1A, solid line) starts at 400°C ($T_{o,red}$) and displays a sharp reduction peak with a maximum (T_{M_1}) at 561°C, asymmetric on the high-temperature side due to a shoulder of H_2 consumption zeroing at about 800°C, along with a small broad peak centred at 955°C (T_{M_4}) (6). The reduction pattern under CO (Fig. 1A, dotted line) is essentially analogous to that obtained under H_2 although it is significantly displaced to higher *T* ($T_{o,red} = 410$°C; $T_{M_1} = 610$°C). Marked differences in the H_2-TPR pattern of the highly loaded VPS 20 catalyst (Fig. 1B, solid line) are observed when compared

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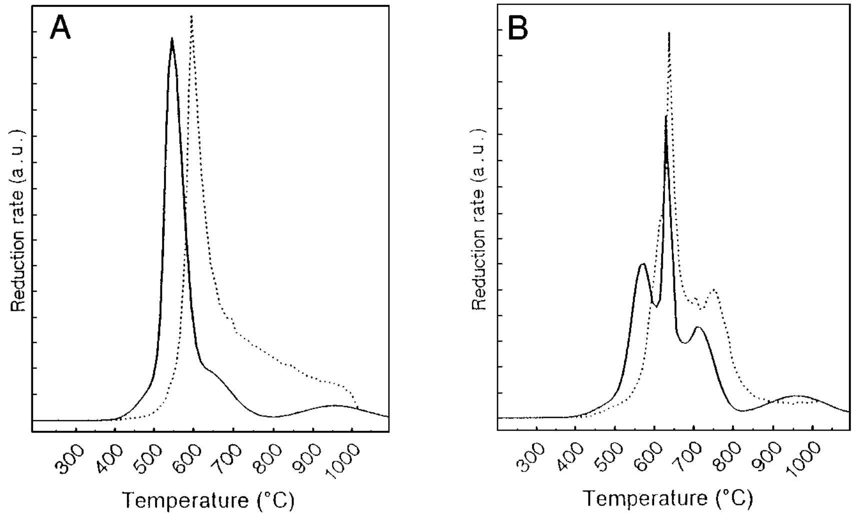


FIG. 1. H_2-TPR (solid lines) and CO-TPR (dotted lines) profiles of (A) VPS 5 and (B) VPS 20 catalysts.

with VPS 5. The T_{M_1} peak decreases considerably in intensity, assuming an asymmetric shape ($T_{M_1} = 584°C$), while two new peaks T_{M_2} (645°C) and T_{M_3} (722°C) appear, the former being the predominant one. Moreover, in comparison with VPS 5 the T_{M_4} feature (968°C) has slightly risen in intensity. The CO-TPR pattern of the VPS 20 sample again bears the main features of the H_2-TPR pattern. There are two main peaks, centred at 655 and 760°C, respectively, slightly shifted to higher temperature in comparison with their H_2-TPR counterparts. In addition, there is a shoulder of CO_2 formation on the low-temperature side of the T_{M_2} peak which appears to be associated with the T_{M_1} reduction peak of the corresponding H_2-TPR pattern. The extent of the integral H_2 (6) and CO consumption for both VPS 5 and VPS 20 samples accounts for the stoichiometric reduction of V^{5+} to V^{3+}.

The photoluminescence spectra at liquid N_2 temperature of VPS 5 (solid line) and VPS 20 (dashed line) catalysts excited by 250-nm light are compared in Fig. 2. The VPS 5 system yields an intense photoluminescence signal between 400 and 650 nm, featuring a well-resolved vibrational structure. The emission spectrum decreases very much in intensity for the VPS 20 system and the vibrational components can hardly be observed in this case.

Several attempts have been made in order to highlight the surface structures (1, 7–9) and the reduction features (8–11) of the V_2O_5/SiO_2 system. It is generally accepted that at low loading vanadia forms highly dispersed "isolated vanadate species" while with increasing the loading level "polymeric two-dimensional species" and "three-dimensional V_2O_5 crystallites" are stabilised on the silica surface. However, the coordination of the V ion in the above surface species is still an undecided issue. In an earlier study dealing with the influence of the V_2O_5 loading on the surface structures of V_2O_5/SiO_2 catalysts we argued that the H_2-TPR features of such systems can be reliably associated with the reduction of various surface V_2O_5 species (6). Indeed, we found that the T_{M_1} peak, predominant in the spectrum of the low-loaded VPS 5 catalyst (Fig. 1A), monitors the reduction of the "isolated vanadyl" species bearing

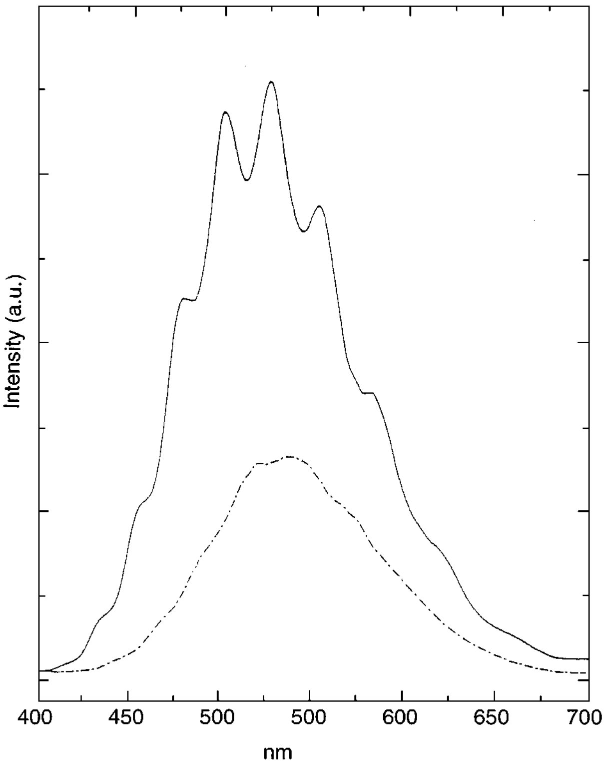
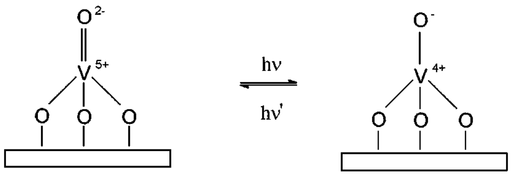


FIG. 2. Photoluminescence spectra of VPS 5 (solid line) and VPS 20 (dashed line) catalysts.



SCHEME 1

tetrahedrally coordinated (pseudo-T_d) V^{5+} centres (6), whereas the shoulder on the high-temperature side of this T_{M_1} peak arises from the reduction of agglomerated octahedrally coordinated (pseudo-O_h) V^{5+} centres (6). At higher V_2O_5 loading, the predominant intensity of the sharp T_{M_2} peak, along with the presence of defined T_{M_3} and T_{M_4} peaks (Fig. 1B), undoubtedly signals the nucleation of monomeric VO_4^{3-} units into polymeric structures, like polyvanadates, with V^{5+} in square–pyramidal (pseudo-S_p) coordination along with the extensive development of crystalline bulk V_2O_5 species, characterized by a more regular octahedral (O_h) coordination symmetry, reducing according to the $V_2O_5 \rightarrow V_6O_{13} \rightarrow V_2O_4 \rightarrow V_2O_3$ sequential path (6).

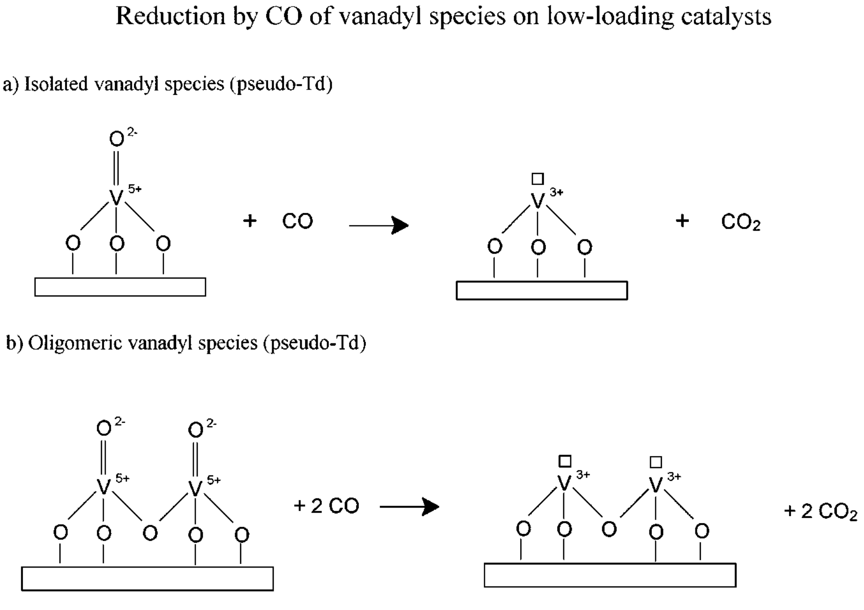
The photoluminescence spectra of the VPS 5 and VPS 20 catalysts match well with the above hypothesis about the surface structures of low- and highly loaded V_2O_5/SiO_2 catalysts. Indeed, the feature of the VPS 5 catalyst (solid line) is an intense and structured signal between 400 and 650 nm which relates to the radiative decay from the charge transfer (CT) excited triplet state of a vanadyl group (12) (Scheme 1).

The energy separations between the vibrational peaks are in agreement with the vibrational energy of a surface V=O bond of a vanadyl group in monomeric or small clustered T_d structures (12). On the other hand, the overall reduced intensity and the virtual absence of vibrational fine structure in the spectrum of the highly loaded VPS 20 catalyst indicates a higher nuclearity of V ions. The extensive formation of agglomerated V_2O_5 structures gives rise to a continuous range of radiative decay states and hence no observable vibrational structure.

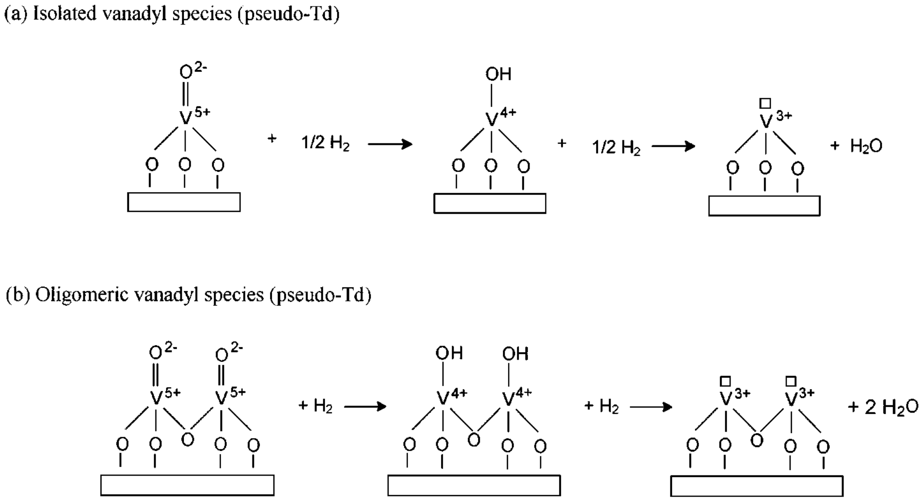
The above findings shed light on the reduction mechanism of vanadium-containing species in low-loaded and in highly loaded catalysts, respectively. The reduction by carbon monoxide, proceeding quite similarly for both low- and highly loaded catalysts, can be attributed exclusively to oxygen abstraction from the coordination sphere of vanadium ions, since the possible intermediate of a surface carbonate must be highly unstable in the studied system (Scheme 2).

The reduction by hydrogen shows a quite different pattern for the two catalysts: the main consumption of hydrogen occurs at much lower temperature on the VPS 5 system containing mainly vanadium in T_d coordination. The reduction of such surface vanadia species could proceed by a different way in H_2 and CO atmospheres. Due to the stability of the –OH groups on the catalyst surface, the H_2 reduction could readily proceed via an electron transfer on "isolated" vanadium ion without any change in the coordination symmetry. This seems to be likely since the corresponding decrease in ligand field stabilization energy for T_d-coordinated V ions, owing to the change in the central ion charge, should be not too high (Scheme 3).

Moreover, on the basis of spectroscopic findings the role and the structure of such V–OH groups have already



SCHEME 2


Reduction by H_2 of vanadyl species on low-loading catalysts

(a) Isolated vanadyl species (pseudo-Td)

(b) Oligomeric vanadyl species (pseudo-Td)

SCHEME 3

been elucidated (7, 8, 10). In particular, Bond and Tahir (8), in reviewing the physicochemical characteristics of monolayer-supported V_2O_5 catalysts, report that such OH groups account well for the marked acidic properties of isolated vanadyl species. Schraml-Marth *et al.* (7) identified by FTIR measurements the presence of V–OH groups, proposing three processes for the generation of V–OH groups on the surface of V_2O_5/SiO_2 surface involving the hydrolysis of V–O–Si bonds, the hydration of vanadyl groups, and the depolymerization of the agglomerated surface vanadia species. However, it is evident that the presence of V–OH groups is to be related to the hydration state of the V_2O_5/SiO_2 system (7, 8).

The reduction of O_h-coordinated vanadium species cannot occur via the above electron transfer mode since the preservation of the octahedral coordination symmetry, in spite of the change in the central ion charge, should imply a much higher energy loss. In this respect, the one-step reduction pattern of T_d-isolated vanadyl species in contrast with the stepwise reduction of O_h V_2O_5 clusters (13) further proves the difficult reduction of the latter species because of the high stability of the coordination symmetry of V ions. Hence, the interaction of this system with hydrogen probably implies the reduction of V^{5+} ions with simultaneous abstraction of oxygen ions from V_2O_5 crystallites. This is likely to be the reason for the similar reduction pattern of the highly loaded system in CO and H_2 atmospheres.

The important consequence of this reduction path is the existence of reduced vanadium ions in T_d symmetry which can activate molecular oxygen by electron transfer ($O_{2(g)} \rightarrow 2O^*_{(ads)}$) (4). Such reduced oxygen species ($O^*_{(ads)}$), due to the absence of an oxygen vacancy in the coordination sphere of isolated surface V centres, cannot be immediately incorporated into the "lattice" according to the following sequential path:

$$\tfrac{1}{2}O_{2(g)} \rightleftarrows O^*_{(ads)} \rightarrow O^{2-}_{(lattice)}. \qquad [1]$$

On the contrary, their lifetime is long enough for them to participate in a catalytic reaction leading to the primary formation of partial oxidation products (4, 5). A completely different path occurs on the highly loaded catalysts. In fact, the reduction of O_h V centres with octahedral coordination proceeds with simultaneous oxygen abstraction giving rise to a lattice vacancy. As a consequence, the surface-activated gas phase oxygen is immediately incorporated into the "lattice" (high r_1 rate) and thus we cannot expect high surface concentrations of partially reduced oxygen species participating in selective oxidation of hydrocarbons (4, 5). The above hypothesis is in good agreement with our findings on the catalytic behaviour of differently loaded vanadia–silica samples in the POM reaction, accounting well for the relationship between reaction rate and density of reduced sites on low- (4) and highly (5) loaded catalysts. Namely, the direct relationship between reaction rate and density of reduced sites (ρ) of low- ($\leq$5 wt.%) loaded V_2O_5/SiO_2 catalyst in POM (4) points to the capability of T_d vanadia species in activating molecular oxygen (4, 5) according to the path [1]. On the other hand, the lack of any direct relationship for highly loaded systems (5) signals the inability of octahedrally coordinated vanadium ions in stabilising surface active oxygen species because of the fast incorporation of the latter into the lattice made possible by the existence of an oxygen lattice vacancy in the reduced state (V^{3+}) of such V_2O_5/SiO_2 systems.

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