

# Oxidative dehydrogenation of propane over mesoporous HMS silica supported vanadia

Rui Zhou<sup>a</sup>, Yong Cao<sup>a</sup>, Shirun Yan<sup>a</sup>, Jingfa Deng<sup>a,\*</sup>, Yuanyan Liao<sup>b</sup> and Bifeng Hong<sup>b</sup>

<sup>a</sup> Department of Chemistry, Fudan University, Shanghai 200433, PR China

E-mail: jfdeng@srcap.stc.sh.cn

<sup>b</sup> State Key Laboratory for Physical Chemistry of the Solid Surface, Xiamen University, Xiamen 361005, PR China

Received 19 March 2001; accepted 14 May 2001

Vanadium-containing mesoporous HMS catalysts have been prepared and characterized for the oxidative dehydrogenation (ODH) of propane. It is demonstrated that the vanadium supported HMS catalysts exhibit a much higher catalytic activity than the literature results obtained over the vanadium supported MCM-41 catalysts in the ODH of propane. The improved catalytic activity of the V-HMS catalysts has been attributed to the presence of high concentration of well-dispersed vanadium species on the surface of the mesoporous HMS materials.

**KEY WORDS:** vanadium; propane; oxidative dehydrogenation (ODH); mesoporous; HMS silica

## 1. Introduction

As an alternative process to upgrade cheaper feedstocks, the selective oxidation of light alkanes to corresponding alkenes has attracted continuously increasing interest in modern petrochemical industry. One recent focus in this area is the oxidative dehydrogenation (ODH) of propane to propylene [1–4]. This process is thermodynamically favored at much lower temperatures since the presence of O<sub>2</sub> inhibits the coke formation prevalent in non-oxidative routes [5].

Supported vanadium oxides have been extensively investigated as selective catalysts in the ODH of propane [5–8]. Intensive efforts have been made for a long time to develop improved catalyst systems that are active at much lower temperatures. Various metal oxides including SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub> and MgO have been extensively investigated as the supporting material in the ODH of propane. Although the vanadium–magnesium mixed oxides (VMgO) have shown to be the most selective and active catalysts reported in literature [9], several recent reports demonstrated that V-containing molecular sieves are also highly selective to the desired oxydehydrogenation products during the ODH of propane [10,11]. More recently, the study of the new type of mesoporous MCM-41 molecular sieves as the vanadium support in the oxidative dehydrogenation of propane has been reported [12]. However, it is only to find that the observed conversion and selectivity to propylene over the vanadium supported silica MCM catalysts are very low compared to the results reported in the literature. The low selectivity to propylene over the vanadium-containing mesoporous silica catalysts has been suggested to be closely related to the effective acidity associated with the MCM catalysts [12]. It is also suggested that a number of influential factors includ-

ing the structural, textural and acidic characteristics may be considered to understand the catalytic behavior of the mesoporous V-containing MCM catalysts.

On the other hand, the well-known family of M41S molecular sieves offers a wide range of catalytically attractive mesoporous materials with varied structural and textural features. A number of mesoporous silicates other than MCM-41 silica can now be routinely prepared *via* a different template assembling approach. One type of mesoporous materials that are of particular interest are the hexagonal mesoporous silicas (HMS), which are claimed to have larger pores, to be more stable and to have thicker pore walls than their MCM-41 counterparts [13]. The unique features associated with the HMS molecular sieve render it a promising candidate as support for various catalysts. Moreover, the synthesis of HMS materials offers additional advantages of the cost-reduction by employing a less expensive and non-toxic surfactant and mild reaction conditions. Consequently, the synthesis and characterization of V-containing HMS materials as well as their applications in catalysis have recently been studied [14]. To our knowledge, the investigation concerning the oxidative dehydrogenation (ODH) of propane over vanadium catalysts employing mesoporous HMS silica as support has yet to be reported.

In the present work, we report the results of the catalytic behavior in the oxidative dehydrogenation of propane of catalysts based on vanadium supported mesoporous HMS silica. The influence of the vanadium incorporation method on the catalytic behavior of the HMS catalysts is also investigated. The chemical and structural characterization of these catalysts has been carried out to understand the relation between the catalytic performance and properties such as the nature and dispersion of the vanadium species in the catalysts.

\* To whom correspondence should be addressed.

## 2. Experimental

### 2.1. Catalyst preparation

Mesoporous HMS silica has been prepared by hydrolysis of TEOS in the presence of dodecylamine ( $C_{12}H_{25}NH_2$ ), water and ethanol as a cosolvent [15]. The use of a cosolvent improved template solubility. In a typical preparation, TEOS was added to a vigorously stirred solution of dodecylamine in ethanol and deionized water, affording a reaction mixture of the following molar composition: 1.0 TEOS : 0.27  $C_{12}H_{25}NH_2$  : 9.09 EtOH : 29.6  $H_2O$ . The reaction mixture was aged at ambient temperature for 18 h in order to obtain the hexagonal mesoporous silica. The obtained crystalline products were recovered by filtration, washed with deionized water, air-dried, and finally calcined in air at 630 °C for 4 h.

The vanadium-impregnated HMS catalysts have been prepared by impregnating the HMS with an aqueous solution of ammonium metavanadate,  $NH_4VO_3$ , at 80 °C. After being air-dried at 110 °C, the V-impregnated silica catalysts were obtained by calcination at 600 °C for 2 h, and they were denoted as  $x$ V-HMS-imp catalysts ( $x$  means the total weight percentage of vanadium). The mechanically mixed vanadium-containing samples labeled as V-HMS-mix have been prepared by heating appropriate well-mixed  $V_2O_5$  and HMS at 600 °C for 2 h. A third method of vanadium introduction has been carried out by adsorption of vanadyl acetyl acetonate ( $VO(AcAc)_2$ ) from a toluene solution consisting of 0.2 g  $VO(AcAc)_2$  and 20 ml toluene. The catalyst was recovered by filtration and then dried at 120 °C. The sample obtained after calcination at 600 °C for 2 h was called V-HMS-ads. Finally, vanadium was also incorporated in the synthesis process of HMS as follows: a mixture of  $VO(AcAc)_2$  alcoholic solution and tetraethyl orthosilicate (TEOS) alcoholic solution was slowly added to a proportional mixture of dodecylamine, ethanol and  $H_2O$  under vigorous stirring at 40 °C. All subsequent synthetic steps follow that for the preparation of the pure HMS silica, and the as-obtained mesoporous vanadium-doped HMS catalyst was designated as V-HMS-syn. 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 ICP-AES after solubilization of the samples in HF/HCl solutions. The X-ray powder diffraction (XRD) of the catalysts were carried out on a Germany Bruker D8Advance X-ray diffractometer using nickel filtered  $Cu K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) in the  $2\theta$  range from 10° to 80°. The textural parameters have been 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 beam splitter. 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 nitrogen atmosphere at 200 °C. Raman spectra were obtained using a confocal microprobe Raman system (LabRam I, Dilor). The excitation wavelength was 632.8 nm from an internal He–Ne laser with a power of 12 mW. All the samples were heated to 500 °C for 1 h *in situ* in airflow before detection. Spectra were recorded with a resolution of  $4 \text{ cm}^{-1}$ .

### 2.3. Reaction tests

The ODH reactions were carried out in a fixed-bed quartz microcatalytic flow reactor at atmospheric pressure with 250 mg catalyst (60–80 mesh) loading. To avoid undesired hot spots in the catalytic bed, the catalysts were diluted with 300 mg quartz powder (40–60 mesh). The gas reaction mixture was constituted of 16.6 mol% propane in air and a total gas flow of  $25 \text{ ml min}^{-1}$ , giving a space velocity of  $6000 \text{ ml h}^{-1} \text{ g}^{-1}$ . The feed and the product gases were analyzed on-line by 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 detector and other reaction products were analyzed employing a Porapak Q column connected to a FID detector.

## 3. Results and discussion

### 3.1. Catalytic activity

The catalytic behavior of the HMS-supported vanadium catalysts has been tested in the oxidative dehydrogenation of propane at different temperatures. The pure silica HMS support was found to be inactive in the reaction at all the experimental conditions. Table 1 compiles the catalytic data for propane oxidation at 500 °C and the selectivity to the main products for the catalysts obtained from different incorporation method at low vanadium contents. As shown in table 1, propylene and  $CO_x$  were the main products produced during the oxidation of propane on all catalysts, whereas O-containing organic compounds were not detected. The variation of the propane conversion demonstrates that it depends on the preparation method. It increases with the vanadium content while the selectivity to propylene changes in a different way. The conversion value of propane over the 1.68V-HMS-mix catalyst was observed to be much lower than its impregnated counterparts although the selectivity to propylene was shown to be similar.

It should be noted that a quite different catalytic behavior has been observed at the initial stage of the ODH reaction over the catalyst of 0.88V-HMS-syn, where the vanadium was structurally incorporated in the HMS synthesis process. Acrolein with a yield up to 7.1% was observed at the beginning of reaction. The detection of an appreciable amount

Table 1  
Catalytic results for ODH of propane over vanadium-loaded HMS catalysts prepared by different synthetic methods.<sup>a</sup>

Catalyst	Vanadium (wt%)	Conversion (%)	Selectivity (%)			Yield of C <sub>3</sub> H <sub>6</sub> (%)
			CO	CO <sub>2</sub>	C <sub>3</sub> H <sub>6</sub>	
0.88V-HMS-syn <sup>a</sup>	0.88	16.2	25.8	18.6	52.2	8.5
0.56V-HMS-imp	0.56	8.7	18.9	16.1	62.2	5.4
1.68V-HMS-mix	1.68	16.3	38.1	24.5	36.2	5.9
2.09V-HMS-ads	2.09	43.8	40.5	33.7	21.8	9.5
1.68V-HMS-imp	1.68	34.5	31.7	29.6	34.7	11.9

<sup>a</sup> This data was obtained after carrying out the ODH reaction of 4 h while other data were obtained at 1 h.

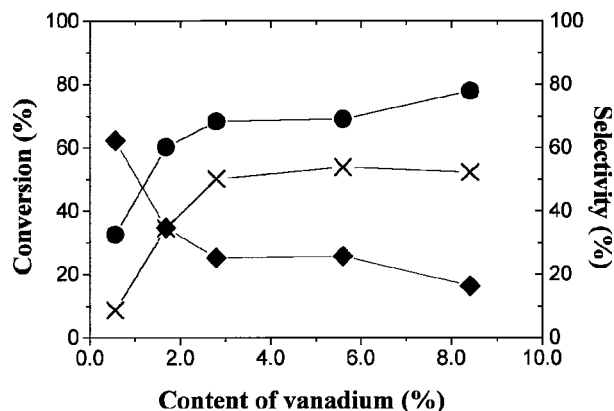


Figure 1. Variation of propane conversion and the selectivity to the main reaction products versus the vanadium content at 500 °C: conversion of propane (x), selectivity of propylene (♦) and CO<sub>x</sub> (●).

of O-containing products over the V-HMS-syn catalyst suggests the presence of a substantial oxidation process during the oxidative dehydrogenation of propane [5]. With the proceeding of the ODH reaction, a gradual decrease in the acrolein formation occurred. After 4 h, only trace acrolein could be detected in the product. The data shown in table 1 list the catalytic data for the 0.88V-HMS-syn catalyst obtained after 4 h of the reaction. Although the 0.88V-HMS-syn catalyst gave a relatively low propane conversion, a high selectivity to propylene was attained.

To further investigate the influence of the vanadium contents on the catalytic behavior of the HMS catalysts, the oxidative dehydrogenation of propane over vanadium-impregnated HMS catalysts with various vanadium contents was investigated. The catalytic activity of the V-HMS-imp catalysts as a function of vanadium loading at 500 °C is shown in figure 1. It is shown that the V-HMS-imp catalysts exhibited a very high selectivity to propylene for samples with low vanadium loading. For samples with higher vanadium loading, the propylene selectivity decreases rapidly at high propane conversions. As a consequence, the maximum propylene yield of 13.9% was obtained over the 5.6V-HMS-imp catalyst with 5.6 wt% of vanadium. This value was much higher than the literature results obtained over the MCM-41-supported vanadia catalyst [12].

Figure 2 plots the oxidative dehydrogenation of propane over the 5.6V-HMS-imp catalyst as a function of reaction temperature. It is found that the catalytic activity of the

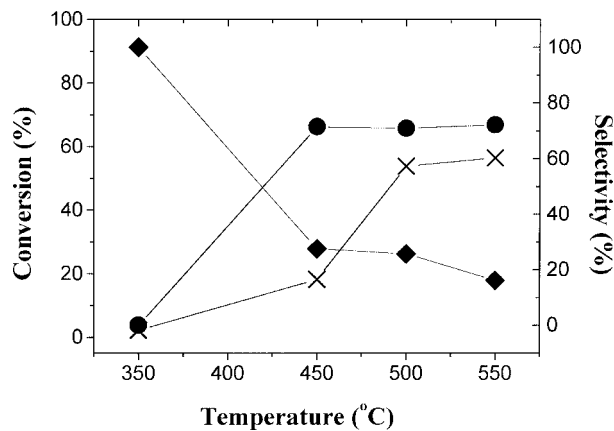


Figure 2. Variation of propane conversion and the selectivity to the main reaction products versus the reaction temperature for the 5.6V-HMS-imp catalyst: conversion of propane (x), selectivity of propylene (♦) and CO<sub>x</sub> (●).

V-HMS-imp catalysts was strongly dependent on the reaction temperature. At reaction temperature lower than 450 °C, the V-HMS catalysts show a very poor catalytic activity. The propane conversion increases rapidly with the reaction temperature, especially at temperature below 500 °C. At the temperature of 550 °C, the propane conversion reaches the highest value. The change behavior of the selectivity to CO<sub>x</sub> is similar to the conversion for propane. In comparison, the continuous decrease of the selectivity to propylene over the temperature range investigated was observed for the 5.6V-HMS-imp catalyst.

### 3.2. Catalyst characterization

The specific surface area ( $S_{BET}$ ) and the cumulative pore volume of the parent HMS have been measured to be 866 m<sup>2</sup> g<sup>-1</sup> and 0.67 cm<sup>3</sup> g<sup>-1</sup>, respectively. Table 2 summarizes the textural results for the low-vanadium-loaded catalysts prepared by various methods. It is seen that the  $S_{BET}$  of the catalysts prepared by the adsorption, impregnation and mechanical mixing methods is lower than that of the unloaded supports and decreases with increasing vanadium content. The results in table 2 also demonstrate that the introduction of the vanadium would cause the loss of the pore volume of the HMS materials. However, both specific surface area and the cumulative pore volume of the structurally incorporated sample (0.88V-HMS-syn) are consid-

Table 2  
Physico-chemical properties of the vanadium-loaded HMS catalysts obtained by different synthetic methods.<sup>a</sup>

Catalyst	$S_{\text{BET}}^{\text{a}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$V_{\text{p}}$ ( $\text{cm}^3 \text{g}^{-1}$ )	Vanadium density ( $\text{VO}_x$ per $\text{nm}^2$ )	$\text{TOF} \times 10^{21}$ ( $\mu\text{mol-C}_3\text{H}_6$ at- $\text{V}^{-1} \text{s}^{-1}$ )
Pure HMS	866	0.67	0	–
0.88V-HMS-syn <sup>a</sup>	1109.6	0.76	0.094	10.15
0.56V-HMS-imp	739.8	0.47	0.089	10.13
1.68V-HMS-mix	725.6	0.46	0.274	3.69
2.09V-HMS-ads	691.9	0.45	0.352	4.78
1.68V-HMS-imp	706.5	0.46	0.281	7.44

<sup>a</sup> This data was obtained after carrying out the ODH reaction of 4 h while other data were obtained at 1 h.

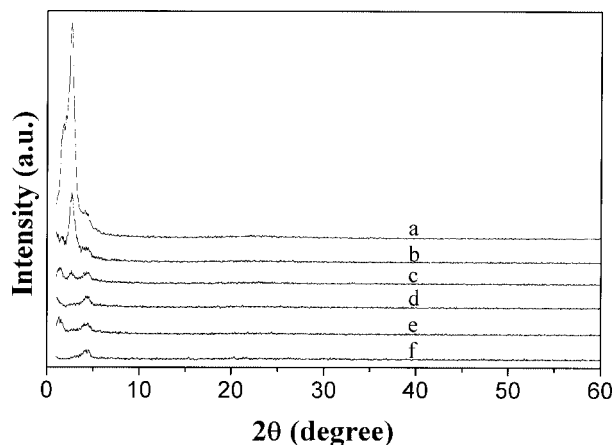


Figure 3. XRD patterns of the  $x$ V-HMS-imp catalysts with different vanadium loading (a) HMS, (b) 1.68 wt%, (c) 2.80 wt%, (d) 5.60 wt%, (e) 8.41 wt% and (f) 16.8 wt%.

erably higher than that of the parent HMS support. The 0.88V-HMS-syn catalyst exhibits high surface area amounts to  $1110 \text{ m}^2 \text{ g}^{-1}$  as well as a large accumulative pore volume of  $0.76 \text{ cm}^3 \text{ g}^{-1}$ . This result suggests that the introduction of vanadium species in the HMS synthesis process may result in beneficial stabilization of the framework of mesoporous HMS. The pore size distribution of the vanadium-loaded HMS materials with low vanadium content shows that the mesoporous structure of the support has been preserved.

The powder X-ray diffraction patterns for the samples prepared by adsorption, incorporation and mechanical mixing methods with low vanadium contents show the characteristic low-angle diffraction peak attributable to the  $d_{100}$  reflection assuming a hexagonal lattice, typical of HMS solids. For the samples prepared by the impregnation method, the gradual attenuation in intensity of the  $d_{100}$  peak was observed with increasing vanadium loading (see figure 3). It is notable that the  $d_{100}$  peak was greatly attenuated on the impregnated samples with vanadium content above 5.6 wt%. This phenomenon may be accountable by considering that the blocking of the hexagonal pore walls of the HMS materials occurred upon vanadium introduction, especially when the vanadium content is very high [16]. In all cases, the absence of diffraction peaks at  $2\theta$  angles higher than  $10^\circ$  seems to exclude the presence of  $\text{V}_2\text{O}_5$  crystallites, thus pointing to a homogeneous distribution of the vanadium species. Dif-

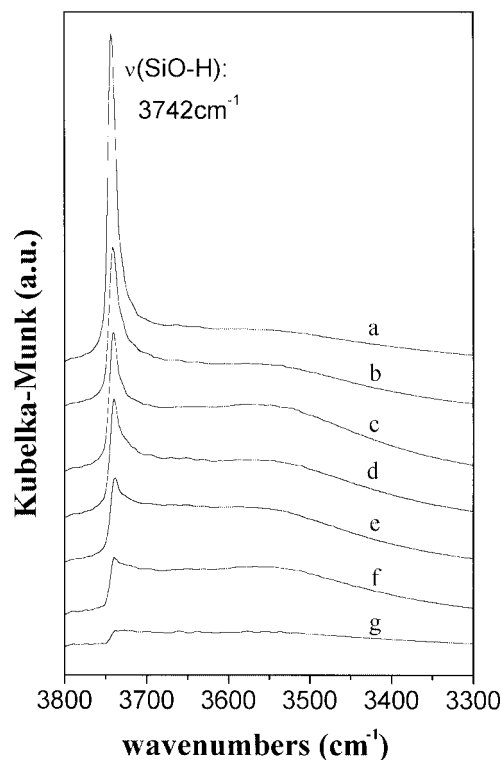


Figure 4. DRIFT spectra of the  $x$ V-HMS-imp catalysts with different vanadium loading: (a) HMS, (b) 0.56 wt%, (c) 1.68 wt%, (d) 2.80 wt%, (e) 5.60 wt%, (f) 8.41 wt% and (g) 16.8 wt%.

fraction features corresponding to crystalline  $\text{V}_2\text{O}_5$  were not detected in all the samples even at the vanadium loading as high as 16.82 wt%. This indicates that the vanadium oxide species can be well dispersed with particle sizes less than 4 nm on the mesoporous HMS supports [17].

Diffuse reflectance FTIR spectroscopy (DRIFTS) has been employed to follow the variation behavior of the hydroxyl groups present on the surface of the impregnated samples as a function of vanadium content. Spectra of the samples under  $\text{N}_2$  atmosphere in the  $3800\text{--}3300 \text{ cm}^{-1}$  range are shown in figure 4. It is shown in figure 4(a) that silanol groups having OH stretching vibrations at  $3742 \text{ cm}^{-1}$  (sharp band),  $3715 \text{ cm}^{-1}$  (shoulder band) and around  $3550 \text{ cm}^{-1}$  (broad band) are clearly identified on pure HMS. The sharp band at  $3742 \text{ cm}^{-1}$  is ascribed to the isolated terminal silanol groups present on the HMS and the bands at 3550 and

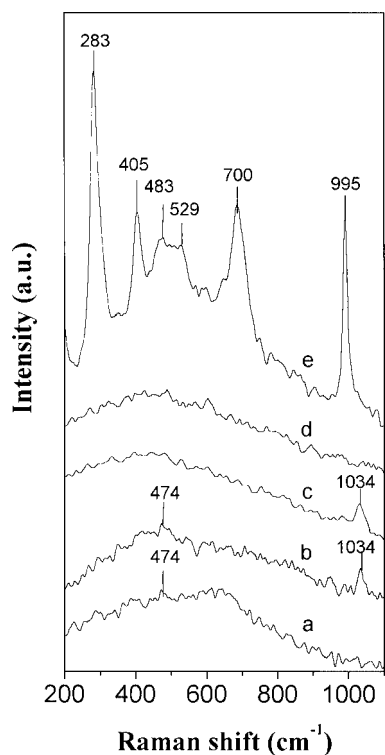


Figure 5. Raman spectra of the V-HMS catalysts prepared by different methods: (a) HMS, (b) 1.68V-HMS-imp, (c) 2.09V-HMS-ads, (d) 0.88V-HMS-syn and (e) 1.68V-HMS-mix.

$3715\text{ cm}^{-1}$  are assigned to silanol groups inside the channels of the HMS with and without strong hydrogen-bonding interactions [18]. The intensity of the band at  $3742\text{ cm}^{-1}$  decreased rapidly as the vanadium loading increases, and almost totally disappeared at 16.8 wt% vanadium loading. 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 in good consistency with the recent results of the vanadium-immobilized MCM-48 silica system obtained by Stucky and co-workers [16].

Laser Raman spectroscopy has been employed to elucidate the molecular nature of the supported vanadium species present on the mesoporous HMS materials. Figure 5(a) shows the Raman spectrum of the pure siliceous HMS that exhibits spectroscopic features similar to amorphous  $\text{SiO}_2$  [19]. Due to the presence of fluorescence interference and low sensitivity in the Raman experiments, the Raman intensity of the pure HMS silica is very weak. Based on previous literature assignments for silicate materials, the weak band at  $474\text{ cm}^{-1}$  is assigned to fourfold siloxane rings [20]. The Raman spectra for the V-HMS catalysts as a function of vanadium incorporation method are shown in figure 5 (b)–(e), respectively. It is seen that the adsorption-derived sample (V-HMS-ads) showed a new band at  $1034\text{ cm}^{-1}$ . The 0.88V-HMS-syn sample exhibited a weaker Raman feature due to the lower vanadium content. This indicates that the vanadium supported on these samples ex-

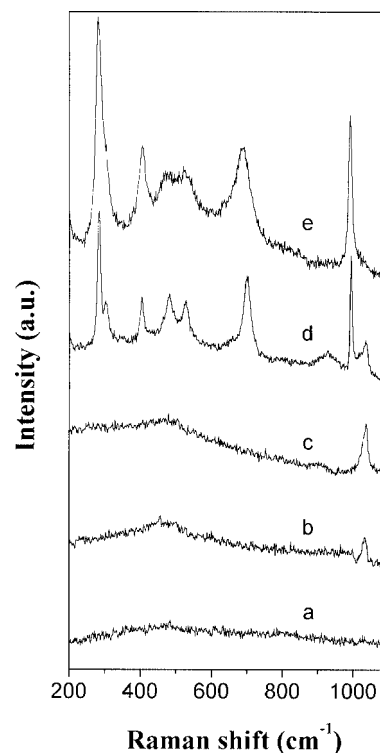
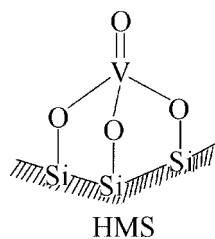


Figure 6. Raman spectra of the  $x$ V-HMS-imp catalyst with different vanadium loading: (a) 1.68 wt%, (b) 2.80 wt%, (c) 5.60 wt%, (d) 8.41 wt% and (e) 16.82 wt%.

ists mainly in the form of isolated vanadium species. Although the XRD results suggest the highly dispersed nature for the vanadium species deposited on the catalyst sample (V-HMS-mix) prepared by calcination after mechanical mixing, strong Raman bands located at 283, 405, 483, 529, 700 and  $995\text{ cm}^{-1}$  (figure 5(e)) have been identified in the Raman spectrum. This is indicative of the presence of microcrystalline  $\text{V}_2\text{O}_5$  in the V-HMS-mix catalyst [21].

Figure 6 illustrates the Raman spectra recorded for the group of HMS catalysts obtained by the wet impregnation method as a function of vanadium content. As shown in figure 6, no Raman features are observed for the samples with low vanadium content of 1.68 wt%. With the increase in vanadium loading, a single band at  $1034\text{ cm}^{-1}$  is seen in the Raman spectrum (figure 6 (b) and (c)), and the intensity increases with the vanadium content. When vanadium content in the sample is above 5.6 wt%, seven additional bands at 283, 303, 405, 483, 529, 700 and  $995\text{ cm}^{-1}$  characteristic of crystalline  $\text{V}_2\text{O}_5$  are detected. The band of  $283\text{ cm}^{-1}$  is assigned to the V–O–V bending mode. Accompanying the observation of the Raman bands associated with bulk  $\text{V}_2\text{O}_5$ , the intensity of the  $1034\text{ cm}^{-1}$  band is attenuated as the content of vanadium is further increased.

Based on the literature assignments, the  $995\text{ cm}^{-1}$  band corresponds to the symmetric stretching frequency of V=O groups present in the bulk [21] while the  $1034\text{ cm}^{-1}$  band is due to the stretching frequency of a terminal V=O group bonded to the HMS support [22]. As a result, the presence of the  $1034\text{ cm}^{-1}$  band unambiguously indicates the existence



Scheme 1.

of isolated vanadium species on the surface of the HMS catalysts. According to the literature, the present isolated vanadium species bonded to the HMS silica support may follow the molecular structure similar to that of the monomeric vanadium species [23] (scheme 1).

It has been well documented that crystalline  $V_2O_5$  can be spontaneously dispersed on some conventional oxide supports from the thermal treatment of the physically mixed sample [24]. In our case, no XRD peaks from crystalline  $V_2O_5$  were detected on the mechanically mixed HMS samples. This seems to point to the highly dispersed nature of the vanadium species over the as-prepared V-HMS-mix catalyst. However, the V-HMS-mix catalyst is observed to exhibit a lower activity than that prepared by impregnation at the same vanadium loading. This can be well explained by the fact that microcrystalline  $V_2O_5$  was present on the V-HMS-mix catalyst as evidenced by the Raman results. The resistance of  $V_2O_5$  dispersion may be due to the repulsion nature between silica and the vanadium species [25].

Turnover frequencies (TOF) for the V-HMS samples prepared *via* various synthetic methods are compared in table 2. In all cases, the vanadium density on all the samples was estimated to be much lower than the monolayer capacity of vanadium on silica ( $1VO_x/nm^2$ ). A quite similar TOF value for propane conversion has been observed over the 0.56V-HMS-imp and 0.88V-HMS-syn catalysts. It therefore seems that, for catalysts with lower vanadium surface density, the vanadium incorporation method has little influence on the catalytic activity of vanadia species. The TOF of 2.09V-HMS-ads and 1.68V-HMS-imp catalysts at relative higher vanadium content were found to be lower than that of the low-vanadium-containing samples. The isolated surface vanadium species have been well established as the active sites in oxidative dehydrogenation of propane [26]. Considering the highly dispersed nature of the vanadium species supported over all catalysts of 0.56V-HMS-imp, 0.88V-HMS-syn, 2.09V-HMS-ads and 1.68V-HMS-imp, it is surprising that 2.09V-HMS-ads and 1.68V-HMS-imp exhibited low TOF values. Here, the influence of the distance on the reaction selectivity over the active sites might be considered to explain the decreased TOF values [17].

#### 4. Conclusions

The mesoporous HMS-silica-supported vanadium catalysts have been prepared and characterized for oxidative dehydrogenation of propane. The mesoporous siliceous HMS

materials have shown to be potential supports for the development of high performance vanadium supported catalysts applicable in ODH reactions. Combined XRD, DRIFTS and Raman results demonstrated that isolated vanadium oxide species with high concentration are well dispersed on the surface of mesoporous HMS silica. The as-prepared vanadium-containing HMS catalysts show a high reactivity as well as selectivity in the oxidative dehydrogenation of propane. Our results show that the highest concentration of isolated vanadium species can be attained at an impregnated catalyst with a 5.6 wt% vanadium content, which allows the selective formation of a maximum propylene yield of  $\sim 13.9\%$  in the oxidative dehydrogenation of propane.

#### References

- [1] R.H.H. Smits, K. Seshan, J.R.H. Ross, L.C.A. van den Oetelaar, J.H.J.M. Helwegen, M.R. Anantharaman and H.H. Brongersma, *J. Catal.* 157 (1995) 584.
- [2] R.B. Watson and U.S. Ozkan, *J. Catal.* 191 (2000) 12.
- [3] S. Sugiyama, Y. Iozuka, E. Nitta, H. Hayashi and J.B. Moffat, *J. Catal.* 189 (2000) 233.
- [4] Q.J. Ge, B. Zhaorigetu, C.Y. Yu, W.Z. Li and H.Y. Xu, *Catal. Lett.* 68 (2000) 59.
- [5] T. Blasco and J.M. López Nieto, *Appl. Catal. A* 157 (1997) 117.
- [6] N. Boisdron, A. Monnier, L. Jalowiecki Duhamel and Y. Barbaux, *J. Chem. Soc. Faraday Trans.* 91 (1995) 2899.
- [7] A.A. Lemonidou, L. Nalbandian and I.A. Vasalos, *Catal. Today* 61 (2000) 333.
- [8] V. Ermini, E. Finocchio, S. Sechi, G. Busca and S. Rossini, *Appl. Catal. A* 198 (2000) 67.
- [9] M. Chaar, D. Patel, M. Kung and H.H. Kung, *J. Catal.* 109 (1988) 463.
- [10] T. Blasco, P. Concepción, J.M. López Nieto and J. Pérez-Pariente, *J. Catal.* 152 (1995) 1.
- [11] L.W. Zatorski, G. Centi, J.M. López Nieto, F. Trifirò, G. Bellusi and V. Fattore, *Stud. Surf. Sci. Catal.* 49 (1989) 1243.
- [12] J. Santamaría-González, J. Luque-Zambrana, J. Mérida-Robles, P. Maireles-Torres, E. Rodríguez-Casllón and A. Jiménez-López, *Catal. Lett.* 68 (2000) 67.
- [13] A. Tuel, *Micropor. Mesopor. Mater.* 27 (1999) 151.
- [14] J.S. Reddy, P. Liu and A. Sayari, *Appl. Catal. A* 148 (1996) 7.
- [15] P.T. Tanev and T.J. Pinnavaia, *Sience* 267 (1995) 865.
- [16] M. Morey, A. Davidson, H. Eckert and G. Stucky, *Chem. Mater.* 8 (1996) 486.
- [17] M.A. Bañares, J.H. Cardoso, F. Agulló-Rueda, J.M. Correa-Bueno and J.L.G. Fierro, *Catal. Lett.* 64 (2000) 191.
- [18] H. Berndt, A. Martin, A. Brückner, E. Schreier, D. Müller, H. Kosslick, G.-U. Wolf and B. Lücke, *J. Catal.* 191 (2000) 384.
- [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. Repelin and G. Lucazezu, *Spectrochim. Acta 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] G. Xiong, C. Li, H.Y. Li, Q. Xin and Z.C. Feng, *J. Chem. Soc. Chem. Commun.* (2000) 677.
- [24] G. Centi, D. Pinelli and F. Trifirò, *Stud. Surf. Sci. Catal.* 67 (1990) 1.
- [25] I.E. Wachs and B.M. Weckhuysen, *Appl. Catal. A* 157 (1997) 67.
- [26] G. Centi, S. Perathoner and F. Trifirò, *Res. Chem. Intermed.* 15 (1991) 49.