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Highly efficient VO_x/SBA-15 mesoporous catalysts for oxidative dehydrogenation of propane

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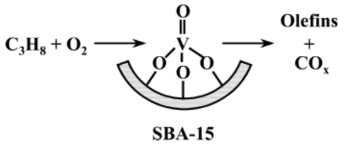
Highly dispersed vanadia species on SBA-15 mesoporous silica have been found to exhibit a highly efficient catalytic performance for the oxidative dehydrogenation (ODH) of propane to light olefins (propene + ethylene).

Light alkenes comprise the most important building blocks in the modern petrochemical industry.[1,2] Oxidative dehydrogenation of light alkanes provides a thermodynamically accessible route to the synthesis of alkenes from alkanes. Vanadia, molybdena and magnesia based catalyst systems have been found to be active and selective for this reaction, but unselective combustion pathways limit alkene selectivities, especially at high conversions.[3,4] Especially in the field of the oxidative dehydrogenation (ODH) of propane to propene, it has been a general consensus that the limited propene selectivity at higher propane conversions is linked with propene adsorption on acid sites and their subsequent oxidation to carbon oxides. Thus, it is challenging to develop new efficient catalyst systems which can allow the production of propene with high selectivity at higher propane conversions.

Although vanadium–magnesium mixed oxides (V–Mg–O) have been reported to be the most selective and active catalysts in the literature,[5] several recent reports demonstrated that V-containing mesoporous molecular sieves are highly selective to the desired propene products during the ODH of propane.[6–9] Particularly, investigations of vanadium-supported mesoporous silica catalysts have shown that the large surface area (> 800 m^2 $\times$ g^{-1}) of the mesoporous materials makes it possible to create highly dispersed, *i.e.*, much more active catalytic sites by incorporating the V species on to the inner walls of the mesoporous silicas.[9] Unfortunately, the yield of olefins from propane did not exceed 30% for all reported catalysts.[5–9]

In the present study, for the first time, a vanadium-containing SBA-15 catalyst with a large pore diameters was prepared and proved to be a highly efficient catalyst for the oxidative dehydrogenation of propane (Scheme 1). SBA-15 is a newly discovered mesoporous silica molecular sieve with tunable uniform hexagonal channels ranging from 50 to 300 Å and thick framework walls (31–64 Å).[10] This is a promising new catalyst support material, especially given its thick walls, which provide a thermal stability that exceeds that for the thinner-walled MCM-41 materials.[11] The introduction of vanadium species onto the inner walls of SBA-15 can provide catalysts with a large concentration of accessible, isolated, and structurally well-defined active sites for the oxidative dehydrogenation of propane. Moreover, it is conceivable that the large pore diameters of the SBA-15 materials (5–30 nm) can make it easy to discharge the produced propene to the outside of the pores, thus preventing the subsequent deep oxidation.

The mesoporous silica materials SBA-15 was prepared according to the literature procedure[10] using Pluronic P123 triblock polymer ($EO_{20}PO_{70}EO_{20}$, M_{av} = 5800, Aldrich) as a template under acidic conditions. Briefly, a solution of $EO_{20}PO_{70}EO_{20}$: 2 M HCl : TEOS : H_2O in 2 : 60 : 4.25 : 15 mass ratio was prepared, stirred for several hours at 40 °C, and then heated at 95 °C for 3 days. The solid products were filtered off and calcined at 500 °C for 5 h. Supported vanadium catalysts on SBA-15 ($n$$VO_x$/SBA-15, n denotes the V_2O_5 content) were prepared by impregnating the SBA-15 with a methanol solution of NH_4VO_3 at 60 °C, and then dried at 120 °C overnight, followed by calcination at 600 °C for 4 h. For comparison, V-containing catalysts supported on MCM-41 and amorphous silica were also prepared using the same procedure. The oxidative dehydrogenation of propane was carried out using a fixed-bed quartz reactor. 0.15 g of the catalyst was loaded in a quartz tubular reactor, and tested under 25 ml min^{-1} (6000 ml h^{-1} g^{-1}) total gas flow consisting of 16.6 mol% propane in air. The products were analyzed by an on-line gas chromatograph.[9]



Scheme 1

The remarkable activity of the VO_x/SBA-15 catalyst can be seen from Table 1. No reaction occurred without catalyst under the reaction conditions used here. Propane was also converted over SBA-15. The introduction of V remarkably increased propane conversion and the selectivity for partial oxidation products. Propene was formed with high selectivity over the SBA-15 catalysts with higher V content and the propene yield was comparable with that obtained over V–Mg–O catalysts.[5] As shown in Table 1, SBA-15 catalysts with low V contents result in the formation of appreciable amount of acrolein. Similar catalytic behaviour has been observed over V-catalysts supported on mesoporous silicas such as MCM-41 and HMS.[7–9] It should be noted that ethylene was yielded in a substantial amount over VO_x/SBA-15 *via* oxidative cracking of propane.[12] It is remarkable that olefin selectivity of up to 80% at a high propane conversion of 41.7% could be achieved over the catalyst 5.0VO_x/SBA-15.

It is also clear from Table 1 that the 5.0VO_x/SBA-15 exhibited much higher C_3H_8 conversion and selectivity to propene than those of mesoporous 5.0VO_x/MCM-41 and amorphous 5.0VO_x/SiO_2. The high selectivity to propene on the former could be related to their highly dispersed V on the large surface of SBA-15 with a large pore diameter as described above. In a comparison of three different silica supports, it is observed that high surface area mesoporous silicas (MCM-41 and SBA-15) are more effective, as demonstrated by the higher activities observed for these supports. Additionally, with a similar V content, SBA-15 is much superior to MCM-41 as a support. Higher dispersion and isolation of the active V-species present on the SBA-15 surface can be attributed to the enhanced catalytic performance in the oxidative dehydrogenation of propane to propene.

Fig. 1 shows the Raman spectra of VO_x/SBA-15, VO_x/MCM-41, VO_x/SiO_2 and crystalline V_2O_5 samples. The absence of sharp peaks at *ca.* 990, 686, 523 cm^{-1} and several others below 400 cm^{-1} (seen in V_2O_5) corresponding to bulk V_2O_5 in the spectra of VO_x/SBA-15 samples indicates that no free V_2O_5 phase was present and the V was highly dispersed in the mesoporous silica-based SBA-15 catalyst. The bands at *ca.* 485 cm^{-1} are assigned to three Si siloxane rings.[13] For all 5.0VO_x/

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Table 1 Catalytic performance of various V-containing catalysts for ODH of propane

Catalyst	S_{BET}/ $m^2\ g^{-1}$	V-Density/ $VO_x\ nm^{-2}$	C_3H_8 Conversion (%)	Selectivity (%)				Yield of propene (%)	TOF × 10^{21}/μmol- C_3H_6 at.-$V^{-1}\ s^{-1}$
				$C_3^=$	$C_3^= + C_2^=$	C_3H_4O	CO_x		
Pure SBA-15	715	—	9.3	22.6	25.5	4.4	70.0	2.1	—
$1.9VO_x$-SBA-15	592	0.21	34.2	46.5	55.8	6.8	30.5	15.9	12.6
$3.3VO_x$-SBA-15	559	0.39	37.4	53.1	64.1	3.5	21.4	19.9	9.0
$5.0VO_x$-SBA-15	478	0.69	41.7	57.0	79.8	—	9.4	23.8	7.1
$8.0VO_x$-SBA-15	458	1.15	34.5	52.0	57.7	—	36.0	17.9	3.3
$16.0VO_x$-SBA-15	448	2.36	33.8	48.4	52.7	—	33.8	16.3	1.5
$5.0VO_x$-SiO_2	222	1.49	25.7	54.3	58.9	1.9	28.1	13.9	4.2
$5.0VO_x$-MCM-41	985	0.34	30.6	57.5	64.9	—	22.9	17.6	5.3

[a] *Reaction conditions*: temperature ~ 600 °C; reaction pressure ~ 1 atm; $C_3^=$: C_3H_6; $C_2^=$: C_2H_4; CO_x: CO_2 + CO. Very small amounts of CH_4 and C_2H_6 were also detected, but are not shown here.

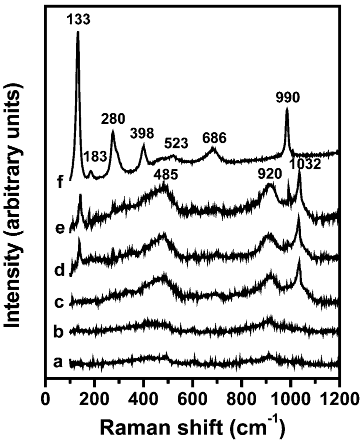

Fig. 1 Laser-Raman spectra of various V-containing catalysts: (a) $1.9VO_x$/SBA-15; (b) $3.3VO_x$/SBA-15; (c) $5.0VO_x$/SBA-15; (d) $5.0VO_x$/MCM-41; (e) $5.0VO_x/SiO_2$; (f) crystalline V_2O_5.

SBA-15, $5.0VO_x$/MCM-41 and $5.0VO_x/SiO_2$ catalysts, the bands at *ca.* 1032 cm^{-1} arise from the isolated tetragonal vanadium species as illustrated in Scheme 1.[9] Bands at 920 cm^{-1} assignable to vanadium species in octahedral coordination were also observed, suggesting the presence of 2D polymeric vanadium species over the three catalysts.[14] For the $5.0VO_x$/MCM-41 and $5.0VO_x/SiO_2$ samples, besides isolated- and polymeric-V species, a trace amount of V_2O_5 (990 and 133 cm^{-1}) was also detected. Thus, the degree of V dispersion on the catalysts can be arranged in the order $5.0VO_x$/SBA-15 > $5.0VO_x$/MCM-41 > $5.0VO_x/SiO_2$, although the SBA-15 catalyst has a much higher vanadium surface density than the MCM-41 sample. This order is in agreement with expectation from the catalytic results shown in Table 1.

To investigate the influence of acidity on the catalytic reactions, NH_3-TPD was performed and the results are shown in Fig. 2. It is seen that the MCM-41- and SiO_2-supported catalyst samples displayed a shoulder at 510–560 °C corresponding to acid sites with medium strength along with the main peak ascribed to weak sites at 205–215 °C. However, it is clear that no appreciable desorption peaks ascribed to medium acid sites were observed on the SBA-15 based catalysts. Takehira *et al.* have proposed that the formation of deep oxidation products (CO_x) is closely related to the interaction of C_3H_6 or allylic intermediates produced on the MCM-41 supported vanadia catalysts with surface medium acid sites during the ODH of propane.[8] Thus, it is likely the desorption of C_3H_6 would be facile over the $5.0VO_x$/SBA-15 catalyst without surface medium acid sites.

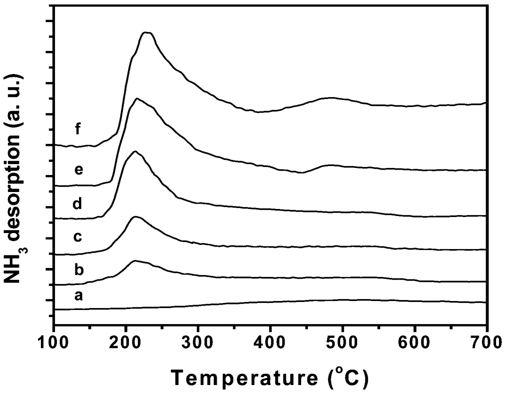

Fig. 2 NH_3-TPD profiles of V-containing catalysts with different V loadings. (a) SBA-15; (b) $1.9VO_x$/SBA-15; (c) $3.3VO_x$/SBA-15; (d) $5.0VO_x$/SBA-15; (e) $5.0VO_x$/MCM-41; (f) $5.0VO_x/SiO_2$.

In conclusion, we have successfully demonstrated that highly dispersed VO_x/SBA-15 catalysts exhibit high catalytic activities for the propene production in the ODH of propane due to the presence of high dispersion and isolation of V species over the surface of SBA-15 materials. The enhanced propene selectivities at higher propane conversions achievable over the VO_x/SBA-15 catalysts has been attributed to the unique large pore diameters and the low surface acidity of the SBA-15 materials, which allow the facile discharge of the target product of propene from the channel of the catalysts.

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