available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article

Preparation and catalytic properties of mesoporous nV -MCM-41 for propane oxidative dehydrogenation in the presence of CO_2

Zai-Fang Han, Xu-Liang Xue, Jian-Min Wu, Wan-Zhong Lang *, Ya-Jun Guo

The Education Ministry Key Laboratory of Resource Chemistry and Shanghai Key Laboratory of Rare Earth Functional Materials, Department of Chemistry and Chemical Engineering, Shanghai Normal University, Shanghai 200234, China

ARTICLE INFO

Article history:

Received 31 December 2017

Accepted 9 February 2018

Published 5 June 2018

Keywords:

Propane dehydrogenation

Vanadium oxide

MCM-41

Mesoporous support

Heterogeneous catalysis

ABSTRACT

The nV -MCM-41 catalysts were prepared by one-step hydrothermal synthesis and applied to the oxidative dehydrogenation of propane (ODHP) in the presence of CO_2 . Several state-of-the-art characterization methods were performed to explore the correlation between catalytic performance and the physicochemical characterizations of the catalysts. Because moderate amounts of V species were introduced into the framework of MCM-41, the catalyst maintained a large specific surface area, a highly ordered mesoporous structure, and highly dispersed V active sites (monomeric and dimeric V oxide species), while the high-vanadium-doping catalysts caused an enhancement in the number of acidic sites and V_2O_5 crystallites. The ODHP reaction showed that the 6.8V-MCM-41 (V content 6.8 wt%) catalyst exhibits high activity and stability, and the C_3H_8/CO_2 molar ratio (1:4) was suitable. The promoting effect of CO_2 on the oxidative dehydrogenation of ODHP was demonstrated as the reaction coupling mechanism and "lattice oxygen" mechanism.

© 2018, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Propene is an important petroleum chemical raw material, used mainly in the production of substances such as polypropene, acrylonitrile, acrylic acid, butanol, octanol, and propene oxide. In recent years, the demand for propene has increased markedly because polypropene has become one of the most important general-purpose plastics. Propene is generally co-produced with ethylene by the steam cracking of naphtha and with gasoline by the fluidized catalytic cracking (FCC) of gasoline. These processes are carried out at high temperatures with low propene selectivity and inevitable coke formation [1,2]. Therefore, it is urgent to find a new technology with less energy intensive processes for propene production [3–5].

Many studies dealing with the oxidative dehydrogenation

(ODH) of light alkanes have been recently reported, with oxidants such as O_2 , N_2O , and CO_2 . Kondratenko *et al.* [6,7] reported that $VO_x/\gamma-Al_2O_3$ and $VO_x/MCM-41$ showed high propene selectivity in ODH of propane (ODHP) with N_2O as an oxidant. However, industrialization would be hindered by the deep oxidation of propane and products or by the high cost of N_2O [8,9].

CO_2 acting as a single mild oxidant, which can effectively inhibit deep oxidation and improve the stability of the catalyst, has been widely used in propane dehydrogenation by many researchers. Moreover, the dehydrogenation reaction coupled with the reverse water-gas shift reaction is an attractive approach to improve the equilibrium conversion in the ODHP process [10]. Previous work indicated that CO_2 was advantageous for maintenance of the metal active sites in a high oxidation state for an $NiMoO_4$ catalyst [11]. Nakagawa *et al.* [12] and

* Corresponding author. Tel/Fax: +86-21-64321951; E-mail: wzlang@shnu.edu.cn

This work was supported by the Ministry of Education of China (PCSIRT_IRT_16R49) and the International Joint Laboratory on Resource Chemistry (IJLRC).

DOI: 10.1016/S1872-2067(18)63048-7 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 39, No. 6, June 2018

Fukudome *et al.* [13] reported that the use of CO₂ as an oxidant markedly promoted the dehydrogenation of propane over the oxidized diamond-supported Cr₂O₃ and V₂O₅ catalysts and over the lattice oxygen of V oxide.

Ordered mesoporous materials are widely employed in the fields of catalysis, adsorption, and biochemistry. The high surface area of ordered mesoporous materials allows the potentially efficient dispersion of active sites, and the uniform pore size in the mesoporous range favors the diffusion of bulky molecules. Among them, MCM-41 has been widely used since it was first reported in 1992 by Mobil Oil Corp. [14,15]. However, MCM-41 in its pure siliceous form shows limited applications in catalytic organic transformations due to a lack of active sites [16,17]. Hence, modification is necessary, which is achieved by incorporating active components into the MCM-41 framework. Many metals have been incorporated into the MCM-41 framework. V has been verified as the active and selective active center in ODHP [18–20]. Shylesh *et al.* [18] reported that V-based catalysts displayed excellent activity toward the epoxidation reaction of bulkier olefins. The V-MCM-41 samples also showed good catalytic performance for the selective oxidation of styrene using hydrogen peroxide as an oxidant [16].

Metal-modified mesoporous silica can be synthesized by either a one-step co-condensation method or post-synthesis treatment. With the one-step method, the active species can be directly incorporated into the pore channels and are better dispersed compared with the impregnation method, contributing to higher catalytic performance.

The reaction mechanism of ODHP by V oxide catalysts supported on silica was examined by density-functional theory (DFT) [19,21]. The active sites are the highly dispersed VO_x species, which can be classified as monomeric and two-dimensional oligomeric V oxide species below the monolayer coverage [22–24]. The reaction involved two-hydrogen abstraction [19]. Single-crystal V₂O₅ (001) was not a good catalyst because the terminal O was too active to release the propene [20], and the bulk V₂O₅ crystallites of three-dimensional particles exhibited low catalytic activity. Therefore, it is expected that V oxide species can be tuned by controlling the extent of their polymerization.

The aim of this work is to synthesize and characterize *n*V-MCM-41 mesoporous molecular sieves and investigate the effects of different V amounts in ODHP in the presence of CO₂. The *n*V-MCM-41 catalysts were prepared by a one-step hydrothermal synthesis. The framework structure, texture, thermal stability, and hydrothermal stability of *n*V-MCM-41 materials were investigated. The selective oxidation of propane was conducted to investigate the potential catalytic applications of the *n*V-MCM-41 sample, and it showed good stability.

2. Experimental

2.1. Catalyst preparation

The catalyst was synthesized by a one-step hydrothermal method using tetraethyl orthosilicate (TEOS) as the silica source and cetyltrimethyl ammonium bromide (CTAB) as the

template. The synthesis steps are as follows. In a typical process, a certain amount of NH₄VO₃ (0.17–0.95 g) was dissolved in 30 mL of deionized water, and 2.5 g of CTAB and 0.4 g of NaOH were dissolved in 150 mL of deionized water. After complete dissolution, the NH₄VO₃ solution was added to the template solution under mechanical stirring. After approximately 30 min, 16.8 mL of TEOS was added dropwise to the mixed solution under mechanical stirring. After stirring for 4 h at 60 °C, the synthesis gel was cooled overnight and then transferred into a Teflon™-lined autoclave and aged at 120 °C for 48 h. The obtained materials were centrifuged, washed five times, dried at 60 °C for 12 h, and then calcined at 550 °C for 4 h. The samples were denoted *n*V-MCM-41, where *n* represents different amounts of V doping varying from 1.9 to 10.6 wt% (ICP results).

2.2. Catalyst characterizations

The V and Si contents in *n*V-MCM-41 were recorded using ICP-AES with a Varian Vista MPX.

The X-ray diffraction (XRD) patterns of *n*V-MCM-41 catalysts were collected on a Bragg-Brentano diffractometer (D/Max-2000, Rigaku Corp., Japan) with monochromatic Cu K_α radiation ($\lambda = 1.5418 \text{ \AA}$). The samples were scanned from 2 θ values of 10° to 60° with a scan speed of 5°/min and from 0.5° to 6° with a scan speed of 0.5°/min. The X-ray tube was manipulated at 40 kV and 30 mA.

The specific surface area, total pore volume, and average pore diameter were measured at –196 °C by the N₂ adsorption-desorption method with an automatic analyzer (NOVA 4000, Quantachrome, Inc., USA). The samples were degassed in a vacuum at 300 °C for 4 h prior to analysis. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method. The total pore volume was calculated from the amount of vapor adsorbed at a relative pressure (P/P_0) close to unity. Pore-size distributions were obtained using the Barrett-Joyner-Halenda (BJH) model.

Fourier transform-infrared (FTIR) spectra of the catalysts were measured using the KBr wafer technique in a Nicolet 3800 FTIR spectrometer (Nicolet Corp., USA). The IR spectra were recorded in the range 4000–400 cm^{–1}.

Raman spectra were recorded using a Jobin Yvon confocal laser Raman system (SuperLabRam II), which was equipped with a He-Ne laser at 632.8 nm with a power of approximately 5 mW. Each spectrum was obtained by three accumulations, and the acquisition time was set at 30 s.

Ultraviolet-visible (UV-vis) spectra of the catalysts were recorded by the diffuse reflectance technique using a spectrophotometer (MPC-3100, Shimadzu, Corp., Japan) in the range 200–600 nm, using BaSO₄ as the reference.

Field-emission scanning-electron-microscopy (FESEM) images of the catalysts were obtained for the analysis of the morphologies of surface particles of mesoporous samples using an S4800 scanning electron microscope.

Transmission-electron-microscopy (TEM) investigations of *n*V-MCM-41 catalytic materials were performed for morphology determinations on a JEM-2010 field-emission transmission

electron microscope operated at 200 kV in a vacuum.

X-ray photoelectron spectroscopy (XPS) was used to analyze the binding-energy values and atomic surface concentration of metal. The XPS measurements were recorded on a Perkin-Elmer PHI 5000C ESCA X-ray photoelectron spectrometer using Al $K\alpha$ radiation. All samples were reduced *in situ* under an H_2 atmosphere at 580 °C for 2.5 h to improve the dispersion of the surface V species. The samples were calibrated using the C 1s binding energy at 284.8 eV as an internal standard.

Temperature-programmed desorption (TPD) of NH_3 and CO_2 measurements was implemented to analyze the acidity and alkalinity of the catalysts. The sample (~0.1 g) was pretreated at 400 °C for 1 h under a helium flow (30 mL/min) before being cooled to 120 °C and saturated with adsorbed gas. After NH_3 adsorption, the sample was purged with He for 15 min. During desorption, a thermal conductivity detector (TCD) was employed to record the TPD profiles from 120 to 800 °C, with a heating rate of 10 °C/min.

Temperature-programmed reduction (TPR) experiments were carried out for the catalysts in a programmable temperature system. The H_2 TPR analysis was tested on a Quantachrome IQ system. The sample (0.1 g) was filled in a quartz reactor, which was heated in a temperature-programmed furnace from room temperature to 800 °C (10 °C/min). The reducing gas was a mixture of H_2 and Ar gas (10% H_2). The H_2 consumption as a function of the reduction temperature was continuously monitored with a TCD cell and recorded.

The samples used for thermogravimetric (TG) analysis were dried at 50 °C in air. TG analysis of the catalysts was performed on a Shimadzu DTG-60H thermogravimetric analyzer. The sample (0.003–0.005 g) was kept under a N_2 atmosphere. The temperature was increased from room temperature to 800 °C at a rate of increase of 20 °C/min.

2.3. Catalytic tests for ODHP reactions

Catalytic tests were performed in a fixed-bed quartz reactor, which was packed with 0.2 g of catalyst with silica wool at at-

mospheric pressure. The temperature in the fixed bed of catalyst particles was monitored with an axially movable thermocouple located inside a quartz capillary. The feed flow consisted of C_3H_8 , CO_2 , and Ar ($C_3H_8/CO_2/Ar$ molar ratio 1/4/4, WHSV = 1.0 h⁻¹). The reaction temperature was controlled at 600 °C. The products were analyzed by gas chromatography (GC, SP-6980). After the reaction, the reactor was cooled to room temperature with pure Ar. The gaseous products (CO and CO_2) were detected by an online TCD and the other products (CH_4 , C_2H_4 , C_2H_6 , C_3H_6 , and C_3H_8) by an FID chromatographic system. The conversion of propane, the selectivity of propene, and the conversion of CO_2 were calculated as follows:

$$C_3H_8 \text{ conversion} = \frac{C_{3H_8 \text{ in}} - C_{3H_8 \text{ out}}}{C_{3H_8 \text{ in}}} \times 100\%$$

$$C_3H_6 \text{ selectivity} = \frac{C_{3H_6 \text{ out}}}{C_{3H_8 \text{ in}} - C_{3H_8 \text{ out}}} \times 100\%$$

$$CO_2 \text{ conversion} = \frac{CO_{2 \text{ in}} - CO_{2 \text{ out}}}{CO_{2 \text{ in}}} \times 100\%$$

where $C_{3H_8 \text{ in}}$ and $C_{3H_8 \text{ out}}$ are the contents of propane in the inlet and outlet streams, respectively, $C_{3H_6 \text{ out}}$ is the content of propylene in the outlet stream, and $CO_{2 \text{ in}}$ and $CO_{2 \text{ out}}$ are the contents of CO_2 in the inlet and outlet streams, respectively.

3. Results and discussion

3.1. Mesoporous structure of *n*V-MCM-41 samples

The small-angle XRD patterns of *n*V-MCM-41 catalysts are shown in Fig. 1(a). One intense peak at $2\theta \approx 2^\circ$ is due to the reflection from the (100) plane of MCM-41. Apart from this, two weak peaks are found in the 2θ range of approximately 4° and can be assigned to the (100) and (200) planes, indicating that long-range order of this mesoporous structure is obtained [25]. With the loading of V in the samples, the intensity of the diffraction peaks decreases, and the main peak is widened, which could affect the ordered pore network of the samples or lead to a decrease in their crystallinity. As shown in Table 1, there is an increase in unit-cell parameter (a_0) owing to the replacement of Si^{4+} (Pauling radius 42 pm) by V^{5+} (Pauling ra-

Fig. 1. Small-(a) and wide-angle (b) XRD patterns of *n*V-MCM-41 samples.

Fig. 2. N₂ adsorption-desorption isotherms of *nV*-MCM-41 samples.

dus 54 pm) as reported in the literature [16,26]. When the V concentration reaches 10.6 wt%, the pore structure of MCM-41 is partially destroyed. This may be due to bulk V oxides blocking the molecular sieve pores and/or to partial collapse of the pore structure.

Figure 1(b) shows the wide-angle XRD patterns of V₂O₅ samples and *nV*-MCM-41 catalysts with varied V contents. In contrast, the samples below 8.8 wt% V content show no characteristic peaks of V₂O₅, suggesting that the V species at low concentrations still exists in an amorphous state, and that V species may be incorporated into the silicate framework or highly dispersed on the surface of mesoporous channels, while the 10.6V-MCM-41 sample shows diffraction peaks of V₂O₅. It can be concluded that the V content is the key factor that determines whether aggregation or formation of bulk V₂O₅ crystallites occurs.

The N₂ adsorption-desorption isotherms are shown in Fig. 2. Typical type-IV isotherms are observed. The capillary condensation shows a sharp increase in the relative pressure (P/P_0) of approximately 0.4 for all *nV*-MCM-41 catalysts, suggesting typical mesoporous structure with uniform pore diameter, and the overall mesoporous structure is well maintained after the addition of V species.

The physical properties, including the specific surface areas (A_{BET}), pore diameters (d_p), and pore volumes (V_p) of

Fig. 3. FTIR spectra of *nV*-MCM-41 samples.

nV-MCM-41 and pure MCM-41 are listed in Table 1. A_{BET} and V_p decrease when an increasing amount of V is incorporated, while d_p maintains a relatively stable size. These behaviors can be ascribed to the formation of V-containing species in the pores, which expand the pore structure [19]. When the V concentration increases to 10.6 wt%, A_{BET} decreases significantly, which can be attributed to the formation of V₂O₅ nanoparticles in the pore system, which block the channels; this is consistent with the following Raman spectroscopy results.

3.2. Physico-chemical characterizations of *nV*-MCM-41 catalysts

The FTIR spectra of the catalysts are shown in Fig. 3; the absorption bands at 802 and 1078 cm⁻¹ over all the catalysts are the Si–O–Si external asymmetric stretching vibration and external symmetric stretching vibration [27], respectively, indicating that the silica framework remains unaffected in terms of V doping. The bands at 458 and 565 cm⁻¹ are due to the Si–O–Si internal tetrahedron vibration absorption peak. The bands at around 1635 and 3465 cm⁻¹ are attributed to the bending vibration of water molecules and the existence of an organic template (CTAB) [28,29]. The characteristic peak of Si–O–V bonding at 960 cm⁻¹ is obscured by the strong Si–O–Si vibrational band of *nV*-MCM-41 [27], which can be taken as

Table 1

Characteristics of synthesized *nV*-MCM-41 and pure MCM-41 samples.

Catalyst	Si/V ^a (molar ratio)	Si/V ^b (molar ratio)	A_{BET}^c (m ² /g)	d_p (nm)	V_p (cm ³ /g)	d_{100} (nm)	a_0^d (nm)	t_w^e (nm)
MCM-41	—	—	1231	2.89	1.061	3.88	4.48	1.59
1.9V-MCM-41	56.98	52.63	1211	2.90	0.960	3.93	4.54	1.64
3.7V-MCM-41	30.46	27.03	1126	2.91	0.890	3.94	4.55	1.64
4.8V-MCM-41	22.35	20.83	959	2.85	0.852	3.96	4.57	1.60
6.8V-MCM-41	15.58	14.71	904	2.93	0.799	3.97	4.58	1.65
8.8V-MCM-41	12.65	11.36	624	2.86	0.694	4.10	4.73	1.87
10.6V-MCM-41	10.61	9.43	208	3.07	0.667	4.36	5.03	2.06

^a In preparation by direct hydrothermal methods; ^b ICP results; ^c BET method using desorption branch; ^d Unit-cell parameter $a_0 = 2d_{100}/3^{1/2}$;

^e Wall thickness $t_w = a_0 - d_p$.

Fig. 4. Raman spectra of pure MCM-41 and *n*V-MCM-41 samples.

proof of the incorporation of V atoms in the V-MCM-41 framework [30,31]. The difference between *n*V-MCM-41 catalysts and pure MCM-41 will be further discussed below.

Raman spectra clearly reveal the differences in *n*V-MCM-41 catalysts, as shown in Fig. 4. All the samples have weaker Raman bands at 488, 600, and 836 cm^{-1} , which are attributed to the SiO_2 support [32]. The band at 1023 cm^{-1} appears in all samples, except for pure MCM-41, and is assigned to the $\text{V}=\text{O}$ stretching vibration of isolated monovanadate VO_4^{3-} [31]. With the increase in V loading, the peak intensity at the 1023- cm^{-1} band increases obviously, and new bands appear gradually at 144, 283, 303, 405, 482, 525, 702, and 997 cm^{-1} , which correspond to V_2O_5 crystallites [32,33]. The sample containing 6.8 wt% V loading has no peak at 997 cm^{-1} , which is attributed to highly dispersed VO_4^{3-} and the absence of V_2O_5 crystallites. With the increase in V loading (8.8 and 10.6 wt%), the peak intensity at 997 cm^{-1} increases strongly since V_2O_5 crystallites gradually accumulate and cover the V-MCM-41. In particular, the catalysts above 6.8-wt% V loading show additional signals at 997 cm^{-1} , and the peak intensity at 1023 cm^{-1} for the

Fig. 5. UV-vis spectra of *n*V-MCM-41 samples.

Fig. 6. XPS analysis of *n*V-MCM-41.

6.8-MCM-41 catalyst is stronger than the catalysts with lower V contents. It is obvious that the 6.8V-MCM-41 catalyst has better V dispersion than the others, which is consistent with the XPS results.

Figure 5 shows the UV-vis spectra of *n*V-MCM-41 catalysts. The presence of intense absorption bands at 261 nm is associated with the $\text{V}-\text{O}-\text{V}$ characteristic absorption band, which is likely due to the $d-d$ charge transfer belonging to highly dispersive tetrahedrally coordinated V^{5+} species incorporated into the silicate framework [34]. The bands at approximately 376 nm are assigned to extra-framework V^{5+} species in distorted octahedral coordinations [35]. The weak absorption bands at 690 nm also indicate the formation of polymeric $\text{V}-\text{O}-\text{V}$ bonds, and dehydrated samples do not have this band [23,31]. The crystalline V_2O_5 exhibits UV-vis absorption over a broad spectral range (220–600 nm), with an instance of V_2O_5 crystal phase in the samples [36]. Therefore, the samples of less than 8.8-wt% V doping suggest the presence of tetrahedrally coordinated V, whereas the higher V doping (10.6 wt%) contains a large amount of V_2O_5 or pentahedrally coordinated V, which is consistent with the wide-angle XRD results.

The XPS technique was applied to analyze the chemical state of elements and the surface composition of the *n*V-MCM-41 catalysts. Fig. 6 shows the XPS spectra of three representative samples. The bands at 515.9 and 517.4 eV of the $\text{V } 2p_{3/2}$ binding energies (BEs) can be assigned to V^{3+} and V^{5+} , respectively. The band at 518.8 eV is attributed to highly dispersed isolated VO_4^{3-} [31]. As can be seen in Table 2, the peak area percentage at 518.8 eV attains a maximum value of 43% for 6.8V-MCM-41, indicating that the sample has better V dispersion than others.

Table 2
XPS results of *n*V-MCM-41 catalysts.

Catalyst	Binding energy (eV)			Si/V ^a
3.7V-MCM-41	515.9 (20%) ^b	517.0 (41%)	518.1 (39%)	52.55
6.8V-MCM-41	515.9 (23%)	517.1 (34%)	518.1 (43%)	38.67
8.8V-MCM-41	516.0 (24%)	517.4 (54%)	518.5 (22%)	22.87

^a Si/V molar ratio by XPS.

^b Values in brackets are fractions.

This result is consistent with the results of the wide-angle XRD and Raman analyses. Compared with Table 1, the Si/V molar ratio of the V-MCM-41 sample determined by XPS (obtained from the surface) is much higher than that determined by ICP, which indicates that most VO_x species tend to disperse in the silicate framework instead of the support surface.

The TG curves of the catalysts are shown in Fig. 7. The weight loss at approximately 100 °C can be ascribed to the loss of surface water, and the weight loss between 200 °C and 450 °C can be assigned to the decomposition of residual template surfactant [37], which results from the association of $\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{N}^+$ with Si-O groups from the surface of the inorganic wall [38]. The weight loss between 450 and 600 °C is attributed to the loss of residual template agent connecting to the center of Si-O-V [39,40], and that above 600 °C is considered to be the result of the removal of water from the condensation of nearby silicon hydroxyl, namely, the dehydroxylation reaction. The weight is almost stable over 600 °C. However, the distribution of successive weight losses depends on the framework or on the substituted Si-to-metal ratio [41].

The reduction behavior of the V oxide species doped on MCM-41 was studied using the H_2 -TPR technique. Fig. 8 shows a gradual increase of hydrogen consumption at approximately 525–550 °C, which is mainly attributed to the amount of V and the reduction of monomeric and oligomeric tetrahedral-like coordinated VO_x species [42–44]. The samples with lower V loading exhibit lower reduction temperatures. The wide-angle XRD and Raman results verify the formation of bulk V_2O_5 or the degree of polymerization of V oxide at high V doping. Therefore, at high V doping, the $n\text{V-MCM-41}$ catalysts exhibit a high-temperature reduction peak. This is the most important reason for the decrease in catalytic activity for ODHP.

The acidic characteristics of the supported $n\text{V-MCM-41}$ catalysts were investigated by NH_3 -TPD, and the results are shown in Fig. 9. It is well known that the dehydrogenation performance of light paraffin is closely related to the acidic properties of a catalyst's surface [28,45]. Obviously, all the catalysts supported on mesoporous silica MCM-41 show a relatively sharp desorption peak from 130–260 °C, which is ascribed to weak Lewis acid sites of the isolated tetrahedral-like coordinated VO_x

Fig. 7. TG curves of $n\text{V-MCM-41}$ samples.

Fig. 8. H_2 -TPR profiles of $n\text{V-MCM-41}$ catalysts.

species [46–49]. The desorption peaks at 260–500 °C and above 500 °C can be ascribed to medium and strong acid sites, respectively. With increasing V doping, it can be seen from the profiles that the intensities of weak- and medium-acid desorption peaks increase and move to the high-temperature zone, indicating the increase in weak- and medium-acid sites. These results imply that the acidity can be improved by increasing V doping.

3.3. Morphology

FESEM images of samples with different V contents are shown in Fig. 10. It can be seen that pure MCM-41 mainly exists as spherical particles with a particle size distribution of 150–250 nm. With a small amount of V doping (1.9 and 3.7 wt%), the spherical particle size becomes large. After the introduction of V species, the morphology of the samples changes from ordered spherical particles to disordered morphologies. During the hydrolytic process, V ions may contact the silica source and be incorporated into the framework, resulting in a

Fig. 9. NH_3 -TPD profiles of $n\text{V-MCM-41}$ samples.

Fig. 10. FESEM images of *n*V-MCM-41 catalysts.

change in catalyst morphology.

TEM images of the 6.8V-MCM-41 sample are displayed in Fig. 11. When the electron beam falls on the sample perpendicular to the pore channel, the pores are seen to be arranged in patches composed of regular rows; when the electron beam is parallel to the pore channel axis, a hexagonal array with a channel dimension of approximately 3 nm is revealed. The TEM images reveal that the highly ordered nanoporous structure of MCM-41 is preserved after loading V oxide into the silicate framework, which is entirely consistent with the small angle XRD and BET results.

3.4. Catalytic performance of *n*V-MCM-41 catalysts in the ODHP reaction

3.3.1. Effect of amounts of V doping

The catalytic activity of *n*V-MCM-41 and pure MCM-41 on the ODHP reaction was evaluated and the results presented in Fig. 12. The pure MCM-41 exhibits very low catalytic activity and propene selectivity. With the loading of V, propane conversion and propene selectivity are both markedly enhanced, and

Fig. 11. TEM images of 6.8V-MCM-41. (a) Parallel to pore direction; (b) Perpendicular to pore channel.

propane conversion gradually increases as the V content increases, until 6.8 wt% is reached. For the 6.8V-MCM-41 catalyst, an initial propane conversion of 58% accompanied by a propene selectivity of ~92% is obtained. When the V doping exceeds 6.8 wt%, the propane conversion gradually decreases for 8.8V-MCM-41 and 10.6V-MCM-41 catalysts, suggesting that over-high vanadium loading in the MCM-41 framework is disadvantageous to propane oxidative dehydrogenation, possibly due to the formation of V_2O_5 crystallites [28,50]. This has been verified by the wide-angle XRD and Raman results. It has been suggested that metal species of octahedrally coordinated V_2O_5 have low activity in the dehydrogenation reaction because of the lack of free coordination sites [24]. As reported in the previous work [51], with a similar V content, mesoporous SBA-15-supported V oxide catalysts exhibited a propane conversion of 40% accompanied by a propene selectivity of ~57% under similar reaction conditions. It is clear that the 6.8V-MCM-41 catalyst exhibits much higher C_3H_8 conversion and propene selectivity than mesoporous, traditional silica-supported VO_x catalysts. The excellent catalytic performance could be related to highly dispersed V oxide on the large specific surface of MCM-41 with a highly ordered mesoporous

Fig. 12. Propane conversion (a) and propene selectivity (b) as a function of time for different catalysts. Reaction conditions: $T = 600\text{ }^{\circ}\text{C}$, $m_{\text{cat}} = 0.2\text{ g}$, $C_3H_8/CO_2/Ar$ (molar ratio = 1/4/4), total flow rate = 15 mL/min.

Fig. 13. CO₂ conversion of 6.8V-MCM-41 catalysts. Reaction conditions: $T = 600\text{ }^{\circ}\text{C}$, $m_{\text{cat}} = 0.2\text{ g}$, $\text{C}_3\text{H}_8/\text{CO}_2/\text{Ar}$ (molar ratio) = 1/4/4, total flow rate = 15 mL/min.

structure, as described by the BET results. The NH₃-TPD results indicate that high V doping increases the number of acidic sites, which reduces propene release from the V active sites, resulting in deep oxidation and carbon deposition.

3.3.2. Effect of CO₂ partial pressure on the ODHP reaction

Fig. 13 shows the CO₂ conversion in the ODHP reaction over 6.8V-MCM-41 catalysts. It can be seen that CO₂ conversion is maintained at 10% throughout the reaction period, which is the same as other $n\text{V-MCM-41}$ catalysts (1.9–10.6 wt% V doping). The reaction mechanism of oxidative dehydrogenation in the presence of CO₂ includes a reaction coupling mechanism [52,53] and a “lattice oxygen” mechanism [54,55], which can be expressed as the reaction coupling of simple propane dehydrogenation with the reverse water-gas shift (RWGS) reaction and the lattice oxygen of isolated tetrahedral VO₄³⁻. It is illustrated in Scheme 1.

The reason that the highest catalytic activity of 6.8V-MCM-41 has a high degree of dispersion of isolated VO₄³⁻ has been verified by Raman and XPS analysis. Scheme 1 shows the reaction and regeneration scheme for the CO₂ oxidative dehydrogenation over $n\text{V-MCM-41}$ catalysts. In the first step,

Scheme 1. Reaction and regeneration cycle mechanism for the CO₂ oxidative dehydrogenation of $n\text{V-MCM-41}$ catalysts.

the O of a vanadyl (O=V) group abstracts a H atom from a secondary C atom of propane. The second H abstraction occurs at the oxygen of the V–O–Si bond, yielding H₂O–V^{III}, or at a fresh vanadyl (O=V) group, yielding two HOV^{IV} species; propene is then released from the V active site. A similar process has been reported by DFT calculation and microkinetic simulation [21].

In this reaction cycle, the presence of CO₂ can make the RWGS reaction proceed toward CO generation, and propene production increases. CO₂ acting as a mild oxidant also prevents the decrease of active sites, which is due to the fast re-oxidation of V³⁺ to V⁵⁺.

Fig. 14 shows the effect of CO₂ partial pressure on 6.8V-MCM-41 catalysts. As can be seen from Fig. 14, propane conversion and propene selectivity significantly increase in the presence of CO₂. With increasing CO₂/C₃H₈ ratios, propane conversion increases gradually, while propene selectivity exhibits almost no variation. Propane conversion with a C₃H₈/CO₂ molar ratio of 1:5 is similar to that with a C₃H₈/CO₂ molar ratio of 1:4 in Fig. 12. It has been verified that moderately increasing the C₃H₈/CO₂ ratio (1:4) is advantageous to the catalytic activity on the propane dehydrogenation reaction, as described in Scheme 1.

Fig. 14. Effect of CO₂ partial pressure on the catalytic performance of 6.8V-MCM-41 catalysts. Reaction conditions: $T = 600\text{ }^{\circ}\text{C}$, $m_{\text{cat}} = 0.2\text{ g}$, $\text{C}_3\text{H}_8/\text{CO}_2/\text{Ar}$ (molar ratio) = 1/ n_1 / n_2 ($n_1 = 1, 3, 5$; $n_2 = 7, 5, 3$), total flow rate = 15 mL/min.

Fig. 15. Reaction-regeneration performance of the 6.8V-MCM-41 catalyst. Reaction conditions: $T = 600\text{ }^{\circ}\text{C}$, $m_{\text{cat}} = 0.2\text{ g}$, $\text{C}_3\text{H}_8/\text{CO}_2/\text{Ar}$ (molar ratio) = 1/4/4, total flow rate = 15 mL/min.

3.3.3. Recycling of catalysts

Figure 15 shows the regeneration performance of the 6.8V-MCM-41 catalyst. After the reaction-regeneration study with four cycles, the catalyst still shows good reactivity. Propane conversion and propene selectivity are almost the same as the initial reactions because the lattice oxygen of isolated VO_4^{3-} is almost completely restored after regeneration by O_2 at $550\text{ }^{\circ}\text{C}$. The regeneration cycle mechanism is demonstrated in Scheme 1. The regeneration performance also benefits from the superior thermal stability of the $n\text{V-MCM-41}$ mesoporous silicon framework, which has been proved by TG analysis. As shown in Fig. 15, propane conversion decreases to approximately 40% after the first 120 min period. This decrease is mainly due to the reduction of the active V sites, which is displayed in Scheme 1. To further investigate the causes of catalyst deactivation, TG analysis of the deactivated 6.8V-MCM-41 catalyst after 120 min of the ODHP reaction was carried out, and the results are shown in Fig. 16. The weight decrease below $200\text{ }^{\circ}\text{C}$ can be ascribed to the loss of surface adsorption water. The weight loss in the range $200\text{--}350\text{ }^{\circ}\text{C}$ can be attributed to

Fig. 16. TGA curve of spent 6.8-MCM-41 catalyst.

coke deposits formed on the surface of the VO_x sites [56]. Coke deposited directly on the surface of active VO_x sites shields them from propane, and consequently, results in catalyst deactivation [57]. The deactivation of catalysts in the ODHP reaction is caused by the reduction of the active V sites and coke deposits formed on the surface of VO_x sites. These factors can be eliminated by oxidative regeneration, and excellent catalytic activity of the 6.8V-MCM-41 catalyst can be maintained after four cycles.

4. Conclusions

The catalytic performance of $n\text{V-MCM-41}$ catalysts prepared by one-step methods was examined in ODHP using CO_2 as an oxidant. The results of XRD, BET, SEM, and TEM analyses confirm that the $n\text{V-MCM-41}$ catalysts maintain a highly ordered mesoporous structure, except for the catalysts with excessively high V loading, which partially destroys the pore structure of MCM-41. FTIR, UV-vis, XPS, Raman, and H_2 -TPR analyses prove the existence of highly dispersed, isolated tetrahedral VO_4^{3-} active sites. As V is doped into the framework of MCM-41, the catalysts maintain a high specific surface area and superior thermal stability. The 6.8V-MCM-41 catalyst exhibits highly active and stable catalytic performance for ODHP, which is due to the high dispersion of isolated VO_4^{3-} . However, upon further increasing the V loading (8.8 and 10.6 wt%), the number of acidic sites and V_2O_5 crystallites increases, which reduces the reaction activity. It is verified that moderately increasing the $\text{C}_3\text{H}_8/\text{CO}_2$ ratio (1:4) of steam is advantageous to the catalytic activity in ODHP. It is worth mentioning that the $n\text{V-MCM-41}$ catalyst performs very well even after four oxidative regenerations.

References

- [1] D. Vitry, J. L. Dubois, W. Ueda, *J. M. Catal. A*, **2004**, 220, 67–76.
- [2] C. A. Carrero, R. Schloegl, I. E. Wachs, R. Schomaeker, *ACS Catal.*, **2014**, 4, 3357–3380.
- [3] M. M. Bettahar, G. Costentin, L. Savary, J. C. Lavalley, *Appl. Catal. A*, **1996**, 145, 1–48.
- [4] M. A. Chaar, D. Patel, M. C. Kung, H. H. Kung, *J. Catal.*, **1987**, 105, 483–498.
- [5] T. Blasco, J. M. L. Nieto, *Appl. Catal. A*, **1997**, 157, 117–142.
- [6] E. V. Kondratenko, M. Cherian, M. Baerns, D. Su, R. Schloegl, X. Wang, I. E. Wachs, *J. Catal.*, **2005**, 234, 131–142.
- [7] E. V. Kondratenko, A. Brückner, *J. Catal.*, **2010**, 274, 111–116.
- [8] Y. M. Liu, W. L. Feng, T. C. Li, H. Y. He, W. L. Dai, W. Huang, Y. Cao, K. N. Fan, *J. Catal.*, **2006**, 239, 125–136.
- [9] S. A. Karakoulia, K. S. Triantafyllidis, A. A. Lemonidou, *Microporous Mesoporous Mater.*, **2008**, 110, 157–166.
- [10] Y. Wang, Y. Ohishi, T. Shishido, Q. H. Zhang, W. Yang, Q. Guo, H. L. Wan, K. Takehira, *J. Catal.*, **2003**, 220, 347–357.
- [11] F. Dury, E. M. Gaigneaux, P. Ruiz, *Appl. Catal. A*, **2003**, 242, 187–203.
- [12] K. Nakagawa, C. Kajita, N. Ikenaga, M. Nishitani-Gamo, T. Ando, T. Suzuki, *Catal. Today*, **2003**, 84, 149–157.
- [13] K. Fukudome, N. Ikenaga, T. Miyake, T. Suzuki, *Catal. Sci. Technol.*, **2011**, 1, 987.
- [14] C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck,

Graphical Abstract

Chin. J. Catal., 2018, 39: 1099–1109 doi: 10.1016/S1872-2067(18)63048-7

Preparation and catalytic properties of mesoporous *nV*-MCM-41 for propane oxidative dehydrogenation in the presence of CO₂

Zai-Fang Han, Xu-Liang Xue, Jian-Min Wu, Wan-Zhong Lang *, Ya-Jun Guo
Shanghai Normal University

nV-MCM-41 catalysts prepared by the one-step method maintain highly ordered mesoporous structures and large specific surface areas. The 6.8V-MCM-41 catalysts exhibit highly dispersed V oxide and excellent catalytic performance in the oxidative dehydrogenation of propane.

- Nature*, **1992**, 359, 710–712.
- [15] J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T. W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins, J. L. Schlenker, *J. Am. Chem. Soc.*, **1992**, 114, 10834–10843.
 - [16] J. Xu, W. Chu, S. Z. Luo, *J. Mol. Catal. A*, **2006**, 256, 48–56.
 - [17] J. Y. Ying, C. P. Mehnert, M. S. Wong, *Angew. Chem. Int. Ed.*, **1999**, 38, 56–77.
 - [18] S. Shylesh, A. P. Singh, *J. Catal.*, **2005**, 233, 359–371.
 - [19] X. Rozanska, R. Fortrie, J. Sauer, *J. Phys. Chem. C*, **2007**, 111, 6041–6050.
 - [20] H. Fu, Z. P. Liu, Z. H. Li, W. N. Wang, K. N. Fan, *J. Am. Chem. Soc.*, **2006**, 128, 11114–11123.
 - [21] X. Rozanska, R. Fortrie, J. Sauer, *J. Am. Chem. Soc.*, **2014**, 136, 7751–7761.
 - [22] A. S. Russell, J. J. Stokes, *Ind. Eng. Chem. Res.*, **1946**, 38, 1071–1074.
 - [23] J. T. Grant, C. A. Carrero, A. M. Love, R. Verel, I. Hermans, *ACS Catal.*, **2015**, 5, 5787–5793.
 - [24] X. L. Xue, W. Z. Lang, X. Yan, Y. J. Guo, *ACS Appl. Mater. Interfaces*, **2017**, 9, 15408–15423.
 - [25] Z. H. Luan, J. Xu, H. Y. He, J. Klinowski, L. Kevan, *J. Phys. Chem.*, **1996**, 100, 19595–19602.
 - [26] C. Mahendiran, T. Maiyalagan, P. Vijayan, C. Suresh, K. Shanthi, *Mechan. Catal.*, **2012**, 105, 469–481.
 - [27] S. Shylesh, A. P. Singh, *J. Catal.*, **2004**, 228, 333–346.
 - [28] J. J. Shi, Y. M. Zhou, Y. W. Zhang, S. J. Zhou, Z. W. Zhang, J. Kong, M. P. Guo, *J. Mater. Sci.*, **2014**, 49, 5772–5781.
 - [29] S. B. Bukallah, A. Bumajdad, K. M. S. Khalil, M. I. Zaki, *Appl. Surf. Sci.*, **2010**, 256, 6179–6185.
 - [30] B. S. Liu, R. Z. Chang, L. Jiang, W. Liu, C. T. Au, *J. Phys. Chem. C*, **2008**, 112, 15490–15501.
 - [31] C. Hess, G. Tzolova-Müller, R. Herbert, *J. Phys. Chem. C*, **2007**, 111, 9471–9479.
 - [32] S. B. Xie, E. Iglesia, A. T. Bell, *Langmuir*, **2000**, 16, 7162–7167.
 - [33] A. Khodakov, B. Olthof, A. T. Bell, E. Iglesia, *J. Catal.*, **1999**, 181, 205–216.
 - [34] X. T. Gao, S. R. Bare, B. M. Weckhuysen, I. E. Wachs, *J. Phys. Chem. B*, **1998**, 102, 10842–10852.
 - [35] S. Bhunia, D. Saha, S. Koner, *Langmuir*, **2011**, 27, 15322–15329.
 - [36] M. L. Peña, A. Dejoz, V. Fornés, F. Rey, M. I. Vázquez, J. M. López Nieto, *Appl. Catal. A*, **2001**, 209, 155–164.
 - [37] D. S. Lee, T. K. Liu, *J. Sol-Gel Sci. Technol.*, **2002**, 24, 69–80.
 - [38] K. J. Chao, C. N. Wu, H. Chang, L. J. Lee, S. f. Hu, *J. Phys. Chem. B*, **1997**, 101, 6341–6349.
 - [39] Y. W. Chen, Y. H. Lu, *Ind. Eng. Chem. Res.*, **1999**, 38, 1893–1903.
 - [40] M. J. Climent, A. Corma, R. Guil-López, S. Iborra, J. Primo, *J. Catal.*, **1998**, 175, 70–79.
 - [41] C. Y. Chen, H. X. Li, M. E. Davis, *Microporous Mater.*, **1993**, 2, 17–26.
 - [42] H. Berndt, A. Martin, A. Brückner, E. Schreier, D. Müller, H. Kosslick, G. U. Wolf, B. Lücke, *J. Catal.*, **2000**, 191, 384–400.
 - [43] B. Solsona, T. Blasco, J. M. López Nieto, M. L. Peña, F. Rey, A. Vidal-Moya, *J. Catal.*, **2001**, 203, 443–452.
 - [44] C. B. Wang, R. G. Herman, C. L. Shi, Q. Sun, J. E. Roberts, *Appl. Catal. A*, **2003**, 247, 321–333.
 - [45] K. Xia, W. Z. Lang, P. P. Li, X. Yan, Y. J. Guo, *J. Catal.*, **2016**, 338, 104.
 - [46] R. Bulánek, P. Čičmanec, S. Y. Hsu, P. Knotek, L. Čapek, M. Setnička, *Appl. Catal. A*, **2012**, 415–416, 29–39.
 - [47] J. Santamaría-González, J. Luque-Zambrana, J. Mérida-Robles, P. Maireles-Torres, E. Rodríguez-Castellón, A. Jiménez-López, *Catal. Lett.*, **2000**, 68, 67–73.
 - [48] W. Liu, S. Y. Lai, H. X. Dai, S. J. Wang, H. Z. Sun, C. T. Au, *Catal. Lett.*, **2007**, 113, 147–154.
 - [49] S. A. Karakoulia, K. S. Triantafyllidis, G. Tsilomelekis, S. Boghosian, A. A. Lemonidou, *Catal. Today*, **2009**, 141, 245–253.
 - [50] K. Chalupka, C. Thomas, Y. Millot, F. Averseng, S. Dzwigaj, *J. Catal.*, **2013**, 305, 46–55.
 - [51] Y. M. Liu, Y. Cao, K. K. Zhu, S. R. Yan, W. L. Dai, H. Y. He, K. N. Fan, *Chem. Commun.*, **2002**, 2832–2833.

- [52] D. B. Fox, E. H. Lee, M. H. Rei, *Product R&D*, **1972**, 11, 444–446.
[53] V. K. Oleg, A. K. Mamedov, *Russ. Chem. Rev.*, **1995**, 64, 877–900.
[54] R. X. Valenzuela, G. Bueno, V. Cortés Corberán, Y. Xu, C. Chen, *Catal. Today*, **2000**, 61, 43–48.
[55] Y. D. Xu, V. C. Corberan, *Progr. Nat. Sci.: Mater. Int.*, **2000**, 10, 22–26.
[56] B. Li, Z. Xu, W. Chu, S. Luo, F. Jing, *Chin. J. Catal.*, **2017**, 38, 726–735.
[57] S. Sokolov, V. Y. Bychkov, M. Stoyanova, U. Rodemerck, U. Bentrup, D. Linke, Y. P. Tyulenin, V. N. Korchak, E. V. Kondratenko, *ChemCatChem*, **2015**, 7, 1691–1700.

n V-MCM-41 催化剂的制备及其催化 CO₂ 氧化丙烷脱氢反应性能

韩再芳, 薛旭良, 吴建民, 郎万中*, 郭亚军

上海师范大学化学化工系, 教育部资源化学重点实验室, 上海市稀土功能材料重点实验室, 上海 200234

摘要: 丙烯是一种重要的化工原料, 其下游产品丰富, 用途广泛, 主要用于生产聚丙烯、丙烯腈、丙烯酸和丁醇等化工产品。丙烯的需求正在不断增长, 而传统的丙烯生产方法如蒸汽裂解和石油催化裂化, 存在反应温度高、积碳严重且丙烯收率较低等问题。因此研制丙烷脱氢制取丙烯的高效催化剂尤为重要。研究发现, 以 CO₂ 作为温和氧化剂进行逆水气变换反应可有效促进丙烷脱氢。催化剂主要由活性组分与载体构成, 本文选择可用于活化丙烷的钒作为主要活性组分。钒氧化物在载体上的高度分散是提高丙烷脱氢反应活性的关键。MCM-41 拥有较大的比表面积和高度有序的介孔结构, 可更有效地分散活性位点。本文采用一步法合成了不同钒含量的 n V-MCM-41 催化剂 (1.9–10.6 wt%), 并研究了其在以下条件下催化丙烷氧化脱氢制丙烯反应性能: 600 °C, 催化剂质量 0.2 g, 进料气体组成 C₃H₈/CO₂/Ar (摩尔比) = 1/4/4, 进料气体总流量 15 mL/min。其中 6.8V-MCM-41 催化剂具有最高的活性, 其初始丙烷转化率达 58%, 丙烯选择性达 92%, 远高于相似反应条件下早期研究的 n V-SBA-15 催化剂。并在四次反应-再生循环中始终保持其原来的高反应活性。本文借助于 N₂ 吸附-脱附、拉曼光谱 (Raman)、X 射线光电子能谱 (XPS) 和热重 (TG) 等手段探究了不同钒含量的 n V-MCM-41 催化剂在丙烷脱氢反应中催化性能差异的原因。

氮气吸附-脱附结果表明, 所有催化剂都存在典型的高度有序的介孔结构, 并没有因为钒组分的掺杂而破坏。 n V-MCM-41 催化剂拥有较大比表面积, 并随钒掺杂量的增加而减小。其中, 10.8V-MCM-41 催化剂的比表面积急剧下降, 可能是由于产生了结晶的 V₂O₅ 阻塞了孔道。Raman 结果表明, 当钒负载量超过 6.8 wt% 时, 出现了 V₂O₅ 的结晶峰。另外根据单分散的四面体钒氧化物的特征峰面积发现, 6.8V-MCM-41 催化剂中钒物种分散度最高, 与其具有最高催化活性结果一致。XPS 结果也进一步证明 6.8V-MCM-41 钒物种的分散度最高。在连续反应过程中 6.8V-MCM-41 催化剂失活较快, 可归结于活性钒位点的还原与催化剂表面的积碳。通过氧化再生, 可恢复催化剂活性, 并且在 4 次再生循环中始终保持其良好稳定的活性。

关键词: 丙烷脱氢; 钒氧化物; MCM-41; 介孔载体; 多相催化

收稿日期: 2017-12-31. 接受日期: 2018-02-09. 出版日期: 2018-06-05.

*通讯联系人. 电话/传真: (021)64321951; 电子信箱: wzlang@shnu.edu.cn

基金来源: 教育部创新团队 (PCSIRT_IRT_16R49); 教育部资源化学国际联合实验室。

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).