

Oxidative dehydrogenation of propane over differently structured vanadia-based catalysts in the presence of O₂ and N₂O

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Abstract

The effect of the nature and distribution of VO_x species over amorphous and well-ordered (MCM-41) SiO₂ as well as over γ-Al₂O₃ on their performance in the oxidative dehydrogenation of propane with O₂ and N₂O was studied using in situ UV–vis, ex situ XRD and H₂-TPR analysis in combination with steady-state catalytic tests. As compared to the alumina support, differently structured SiO₂ supports stabilise highly dispersed surface VO_x species at higher vanadium loading. These species are more selective over the latter materials than over V/γ-Al₂O₃ catalysts. This finding was explained by the difference in acidic properties of silica- and alumina-based supports. C₃H₆ selectivity over V/γ-Al₂O₃ materials is improved by covering the support fully with well-dispersed VO_x species. Additionally, C₃H₆ selectivity over all materials studied can be tuned by using an alternative oxidising agent (N₂O). The improving effect of N₂O on C₃H₆ selectivity is related to the lower ability of N₂O for catalyst reoxidation resulting in an increase in the degree of catalyst reduction, i.e. spatial separation of active lattice oxygen in surface VO_x species. Such separation favours selective oxidation over CO_x formation.

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1. Introduction

Oxidative dehydrogenation (ODH) of lower alkanes to high-value added olefins is an attractive field of oxidative heterogeneous catalysis because such operation offers an economical alternative to the existing technologies of alkene production by thermal dehydrogenation, which is thermodynamically limited, and energy demanding. Additionally, the ODH operation does not suffer from catalyst deactivation by coking; therefore, stable catalytic performance is enabled. Numerous catalytic systems have been evaluated for the oxidative dehydrogenation of propane (ODP) to propene and the relevant results have been recently reviewed [1,2]. Vanadium- and molybdenum-based catalytic materials are claimed to be the most active and selective ones for the ODP reaction with O₂ [3–5]. Different properties of the solid material such as reducibility, acidity and basicity, co-ordination geometry and dispersion of VO_x species have been identified as

being important in affecting catalytic performance [6–11]. However, all these factors are still being debated.

The present work aims at understanding the role of support (MCM-41, amorphous SiO₂ and γ-Al₂O₃) on the structure and catalytic performance of VO_x species in the ODP reaction. For comparing activity of various catalytic materials, apparent turnover frequencies (TOFs) for propane conversion were obtained from steady-state reaction rates determined under differential conditions. Attention is particularly focussed on the effect of different oxidising agents (O₂ and N₂O) on activity and selectivity of VO_x species in the ODP reaction.

2. Experimental

V/SiO₂ materials were prepared by impregnating SiO₂ with a predetermined amount of vanadium acetyl acetate ([CH₃COCH=C(O–)CH₃]₂VO) in toluene. The resulting catalyst precursor was calcined at 823 K for 12 h in air. Details of preparation of V/γ-Al₂O₃ and V/MCM-41 samples have been reported previously [9,12]. The catalysts are denoted below by their amount of vanadium loading, e.g. V(2.9)/SiO₂ contains 2.9 wt.% of V in the sample. All materials were characterised by XRD, UV–vis and H₂-TPR for identifying

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structural properties as well as for deriving insights into the distribution and reducibility of surface as well as near surface VO_x species. H_2 -TPR measurements were performed by heating 20–100 mg of sample with 20 K/min up to 1073 K in a gas mixture of hydrogen (10 vol.% in argon for V/SiO₂ and V/MCM-41 as well as 5 vol.% in neon for V/Al₂O₃) with a total flow rate of 50 cm³_{STP} min⁻¹. Apparent vanadium surface density S_V was calculated according to Eq. (1):

$$S_V = \frac{N_V}{S_{\text{BET}}} \quad (1)$$

where N_V is the number of vanadium atoms per gram of catalyst (atoms/g) and S_{BET} is the catalyst specific surface area.

For characterizing the performance of the catalytic materials, continuous flow experiments were performed at atmospheric pressure and different temperatures (673–773 K) in an U-shaped fixed-bed reactor ($\varnothing_{\text{i.d.}} = 6$ mm) made of quartz. The following reaction feeds were used: $\text{C}_3\text{H}_8:\text{O}_2:\text{N}_2 = 30:15:55$ and $\text{C}_3\text{H}_8:\text{N}_2\text{O}:\text{Ne} = 30:30:40$ (for V/ γ -Al₂O₃ catalytic materials) as well as $\text{C}_3\text{H}_8:\text{O}_2:\text{N}_2 = 40:20:40$ and $\text{C}_3\text{H}_8:\text{N}_2\text{O}:\text{Ne} = 40:40:20$ (for V/MCM-41 and V/SiO₂). The initial rates of products formation and turnover frequencies (TOFs) were determined at degrees of propane conversion of less than 4% according to Eqs. (2) and (3), respectively. The rate units was defined as $n_{\text{C}_3\text{H}_8} \text{ s}^{-1} \text{ g}^{-1}$, where $n_{\text{C}_3\text{H}_8}$ is the number of moles of propane converted to a certain reaction product, g the mass of catalyst, and TOF is the number of propane molecules converted per V atom and second.

$$r_i = \frac{F_i C(i)}{22400 m_{\text{cat}} \nu_i \times 100} \quad (2)$$

$$\text{TOF} = \frac{r_{\text{C}_3\text{H}_6} + r_{\text{CO}} + r_{\text{CO}_2}}{n_V} \quad (3)$$

where F_i is the total volumetric flow (ml/s), m_{cat} the catalyst mass (g), $C(i)$ is the concentration of propene, CO and CO₂ at the reactor outlet (vol.%), ν_i is the respective stoichiometric coefficient and n_V is the number of vanadium moles per gram of catalyst (mol/g).

3. Results and discussion

3.1. Catalyst characterisation

The specific surface areas (S_{BET}), apparent vanadium surface densities, phase composition from XRD analysis, and T_{max} of hydrogen consumption in temperature-programmed reduction (TPR) tests are shown in Table 1. The S_{BET} values of V/MCM-41 and V/SiO₂ materials do not strongly depend on vanadium loading up to 5 wt.%. For V/ γ -Al₂O₃ materials, such possible vanadium loading is, however, lower (1 wt.%). The S_{BET} values of V(11.2)/MCM-41, V(4.6)/ γ -Al₂O₃ and V(9.5)/ γ -Al₂O₃ are significantly lower than those

Table 1
Surface and bulk properties of different vanadia-based materials

Catalysts	S_{BET} (m ² g ⁻¹)	Vanadium surface density (V/nm ²)	XRD	H ₂ -TPR, T_{max} (K)
V(0.6)/MCM-41	892	0.08	Amorphous	788
V(1.2)/MCM-41	807	0.17	Amorphous	798
V(2.7)/MCM-41	871	0.37	Amorphous	801
V(5.3)/MCM-41	790	0.79	Amorphous	805
V(11.2)/MCM-41	52	25.4	V ₂ O ₅	823, 873
V(0.4)/SiO ₂	263	0.17	Amorphous	785
V(0.9)/SiO ₂	257	0.41	Amorphous	801
V(1.5)/SiO ₂	245	0.71	Amorphous	801
V(2.9)/SiO ₂	227	1.38	Amorphous	806
V(0.5)/ γ -Al ₂ O ₃	124	0.48	Amorphous	868
V(1)/ γ -Al ₂ O ₃	121	0.97	Amorphous	868
V(4.6)/ γ -Al ₂ O ₃	48	11.3	V ₂ O ₅ , γ -Al ₂ O ₃	878, 936
V(9.5)/ γ -Al ₂ O ₃	8.7	129	V ₂ O ₅ , γ -Al ₂ O ₃	910, 936, 1001

of the other V/MCM-41 and V/ γ -Al₂O₃ catalytic materials indicating that the microstructure of MCM-41 and γ -Al₂O₃ is influenced by the comparatively high loading of vanadium. This is explained by the fact that the support surfaces are fully covered by larger vanadia crystallites and that pores of alumina and silica are plugged by vanadia. Intense peaks corresponding to V₂O₅ were identified in XRD-patterns of V(4.6)/ γ -Al₂O₃, V(9.5)/ γ -Al₂O₃ and V(11.2)/MCM-41 (Table 1), i.e. in samples with the lowest BET values. Accordingly, H₂-TPR profiles of these three samples have several maxima (Table 1). To derive further insights into the degree of vanadium site isolation and reducibility of VO_x species, catalytic materials were characterised by in situ UV–vis diffuse reflectance spectroscopy. UV–vis spectra of selected V/MCM-41, V/SiO₂ and V/ γ -Al₂O₃ materials are compared in Fig. 1. The UV–vis spectra are essentially the same for all V/MCM-41, V/SiO₂ and V/ γ -Al₂O₃ catalysts with vanadium loadings up to 5, 2.9 and 1 wt.%, respectively. For these samples, the ligand to metal charge transfer (LMCT) bands at 224, 275 and 310 nm are identified. These bands are characteristic of highly dispersed VO_x species [13]. Thus, the same surface VO_x species are present in all of these catalysts. New broad UV–vis bands between 400 and 600 nm appear in V(4.6)/ γ -Al₂O₃, V(9.5)/ γ -Al₂O₃ (not shown) and V(11.2)/MCM-41. These bands originate from the extensively polymerised VO_x sites present in crystalline V₂O₅ nanoparticles [14]. This is in agreement with the XRD and H₂-TPR results shown in Table 1. Independent of the support, both, polymerised and highly dispersed VO_x species are reduced in flows of H₂ (Table 1) or C₃H₈ (results are not shown). The reduced surface VO_x species are easily reoxidized to surface V⁵⁺ species. These results support the assumption that the ODP reaction over the catalysts used proceeds via a Mars–van-Krevelen sequence.

Thus, depending upon the vanadium loading, VO_x species of different degrees of polymerisation exist in the catalysts studied. As compared to the alumina support differently structured SiO₂ supports (amorphous silica and MCM-41) enable stabilisation of VO_x species of lower degrees of

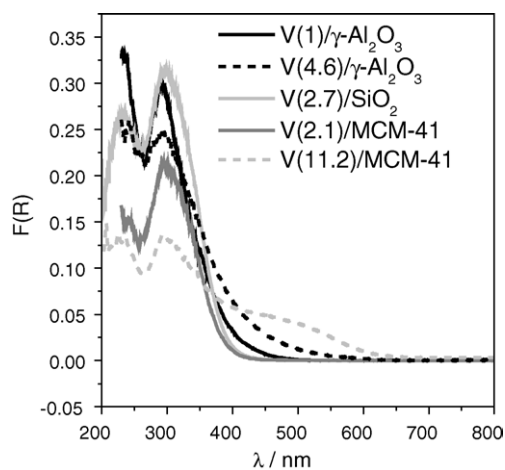


Fig. 1. UV-vis-DRS spectra of different materials during pre-treatment in an $O_2/N_2 = 20/80$ mixture at 773 K.

polymerisation at higher vanadium loading. This is due to higher specific surface areas of the latter supports as compared to $\gamma\text{-Al}_2\text{O}_3$.

3.2. Reactivity of various VO_x species in the ODP reaction with O_2 and N_2O

The effect of vanadium surface density on the rate of propane consumption per V atom, i.e. the apparent turnover frequency (TOF), is shown in Fig. 2. For both N_2O and O_2 , TOFs pass through a maximum at ca. 1 V/nm^2 for all the catalytic materials. For a given vanadium surface density, the TOF values obtained with N_2O as oxidant is lower than with O_2 . According to [9], the lower activity of N_2O is explained by the lower ability of N_2O for reoxidation of reduced VO_x sites.

A similar dependence of TOFs on vanadium surface density has been previously found for the oxidative dehydrogenation of ethane and propane over $V/\text{Al}_2\text{O}_3$ materials using O_2 as oxidant [15]. Since the TOF values for materials with vanadium surface densities up to 1 V/nm^2 do not significantly depend on the

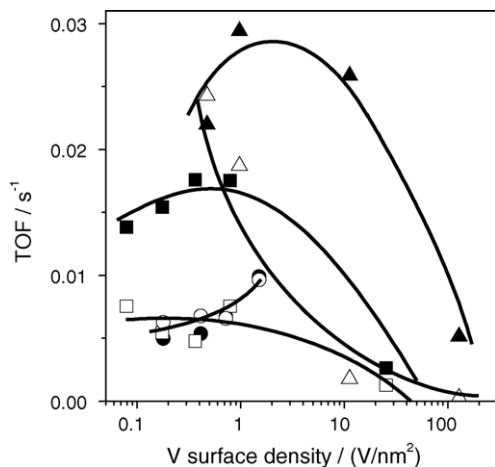


Fig. 2. TOF of propane consumption at 748 K vs. apparent V surface density: $V/\text{MCM-41}$ (■, □), V/SiO_2 (●, ○) and $V/\gamma\text{-Al}_2\text{O}_3$ (▲, △). Open symbols for N_2O -containing mixtures, solid symbols for O_2 -containing mixtures.

vanadium surface densities, these materials should possess VO_x species of similar structure and reactivity. From the results of catalyst characterisation in Section 3.1, highly dispersed surface VO_x species are concluded to be stabilised over these materials. The decrease of TOFs at vanadium surface densities above 1 V/nm^2 in Fig. 2 is explained by changing the structure of surface VO_x species. Not only highly dispersed surface VO_x species but also three-dimensional V_2O_5 clusters appear over materials with high vanadium surface densities (Table 1, Fig. 1). In such clusters, only a small part of surface VO_x species is accessible for the ODP reaction, while bulk VO_x species do not actively participate in the reaction. These species were found to be active for propane oxidation in a periodic mode of operation, i.e. alternating feeding of O_2 and C_3H_8 [16].

3.3. Selectivity determining factors in the ODP reaction

Fig. 3 demonstrates that C_3H_6 selectivity over $V(2.9)/\text{SiO}_2$ and $V(2.7)/\text{MCM-41}$ is very close. The selectivity is, however, influenced by oxidising agents (O_2 and N_2O) being higher with N_2O than with O_2 . As compared to these materials, C_3H_6 selectivity is significantly lower over $V(1)/\gamma\text{-Al}_2\text{O}_3$ using both O_2 and N_2O . Since apparent vanadium surface densities, structure and distribution of VO_x species over $V(2.9)/\text{SiO}_2$, $V(2.7)/\text{MCM-41}$ and $V(1)/\gamma\text{-Al}_2\text{O}_3$ are very similar (Section 3.1), the support itself is concluded to influence catalytic performance of the supported vanadia-based catalysts. The differences between the alumina- and silica-supported catalysts can be related to their acid–base properties. $\gamma\text{-Al}_2\text{O}_3$ is well known to be a stronger acidic support than silica. Based on the values of apparent surface density of vanadium (Table 1), it is concluded that the surface area of $V(1)/\gamma\text{-Al}_2\text{O}_3$ exposes a significant fraction of free alumina, on which adsorption of propene occurs. The adsorbed propene transforms further to CO_x as previously suggested [17,18]. Taking into account the

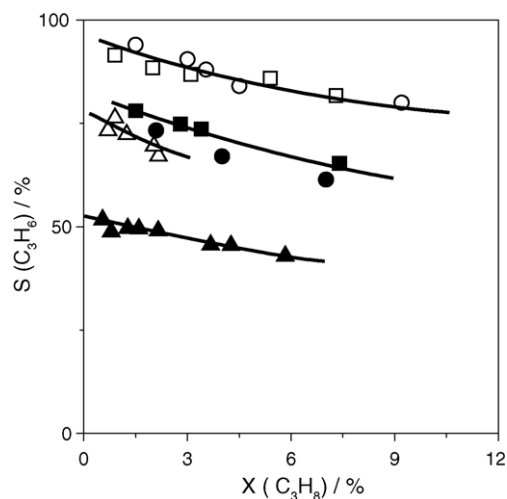


Fig. 3. Relationship between selectivity and propane conversion over $V(2.7)/\text{MCM-41}$ (■, □), $V(2.9)/\text{SiO}_2$ (●, ○) at 748 K and $V(1)/\gamma\text{-Al}_2\text{O}_3$ (▲, △) at 723 K. Open symbols for N_2O -containing mixtures, solid symbols for O_2 -containing mixtures.

present and earlier observations as well as the fact that CO_x products are mainly formed via consecutive propene combustion, C₃H₆ selectivity is suggested to be a function of the rates of propene desorption and its consecutive oxidation. The higher the ratio of the rates of propene desorption to oxidation of propene, the higher is propene selectivity.

Besides the influence of the support material on catalytic performance of V-based catalysts in the ODP reaction, their catalytic performance can be further tuned by applying N₂O instead of O₂ as shown in Fig. 3. This improving effect of N₂O on propene selectivity is assumed to be due to the fact that catalyst reoxidation by N₂O is less favourable than by O₂ [9]. This causes a decrease in the steady-state concentration of active surface lattice oxygen of VO_x species, i.e. the surface density of oxidising sites decreases. Such a decrease favours selective propane oxidation to propene over CO_x formation, since only one to two lattice oxygen are necessary in an active site for the former reaction. Active sites having more than two lattice oxygen species favour the formation of waste products, i.e. CO and CO₂. Such a hypothesis of active site isolation in selective oxidation of hydrocarbons was first formulated and published by Callahan and Grasselli [19].

The effect of the oxidising agent on the catalytic performance can be also related to the nature of oxygen species originating from O₂ and N₂O. Since molecular oxygen consists of two oxygen atoms, both polyatomic (O₂⁻, O₂²⁻) and monoatomic (O, O⁻ or O²⁻) species can be formed from O₂. All these species were identified over various oxide materials [20]. In contrast to molecular oxygen, decomposition of N₂O results in the formation of one atomic oxygen species only [21]. Although direct experimental evidence is not available at this stage, it has been suggested that atomic oxygen species (O, O⁻, O²⁻) are responsible for selective oxidation, while polyatomic oxygen species (O₂²⁻, O₃²⁻) take part in CO_x formation [22–24].

4. Conclusions

This study has shown that the nature of VO_x species, i.e. highly dispersed versus polymerised ones, depends on their apparent surface density and the supporting material. High-surface amorphous SiO₂ and MCM-41 enable stabilisation of highly dispersed surface VO_x species at vanadium loading up to 5 wt.% as compared to only up to 1 wt.% on γ-Al₂O₃. This is due to lower specific surface area of γ-Al₂O₃. The apparent TOFs (rates of propane consumption per vanadium atom) in the ODP reaction are a function of vanadium surface densities, supporting material and oxidising agent (O₂ or N₂O). TOFs with O₂ are higher than those with N₂O due to the lower ability

of N₂O for catalyst reoxidation. However, C₃H₆ selectivity is improved in the presence of N₂O. Additionally, C₃H₆ selectivity depends on the support material at similar vanadium surface densities. Strongly acidic supports like γ-Al₂O₃ ought to be fully covered by small VO_x aggregates in order to achieve a high selectivity in ODP. For weakly acidic supports like SiO₂, highly dispersed surface VO_x species perform similarly for vanadium surface densities up to 1 V/nm².

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