Highly effective oxidative dehydrogenation of propane over vanadia supported on mesoporous SBA-15 silica

Yong-Mei Liu, Yong Cao, Shi-Run Yan, Wei-Lin Dai, and Kang-Nian Fan *

Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Department of Chemistry,
Fudan University, Shanghai 200433, P.R. China

Received 4 December 2002; accepted 7 March 2003

Vanadia-containing mesoporous SBA-15 catalysts were prepared and characterized for the oxidative dehydrogenation (ODH) of propane. It is demonstrated that the vanadia-supported SBA-15 catalysts exhibit a much higher catalytic activity than those reported in the literature obtained over vanadium-supported mesoporous MCM-41 catalysts in the ODH of propane. The high catalytic performance of the mesoporous SBA-15 catalysts is attributed to the particularly large pore diameters and low surface acidity.

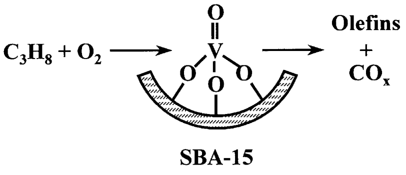
KEY WORDS: vanadium; propane; oxidation dehydrogenation (ODH); mesoporous; SBA-15 silica.

1. Introduction

The increasing need to upgrade low-cost feedstocks has greatly stimulated research on the selective oxidation reactions of light alkanes as an alternative to the production of the more expensive alkenes. In this regard, much attention has been paid recently to the oxidative dehydrogenation (ODH) of alkanes to give the corresponding alkenes, which is thermodynamically favored because the presence of O_2 inhibits the coke formation prevalent in conventional non-oxidative routes [1–4]. 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 [5,6]. Especially in the field of the ODH of propane to propene, it has been well established that the limited propene selectivity at higher propane conversions is linked with propene adsorption on acidic sites and their subsequent combustion to carbon oxides. Thus, new, efficient catalyst systems that can allow the production of propene with high selectivity at higher propane conversions are highly desirable.

Although vanadium–magnesium mixed oxides (V–Mg–O) have been reported to be the most selective and active catalysts [7], several recent reports have demonstrated that V-containing mesoporous molecular sieves are also highly selective to the desired propene products during the ODH of propane [8–11]. The investigations of vanadium-supported mesoporous silica catalysts have shown that the large surface area (>800 m^2/g) of mesoporous materials such as MCM-41, MCM-48 and HMS makes it possible to create highly dispersed, i.e., much more active, catalytic sites by incorporating the vanadium species on to the inner walls of the mesoporous silicas [11]. Unfortunately, to the best of our knowledge, the yield of alkenes from propane has not exceeded 30% up to now using any of the reported catalysts [7–11].

On the other hand, the discovery of mesoporous SBA-15 silica may open up new opportunities for the design of more efficient catalysts for the ODH of light alkanes. Recently, we reported in a communication that the use of mesoporous SBA-15 silica as a support can allow the generation of a highly efficient vanadia catalyst (see scheme 1 in ref. 12) which exhibits a high selectivity (80%) to alkenes at high propane conversions (42%) in the ODH of propane [12]. 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) [13]. SBA-15 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 [14]. The introduction of vanadium species on to the inner walls of SBA-15 can provide catalysts with a large concentration of accessible, isolated, and structurally well-defined active sites for the ODH of propane.



Scheme 1.

---

* To whom correspondence should be addressed.
E-mail: knfan@fudan.edu.cn

1011-372X/03/0500-0061/0 © 2003 Plenum Publishing Corporation

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 subsequent deep oxidation.

In this paper, we report detailed results of the catalytic behavior in the ODH of propane of catalysts based on vanadium-supported mesoporous SBA-15 silica. The influence of the vanadium incorporation method on the catalytic behavior of the vanadium-containing SBA-15 catalysts was also investigated. The chemical and structural characterization of these catalysts was carried out to elucidate the relationship between the catalytic performance and physicochemical properties such as the molecular nature and dispersion of the vanadium species in the catalysts.

2. Experimental

2.1. Catalyst preparation

Mesoporous SBA-15 silica was prepared according to the literature procedure using Pluronic P123 triblock polymer ($EO_{20}PO_{70}EO_{20}$, $M_{av} = 5800$; Aldrich) as template in acidic conditions [14]. Briefly, a solution of $EO_{20}PO_{70}EO_{20}$–2 M HCl–TEOS–H_2O (2 : 60 : 4.25 : 15) (mass ratio) was prepared, stirred for several hours at 40 °C, and then hydrothermally treated at 95 °C for 3 days. The solid products were recovered by filtration and calcined at 500 °C for 5 h to obtain a white powder of SBA-15.

The vanadium-impregnated SBA-15 catalysts ($x$$VO_x$–SBA-imp, where x denotes the weight content of V_2O_5) were prepared by impregnating the SBA-15 with a methanolic solution of NH_4VO_3 at 60 °C, and then dried at 120 °C overnight, followed by calcination at 600 °C for 4 h. The mechanically mixed vanadium-containing samples labeled VO_x–SBA-mix were prepared by heating appropriate well-mixed V_2O_5 and SBA-15 at 600 °C for 4 h. A third method of vanadium introduction was carried out by adsorption of $VO(SO_4)_2$ from an aqueous solution consisting of 1 g of $VO(SO_4)_2$ and 20 ml of H_2O. The catalyst was recovered by filtration and dried at 120 °C. The sample obtained after calcination at 600 °C for 4 h was denoted VO_x–SBA-ads. All synthesized catalysts were pressed, followed by grinding to 60–80-mesh particles for catalytic testing.

2.2. Catalyst characterization

The vanadium contents in all catalysts were measured by inductively coupled plasma atomic emission spectrometry (ICP-AES) after dissolution of the samples in HF/HCl solutions. The X-ray powder diffraction (XRD) of the catalysts was carried out on a Bruker D8 Avance X-ray diffractometer using nickel-filtered Cu K_α radiation ($\lambda = 1.5418$ Å) in the 2θ range from 1 to 80°. The textural parameters were measured using the BET method by N_2 adsorption and desorption at 77 K in a Micromeritics TriStar system. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) characterization of the catalysts was performed using a Bruker Vector 22 instrument equipped with a DTGS detector and a KBr beamsplitter. Catalysts were placed in a sample cup inside a Harrick diffuse reflectance cell equipped with KBr windows and a thermocouple mount that allowed direct measurement of the sample temperature. All spectra were collected in a nitrogen atmosphere at 200 °C. Raman spectra were obtained using a confocal microprobe Raman system (Lab Ram Infinity). The excitation wavelength was 514.5 nm from an internal Ar^+ laser with a power of 8 mW. All the samples were heated to 500 °C in dry air flow for 1 h before detects. Spectra were recorded with a resolution of 4 cm^{-1}. The NH_3 temperature-programmed desorption (TPD) was performed between 100 and 700 °C, with a heating rate of 10 °C/min. After pretreatment in a gas flow of He (20 ml/min) and O_2 (10 ml/min) at 600 °C, the sample was degassed in vacuum. The adsorption of NH_3 was carried out at 120 °C and a pressure of 2.67 kPa for 1 h, then the NH_3 that remained in the gas phase was purged by He. TPD was performed in a flow of He (15 ml/min) and the desorbed NH_3 was detected by mass spectrometry.

2.3. Reaction tests

The ODH reactions were carried out in a fixed-bed quartz microcatalytic flow reactor at atmospheric pressure with a 150 mg catalyst (60–80-mesh) loading. The gas reaction mixture was constituted of 16.6 mol% propane in air and a total gas flow of 12 ml/min, giving a space velocity of 4800 ml/h/g. The feed and the product gases were analyzed on-line using a gas chromatograph (Type GC-122, Shanghai). Permanent gases (N_2, O_2, CO, CO_2) were separated using a TDX-01 column connected to a TCD and other reaction products were analyzed employing a Porapak Q column connected to an FID.

3. Results and discussion

3.1. Catalytic activity

The catalytic behaviors of the SBA-15-supported vanadium catalysts were tested in the ODH of propane at different temperatures. No reaction occurred without a catalyst under the reaction conditions used here. However, it has been observed that propane could be converted over parent SBA-15 [12]. The introduction of vanadium remarkably enhanced the propane conversion and the selectivity for partial oxidation products.

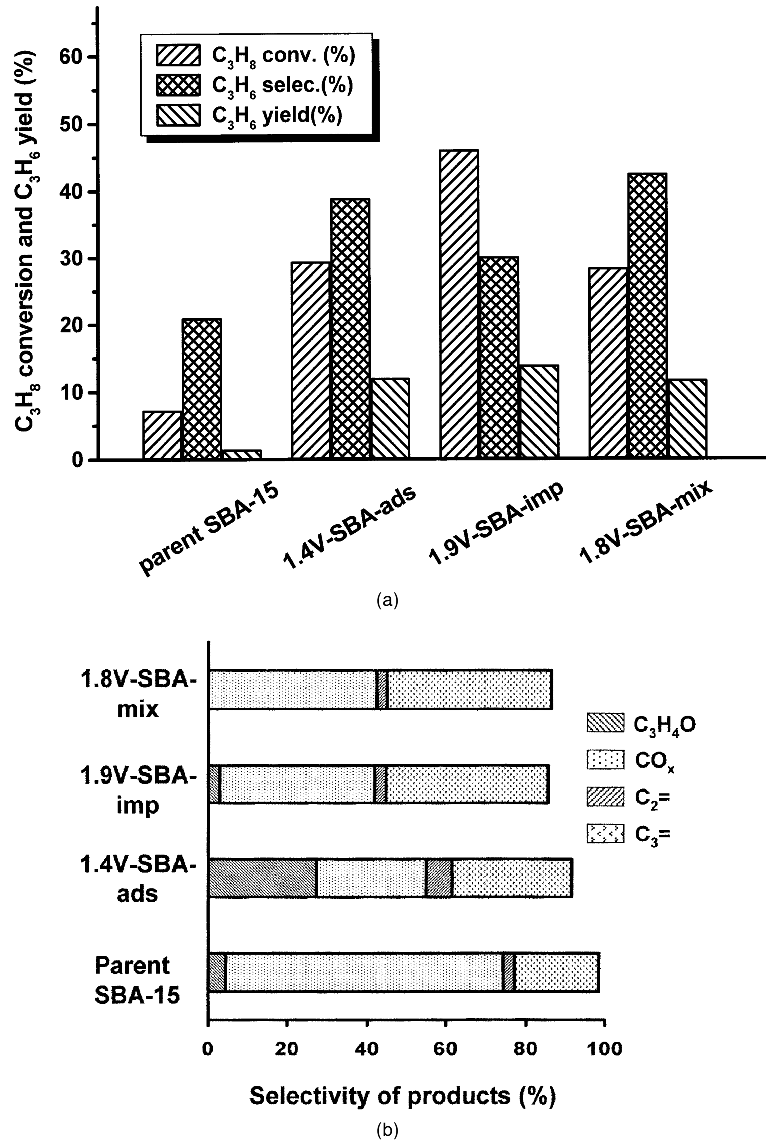


Figure 1. Propane conversion, propene yield (a) and product distribution (b) of vanadium-loaded SBA-15 catalysts prepared by different synthetic methods. Reaction conditions: temperature, ~550 °C; reaction pressure ~1 atm; C_3=, C_3H_6; C_2=, C_2H_4; CO_x, $CO_2 + CO$. Very small amounts of CH_4 were also detected, but are not shown here.

Figure 1 shows the propane conversion, propene yield and product distribution obtained at 550 °C over SBA-15 catalysts derived by different methods at low vanadium content. As shown, propene and CO_x were the main products produced during the oxidation of propane on all catalysts, and small amounts of ethylene produced via oxidative cracking of propane were also detected (the additional 10–15% unaccounted for product mixture is CH_4 and C_2H_6). It is notable that an appreciable amount of acrolein was detected over the SBA-15 catalyst obtained by the adsorption method, suggesting the presence of a substantial further oxidation process during the ODH of propane in this case [15]. The variation of the propane conversion demonstrates that it depends strongly on the preparation method. The conversion of propane over the V–SBA-mix catalyst was observed to be much lower than for its impregnated counterparts, although the selectivity to propene was similar.

To investigate further the influence of the vanadium content on the catalytic behavior of the SBA-15 catalysts, the oxidative dehydrogenation of propane over vanadium-impregnated SBA-15 catalysts with various vanadium contents was investigated. The catalytic activity of the V–SBA-imp catalysts as a function of vanadium loading at 550 °C is shown in figure 2. It is interesting that the V–SBA-imp catalysts exhibited a very high selectivity to propylene for samples with medium vanadium loadings. With increasing vanadium content, the V–SBA-imp catalysts show a decrease in propane conversion when the vanadium content in the catalyst is <5.0 wt%. However, the selectivity to propene changes in a different way, attaining the highest value over the 5.0V–SBA-imp catalyst. As a

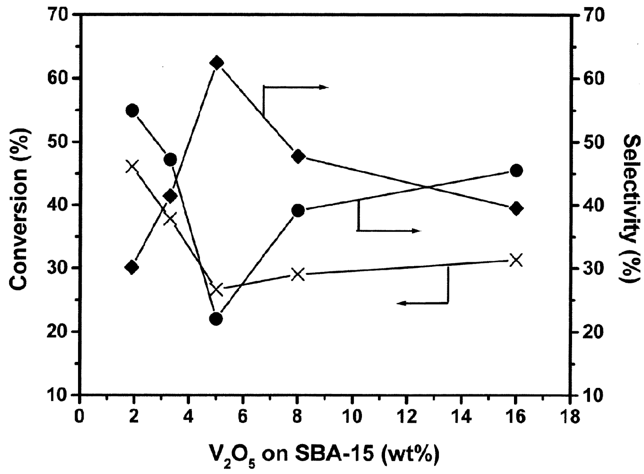


Figure 2. Variation of propane conversion and the selectivity to the main reaction products versus the vanadium content over the *x*V–SBA-imp catalysts at 550 °C: conversion of propane (×), selectivity of propene (◆) and CO_x (●).

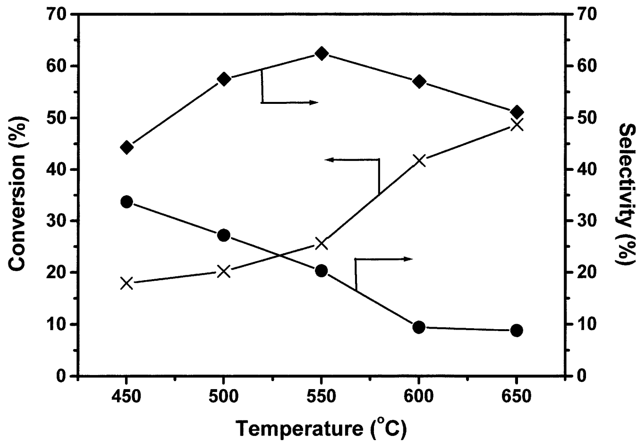


Figure 3. Variation of propane conversion and the selectivity to the main reaction products versus the reaction temperature for the 5.0V–SBA-imp catalyst: conversion of propane (×), selectivity of propene (◆) and CO_x (●).

consequence, a maximum propene yield of 16.0% was obtained over the V–SBA-imp catalyst with 5.0 wt% of vanadium at 550 °C. This value was much higher than the recent literature results obtained over vanadium-supported MCM catalysts [4].

The catalytic activity of the V–SBA-imp catalysts was also found to be strongly dependent on the reaction temperature. To determine the possible low-temperature performance of the V–SBA-imp catalysts, the catalytic performance of the 5.0V–SBA-imp catalyst at temperatures between 450 and 650 °C was investigated. Figure 3 plots the ODH of propane over the 5.0V–SBA-imp catalyst as a function of reaction temperature. It was found that the 5.0V–SBA-imp catalysts show a poorer catalytic activity at a reaction temperature of 450 °C. The propane conversion increases rapidly with increase in reaction temperature, especially below 600 °C. At 650 °C, the propane conversion reaches the highest value. It is noticeable that the change in behavior of the selectivity to CO_x is the reverse of the conversion for propane over the temperature range investigated, which is completely different to the results obtained over V–MCM-41 or V–HMS catalysts [8,11]. In comparison, the selectivity to propene shows a maximum value of 62.4% at 550 °C, indicative of the highly selective nature of the 5.0V–SBA-imp catalyst for the ODH of propane. It should also be noted that ethylene was obtained in substantial amounts over VO_x/SBA-15 via oxidative cracking of propane at 600 °C [16]. It is remarkable that an alkene selectivity of up to 80% at a high propane conversion of 41.7% could be achieved over the 5.0V–SBA-imp catalyst at 600 °C.

3.2. Catalyst characterization

The specific surface area (S_{BET}) and the cumulative pore volume of the parent SBA-15 were measured as 713 m^2/g and 1.25 cm^3/g, respectively. Table 1 summarizes the results for the low-vanadium loaded catalysts prepared by the impregnation method. It can be seen that the S_{BET} of the vanadium-impregnated catalysts is lower than that of the unloaded supports and decreases with increasing vanadium content. The results in table 1 clearly demonstrate that the introduction of vanadium would cause a decrease in the pore volume of the

Table 1
Physicochemical properties of various vanadia-supported SBA-15 catalysts[a]

Catalyst	S_{BET} (m^2/g)	V_p (cm^3/g)	D_{BJH} (nm)	Vanadium density (VO_x per nm^2)	TOF × 10^{21} (μmol C_3H_6 at-V^{-1}s^{-1})
SBA	713.1	1.25	7.7	—	—
1.8V–SBA-mix	546.7	0.87	5.9	0.19	8.4
1.4V–SBA-ads	557.6	0.95	6.5	0.15	12.4
1.9V–SBA-imp	591.6	1.09	7.1	0.20	11.0
3.3V–SBA-imp	558.9	0.99	7.0	0.39	7.1
5.0V–SBA-imp	477.7	0.88	6.4	0.69	4.8
8.0V–SBA-imp	458.3	0.73	6.0	1.16	2.6
16.0V–SBA-imp	448.1	0.75	5.2	2.40	1.2

[a] Reaction conditions: temperature ~550 °C; reaction pressure ~1 atm.

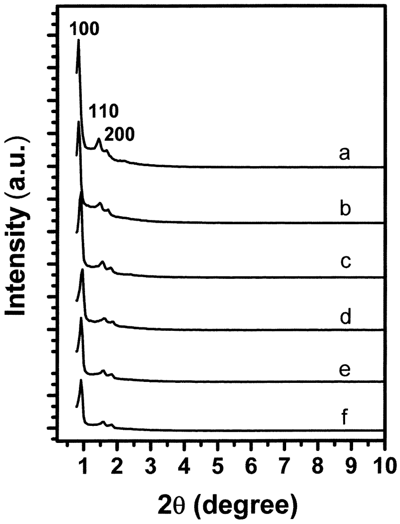


Figure 4. XRD patterns of the *x*V–SBA-imp catalysts with different vanadium loadings: (a) pure SBA-15; (b) 1.9V–SBA-imp; (c) 3.3V–SBA-imp; (d) 5.0V–SBA-imp; (e) 8.0V–SBA-imp; (f) 16.0V–SBA-imp.

SBA-15 materials. This decreasing trend is also shown by the data for pore size distributions (D_{BJH}). With increasing vanadium loading, D_{BJH} decreases from 7.7 nm for parent SBA-15 to 5.6 nm for the V–SBA-imp catalyst with 16 wt% of V_2O_5. It is also noticeable that the pore size distribution is narrow, indicating that the regular mesoporous structure of the support has been preserved after vanadium introduction.

The powder X-ray diffraction patterns for the samples prepared by impregnation show the characteristic low-angle diffraction peak. All samples show well-resolved patterns with a prominent diffraction peak (100), two additional weak diffraction peaks indexed to (110) and (200) reflections and a poorer intensity diffraction peak indexed to (210), which match well with the pattern reported for SBA-15 [14], indicating that all xVO$_x$–SBA-15 products prepared by impregnation have well-ordered hexagonal mesostructures. However, the diffraction peaks of V–SBA-imp samples all shift to higher 2θ values compared with SBA-15. This may result from the constriction of their frameworks with further vanadium loading during the calcination procedure. In addition, a gradual attenuation in intensity of the d_{100} peak was observed with increasing vanadium loading (see figure 4). This phenomenon may be accounted for by considering that partial blocking of the hexagonal pore walls of the SBA-15 materials occurs upon vanadium introduction, especially when the vanadium content is very high [17]. In all cases, the absence of diffraction peaks at 2θ angles $>10^\circ$ (not shown) seems to exclude the presence of V_2O_5 crystallites. Diffraction features corresponding to crystalline V_2O_5 were not detected in any of the samples even at vanadium loadings as high as 16.0 wt%. This indicates that the VO_x species can be well dispersed on the mesoporous SBA-15 supports [18].

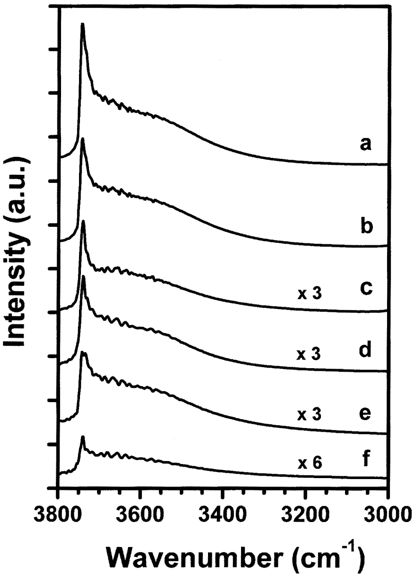


Figure 5. DRIFT spectra of the *x*V–SBA-imp catalysts with different vanadium loadings: (a) pure SBA-15; (b) 1.9V–SBA-imp; (c) 3.3V–SBA-imp; (d) 5.0V–SBA-imp; (e) 8.0V–SBA-imp; (f) 16.0V–SBA-imp.

DRIFTS was employed to follow the variations in the behavior of the hydroxyl groups present on the surface of the impregnated samples as a function of vanadium content. Spectra of the samples under an N_2 atmosphere in the 3800–3000 cm^{-1} range are shown in figure 5. For convenience of comparison, the infrared spectrum of the pure siliceous SBA-15 support is also included. In figure 5(a), silanol groups having an OH stretching vibration at 3740 cm^{-1} (sharp band) are clearly identified on pure SBA-15. The sharp band at 3740 cm^{-1} is ascribed to the isolated terminal silanol groups present on the SBA-15 [11]. The intensity of the band at 3740 cm^{-1} decreased rapidly as the vanadium loading increased, and almost totally disappeared at 16.0 wt% vanadium. The strong decrease in intensity of the isolated terminal silanol groups with increasing vanadium loading can be attributed to the reaction of vanadium oxide species with the isolated terminal silanol groups during the catalyst preparation process. This observation is consistent with the recent results for the vanadium-immobilized mesoporous HMS silica systems reported by Zhou *et al.* [11].

Laser Raman spectroscopy was employed to elucidate the molecular nature of the supported vanadium species present on the mesoporous SBA-15 materials. Figure 6(a) shows the Raman spectrum of the pure siliceous SBA-15 that exhibits spectroscopic features similar to those of amorphous SiO_2 [19]. Owing to the presence of fluorescence interference and low sensitivity in the Raman experiments, the Raman intensity of the pure SBA-15 silica is very weak. Based on previous literature assignments for silicate materials, the weak band at 480 cm^{-1} is assigned to fourfold siloxane rings [20]. The Raman spectra for the V–SBA-imp catalysts as a

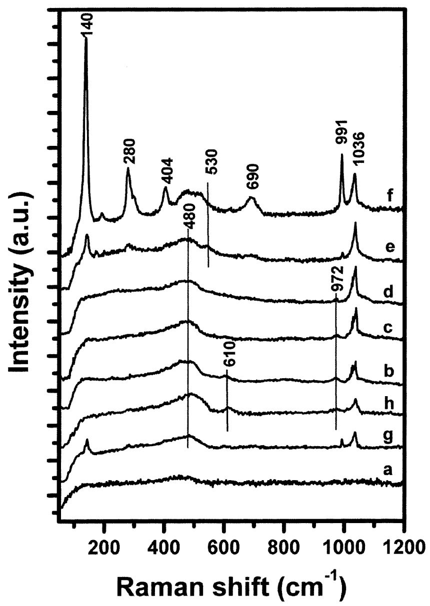


Figure 6. Raman spectra of the *x*V–SBA catalysts with different vanadium loadings: (a) pure SBA-15; (b) 1.9V–SBA-imp; (c) 3.3V–SBA-imp; (d) 5.0V–SBA-imp; (e) 8.0V–SBA-imp; (f) 16.0V–SBA-imp; (g) 1.8V–SBA-mix; (h) 1.4V–SBA-ads.

function of vanadium content are shown in figure 6(b)–(f). As shown in figure 6(b), new bands at 610, 972 and 1036 cm^{-1} are observed for the samples with a low vanadium content of 1.9 wt%. With increase in vanadium loading, the intensity of the band at 1036 cm^{-1} increases with the vanadium content (figure 6(c) and (d)). When the vanadium content in the sample is >8.0 wt%, six additional bands at 140, 280, 404, 530, 690 and 991 cm^{-1} characteristic of crystalline V_2O_5 are detected. Although the XRD results suggest the highly dispersed nature for the vanadium species deposited on the catalyst sample prepared by impregnation at high vanadium content or mechanical mixing, sharp Raman bands associated with microcrystalline V_2O_5 (figure 6(g)) suggest that laser Raman technique is more sensitive than XRD in crystalline V_2O_5 identification over V–SBA catalysts [11]. The band of 280 cm^{-1} is assigned to the V–O–V bending mode. In addition to the observation of the Raman bands associated with bulk V_2O_5, the intensity of the 1036 cm^{-1} band is attenuated as the content of vanadium is further increased.

Based on literature assignments, the 991 cm^{-1} band corresponds to the symmetric stretching frequency of V=O groups present in the bulk [21] and the 1036 cm^{-1} band is due to the stretching frequency of a terminal V=O groups bonded to the SBA-15 support [22]. As a result, the presence of the 1036 cm^{-1} band unambiguously indicates the existence of isolated vanadium species on the surface of the V–SBA-imp catalysts. It is also interesting that the identification of the weak bands at 610 and 972 cm^{-1} attributable to the V–O–V symmetric stretch and O–V–O stretch over the 1.9V–SBA-imp catalyst suggests the presence of polymeric vanadia species over the SBA-15 surface even at very low vanadium loadings.

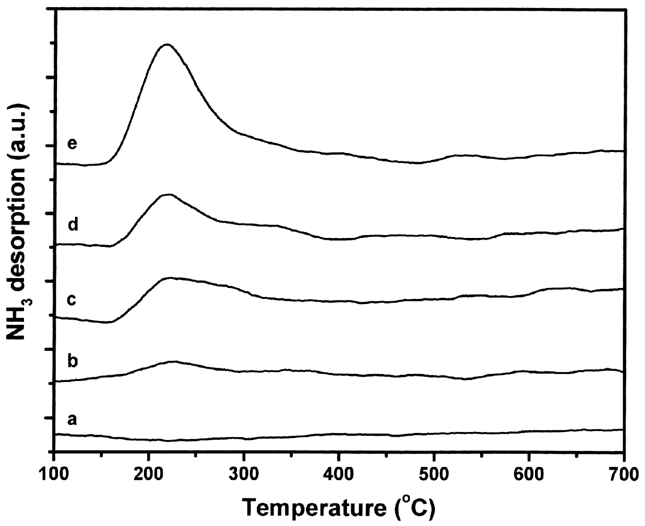


Figure 7. NH_3 TPD profiles of the *x*V–SBA-imp catalysts with different vanadium loadings: (a) SBA-15; (b) 3.3V–SBA-imp; (c) 5.0V–SBA-imp; (d) 8.0V–SBA-imp; (e) 16.0V–SBA-imp.

To investigate the influence of acidity on the catalytic reactions, NH_3 TPD was performed and the results are shown in figure 7. For the parent SBA-15, no appreciable desorption corresponding to the presence of acidic sites is observed. However, it is seen that all the SBA-15-supported catalyst samples displayed a wide peak at 205–220 °C corresponding to weak sites and the intensity of the peak increased with increasing vanadia loading. This result indicates that incorporation of vanadium induces a moderate development of acidity [4]. It is also clear that no appreciable desorption peaks ascribed to medium acidic sites in the temperature range 510–560 °C were observed on the vanadium-containing SBA-15 catalysts with vanadium loadings <8 wt%. For the 16.0V–SBA-imp catalyst, a weak shoulder at 510–560 °C corresponding to acidic sites with medium strength was developed. Zhang *et al.* proposed that the formation of deep oxidation products (CO_x) is closely related to the interaction of C_3H_6 or allylic intermediates with surface medium acidic sites during the ODH of propane over MCM-41-supported vanadia catalysts [23]. Hence it is likely that the desorption of the target product of C_3H_6 would be facile over the 5.0V–SBA-imp catalyst without surface medium acidic sites.

In our experiments, the V–SBA-ads catalyst obtained by adsorption demonstrated a unique catalytic behavior in ODH reactions as compared with the catalysts prepared by other methods. It is surprising to find that up to ~8.3% of acrolein is obtained over the 1.4V–SBA-ads catalyst. The detection of appreciable amounts of O-containing products in the ODH of propane over the V–SBA-ads catalyst suggests that a different reaction mechanism may be involved in the acrolein formation process. In our case, at least part of the VO_4 units was structurally incorporated into the SBA-15 framework of the 1.4V–SBA-ads catalyst. According to the alkane activation mechanism on isolated VO_4 units proposed by Blasco *et al.* [17,18,24], both the V=O double bond character and the strength of the bridging V–O–R oxygen bond are essential factors in the final product distribution. Considering the unique structural features associated with the isolated VO_4 units in the V–SBA-ads catalyst, it would be easier to generate the V–O–R bond than the V–R bond formation owing to the steric hindrance to the approach of propane molecules to the active sites. Therefore, this would favor the formation of acrolein in the reaction products.

Turnover frequencies (TOF) for the V–SBA samples prepared via various synthetic methods and with various vanadium contents are also compared in table 1. It can be seen that the vanadium density on the samples with vanadia loadings <5 wt% was estimated to be much lower than the monolayer capacity of vanadium on silica ($1VO_x/nm^2$). We obtained a remarkable TOF value as high as $12.4\,\mu mol\ C_3H_6\,at\text{-}V^{-1}s^{-1}$ on the V–SBA-ads catalyst, which suggests that the vanadium incorporation method has a strong influence on the catalytic activity of vanadia species. The isolated surface vanadium species have been well established as the active sites in the ODH of propane [25]. Considering the highly dispersed nature of the vanadium species supported over all catalysts with vanadium densities $<1VO_x/nm^2$, it seems surprising that the SBA-15 catalysts exhibited decreased TOF values with increasing vanadium content. Here, the presence of small amounts of polymeric vanadia species and the influence of the distance on the reaction selectivity over the active sites might be considered to explain the decreased TOF values [18].

4. Conclusions

Mesoporous SBA-15 silica-supported vanadium catalysts were prepared and characterized for the ODH of propane. The mesoporous siliceous SBA-15 materials were shown to be promising supports for the development of high-performance vanadium-supported catalysts applicable in ODH reactions. Combined XRD, DRIFTS, NH_3 TPD and laser Raman results demonstrated that isolated vanadium oxide species with high concentration are well dispersed on the surface of mesoporous SBA-15 silica. The as-prepared vanadium-containing SBA-15 catalysts show high reactivity and selectivity in the oxidative dehydrogenation of propane. Our results show that the highest catalytic performance can be attained with an impregnated catalyst with a 5.0 wt% vanadium content, which allows the selective formation of propene with a maximum yield of $\sim$23.4% in the ODH of propane. The high catalytic activity of the present V–SBA-15 catalysts in the ODH reaction of propane is attributed to the particularly large pore diameters and low surface acidity in the SBA-15 catalysts.

Acknowledgments

Financial support from the National Natural Science Foundation of China (Grant Nos. 20203003 and 20073009) and the Committee of Shanghai Science and Technology (Grant Nos. 0112NM076 and 02QA14006) is gratefully acknowledged.

References

[1] H.H. Kung, Adv. Catal. 40 (1994) 1.

[2] M.M. Bettahar, G. Costentin, L. Savary and J.C. Lavalley, Appl. Catal. A 145 (1996) 1.

[3] T. Blasco and J.M. López-Nieto, Appl. Catal. A 157 (1997) 117.

[4] J. Santamaría-González, J. Luque-Zambrana, J. Mérida-Robles, P. Maireles-Torres, E. Rodríguez-Casallón and A. Jiménez-López, Catal. Lett. 68 (2000) 67.

[5] S. Sugiyama, Y. Iozuka, E. Nitta, H. Hayashi and J.B. Moffat, J. Catal. 233 (2000) 189.

[6] T. Blasco and J.M. López Nieto, Appl. Catal. A 117 (1997) 157.

[7] M. Chaar, D. Patel, M. Kung and H.H. Kung, J. Catal. 463 (1988) 109.

[8] J. Santamaría-González, J. Luque-Zambrana, J. Mérida-Robles, P. Maireles-Torres, E. Rodríguez-Casallón and A. Jimínez-López, Catal. Lett. 67 (2000) 68.

[9] B. Solsona, T. Blasco, J.M. López Nieto, M.L. Peña, F. Rey and A. Vidal-Moya, J. Catal. 443 (2001) 203.

[10] Q. Zhang, Y. Wang, Y. Ohishi, T. Shishido and K. Takehira, J. Catal. 308 (2001) 202.

[11] R. Zhou, Y. Cao, S.R. Yan, J.F. Deng, Y.Y. Liao and B.F. Hong, Catal. Lett. 107 (2001) 75.

[12] Y.M. Liu, Y. Cao, K.K. Zhu, H.Y. He, S.R. Yan, W.L. Dai and K.N. Fan, J. Chem. Soc., Chem. Commun. (2002) 2832.

[13] D.Y. Zhao, J.L. Feng, Q.S. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka and G.D. Stucky, Science 548 (1998) 279.

[14] J. Jarupatrakorn and T.D. Tilley, J. Am. Chem. Soc. 8380 (2002) 124.

[15] K.M. Reddy, I. Moudrakovvski and A. Sayari, J. Chem. Soc., Chem. Commun. (1994) 2373.

[16] M.L. Kaliya, S.B. Kogan, N. Froumin and M. Herskowitz, Catal. Commun. 3 (2002) 327.

[17] Q. Zhang, Y. Wang, Y. Ohishi, T. Shishido and K. Takehira, J. Catal. 202 (2001) 308.

[18] M.A. Bañares, J.H. Cardoso, F. Agulló-Rueda, J.M. Correa-Bueno and J.L.G. Fierro, Catal. Lett. 64 (2000) 191.

[19] G.T. Went, S.T. Oyama and A.T. Bell, J. Phys. Chem. 94 (1990) 4240.

[20] K.J. Chao, C.N. Wu, H. Chang, L.J. Lee and S.F. Hu, J. Phys. Chem. B 101 (1997) 6341.

[21] L. Abello, E. Husson, Y. Replin and G. Lucazezu, Spectrochim. Acta, Part A 39 (1983) 641.

[22] Z.H. Luan, P.A. Meloni, R.S. Czernuszewicz and L. Kevan, J. Phys. Chem. B 101 (1997) 9046.

[23] Q. Zhang, Y. Wang, Y. Ohishi, T. Shishido and K. Takehira, J. Catal. 202 (2001) 308.

[24] A. Khodakov, B. Olthof, A.T. Bell and E. Iglesia, J. Catal. 181 (1999) 205.

[25] M. Morey, A. Davidson, H. Eckert and G. Stucky, Chem. Mater. 8 (1996) 486.