Importance of nanostructured vanadia for selective oxidation of propane to acrylic acid

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Highly dispersed nanostructured vanadia supported on mesoporous silica SBA-15, prepared by controlled grafting/ion-exchange, has been found to exhibit high selectivities in propane partial oxidation to acrylic acid demonstrating its unique potential for mixed metal oxide catalyst development.

There is great interest in partial oxidation of low alkanes for producing light oxygenated compounds due to their global abundance and the possibility to obtain the desired products through less expensive processes and with a lower environmental impact.[1,2] However, for the selective oxidation of alkanes there have been only a few successful commercial examples, like maleic anhydride formation starting from *n*-butane.[3] Partial oxidation of propane to acrylic acid, although very promising, is not widely studied in academia.[4] Most of the catalyst systems developed for selective oxidation of propane to acrylic acid so far include V as an essential element and belong to one of the following three catalyst systems: vanadium pyrophosphate (VPO) type catalysts, heteropoly acids and salts, and multi-component mixed oxide catalysts. Currently, the most effective catalysts are those of Mo- and V-based mixed metal oxides, such as Mo–V–Te–Nb oxides.[4] However, a major drawback of the mixed metal oxide catalysts appears to be the difficulty in controlling the preparation parameters and therefore the catalyst structure, *i.e.* the formation of the active phases or sites.[4] In general, very little has been reported concerning the origin of the high catalytic performance of these systems. The existence of a well-ordered surface resembling the structure of the bulk is dubious regarding the surface free energy and the harsh working conditions (400 °C, steam, *etc.*). On the other hand, it is well known that the active surface requires oxygen defects to expose metal sites to the reactants,[5] as may be found *e.g.* in an array of linked metal–oxo clusters supported by the bulk.[6] Therefore, it is challenging to develop catalyst systems which mimic the properties of the active catalyst surface, but at the same time isolate the intrinsic properties of the different catalyst components.

In the present study, for the first time, a catalyst with uniform active vanadium sites supported on SBA-15 was prepared by controlled grafting/anion exchange synthesis and proved to be highly selective in propane partial oxidation to acrylic acid. SBA-15 is a mesoporous silica material with uniform hexagonal channels, which can be tuned from 5 to 30 nm, and a very narrow pore size distribution.[7] Therefore, SBA-15 allows for rigorous control of the surface geometry at the mesoscale, which is an important ingredient for the design of catalysts.[8] SBA-15 possesses a large internal surface area (>800 m^2 g^{-1}), which allows for the dispersion of a large number of catalytically active sites. Its large pores permit access to bulky reagents. Furthermore, the thick framework walls (3.1–6.4 nm) provide high hydrothermal stability that exceeds those of the thinner-walled MCM-41 materials.[9] By anchoring vanadium oxide species onto the surface of the inner walls of SBA-15, a large density of accessible, isolated, and uniform active sites is obtained.[10] Therefore, mesoporous silica SBA-15 acts as an inert diluent, which should stabilize the nanostructured surface vanadium oxide in its highly dispersed state during reaction preventing it from sintering.

The mesoporous silica SBA-15 was synthesized according to the literature using Pluronic P123 triblock copolymer ($EO_{20}PO_{70}EO_{20}$, BASF). The preparation of SBA-15 supported vanadia catalysts (V_xO_y/SBA-15) is described elsewhere.[10] Briefly, functionalization of SBA-15 was achieved by stirring SBA-15 in toluene at 65 °C and adding 3-aminopropyltrimethoxysilane. The contents were filtered and washed with toluene. This white powder was stirred in 0.3 M HCl. The contents were filtered again, washed and dried in air overnight (functionalized SBA-15). For 3.3 wt% V/SBA-15, 73 mg of butylammonium decavanadate were added to a suspension of 1 g functionalized SBA-15 in water. The contents were stirred, filtered, washed and dried in air. The powder was calcined at 550 °C for 12 hours. The V content was determined by AAS. Reactivity experiments were carried out in a Nanoflow catalytic reactor with twelve fixed bed quartz tubular reactor. The feed flow rate of each reactor was fixed at a gas hourly space velocity (GHSV) of 1200 h^{-1} (at STP) with a standard catalytic bed volume of 0.5 ml. The feed composition was propane–oxygen–nitrogen–steam (1 : 2.2 : 17.9 : 14.1). The products were analyzed by two on-line gas chromatographs.

The TEM image shown in Fig. 1 corresponds to the final 3.3 wt% V/SBA-15 catalyst and confirms that the pore structure of the support material was conserved throughout the synthesis (see Table 1). XPS analysis revealed the presence of O, V, Si. No C was observed. Vanadium was present mainly as V^{5+} (75%), besides V^{3+}. Fig. 2 shows the UV-VIS diffuse reflectance and Raman (532 nm, 10 mW) spectra of dehydrated 3.3 wt% V/SBA-15 and SBA-15. Deconvolution gives rise to bands at 250 and 292 nm, respectively. The positions of their maxima agree well with those of the orthovanadate reference compounds Na_3VO_4 and $Mg_3V_2O_8$.[10] The corresponding Raman spectrum is dominated by a band at 1040 cm^{-1}, which has been assigned to isolated tetrahedral VO_4

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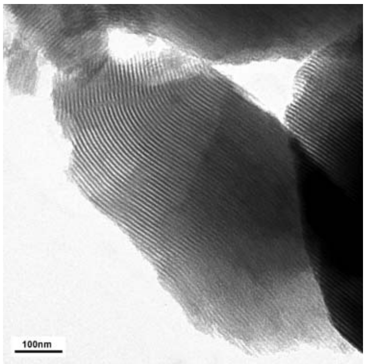

Fig. 1 TEM image of 3.3 wt% V/SBA-15.

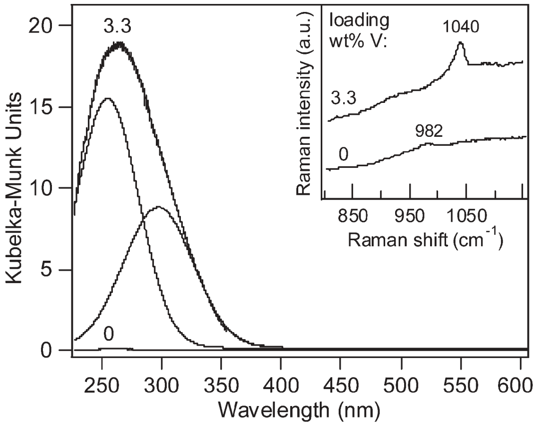

Fig. 2 UV-VIS diffuse reflectance spectra of bare SBA-15 and dehydrated 3.3 wt% V/SBA-15 together with the results from the deconvolution. The inset shows the corresponding Raman spectra.

Table 1 Catalytic performance of V_xO_y/SBA-15 for partial oxidation of propane

Catalyst	S_{BET}/ $m^2\ g^{-1}$	D_{BJH}/Å	V density/ V nm^{-2}	Time on stream/min	C_3H_8 conversion (%)	Selectivity (%)				Yield of acrylic acid (%)
						AA	C_3H_6	AceA	CO_x	
bare SBA-15	878	61	0	165	0	0	0	0	0	0
3.3 wt% V/SBA-15	491	50	0.8	165	8	84	10	2	4	6.8
				345	5	86	13	1	0	4.5

[a] D_{BJH} values were calculated from the adsorption branch of the nitrogen adsorption isotherm. [b] *Reaction conditions:* temperature: 400 °C; reaction pressure: 1 atm; AA: acrylic acid; AceA: acetic acid; CO_x: CO + CO_2.

with three V–$O_{support}$ bonds and one V=O bond.[11] The band at 982 cm^{-1} is characteristic of Si–OH stretching of surface hydroxyls.[12]

Table 1 shows the remarkable selectivities of V_xO_y/SBA-15. No reaction occurred without catalyst under the reaction conditions used here. Similarly, bare SBA-15, although of about twice the surface area of 3.3 wt% V/SBA-15, did not give rise to any propane conversion. Importantly, our reactivity results show that besides acrylic acid and propene only little acetic acid and CO_x is formed. After about 6 hours on stream, a small decrease in propane yield is observed probably due to steam-induced volatilization of vanadia.[13] Previously, silica SBA-15 supported vanadia has proved to be an efficient catalyst for oxidative dehydrogenation (ODH) of propane at temperatures within 500 °C–600 °C.[14] Our results show that the presence of steam significantly reduces the barrier for propane activation and shifts the product spectrum from propylene to acrylic acid. Recently, propane partial oxidation has been studied over 3.5 wt% V/γ-Al_2O_3 at 380 °C and a H_2O/propane ratio of 7.5.[15] Propylene formation but no oxygenated products were observed besides CO_x. These results are indicative of a strong influence of the support properties on the outcome of the reaction. At the V loading used, SBA-15 allows for a higher dispersion of vanadia compared to alumina (137 $m^2\ g^{-1}$). More importantly, in contrast to V_xO_y/γ-Al_2O_3,[15] V_xO_y/SBA-15 possesses only weak acid sites.[14] Previous studies have shown an increase in selectivity to partial oxidation products upon reduction of the total acidity.[16] Thus, it is likely that high selectivities for acrylic acid, *i.e.*, suppression of non-selective oxidation products, would be favored over weak acid sites.

In conclusion, we have demonstrated that highly dispersed vanadium oxide supported on silica SBA-15 exhibits high selectivities in propane partial oxidation to acrylic acid. While highlighting the potential of nanostructured vanadia for mixed metal oxide catalyst development, our results have also important implications for the understanding of selective activation of small alkanes by other complex metal oxide catalysts such as VPO.

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