Synthesis of V-MCM-41 by template-ion exchange method and its catalytic properties in propane oxidative dehydrogenation

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Vanadium has been introduced to MCM-41 without collapse of the mesoporous structure by exchanging VO^{2+} ions in the aqueous solution with the template cations in the uncalcined MCM-41. This template-ion exchange (TIE) method provides tetrahedrally coordinated vanadyl species dispersed in the channel of MCM-41. Such synthesized V-MCM-41 shows higher catalytic activity in the oxidative dehydrogenation of propane than that prepared by direct hydrothermal method.

KEY WORDS: V-MCM-41; template-ion exchange; oxidative dehydrogenation; propane

1. Introduction

MCM-41 opens an opportunity for the design of catalytically active sites inside the uniform channels with controllable nano-order pore diameter [1–3]. Vanadium-containing MCM-41 (V-MCM-41) has received particular attention since many oxidation catalysts contain vanadium as an active component [4–8]. In the literature, vanadium was mainly introduced to MCM-41 by a direct hydrothermal method, in which the vanadium source such as $VO(SO_4)$ or $VO(C_2O_4)$ was directly added to the synthesis gel comprising silica source and surfactant template before hydrothermal synthesis. A large part of vanadium sites, however, seems difficult to be accessed during the catalytic reactions because of their incorporation inside the framework of MCM-41 by this method [5,7]. The conventional impregnation method, on the other hand, could produce vanadium species on the surface of the siliceous wall and thus could be accessed in catalytic reactions [8]. However, this method cannot ensure that the V species is introduced into the mesopore of MCM-41. Moreover, it has been reported that the mesoporous structure of MCM-41 is destroyed to some extent and some “bulk-like” V_2O_5 also appears by the impregnation method [8]. A method by the reaction of vanadium triisopropoxide with the surface silanol groups has been reported to prepare the pseudotetrahedral $O_{3/2}V{=}O$ centers immobilized on the wall of MCM-48 [9]. Further development of other methods effective for the introduction of active vanadium sites into the mesopore of MCM-41 would thus be highly desirable.

In a communication, Iwamoto and coworkers [10] reported that the template cations in the uncalcined MCM-41 could partly be exchanged by Mn^{2+} in aqueous solution without destroying the mesoporous structure. In this paper, we report our attempt to synthesize V-MCM-41 by the TIE method, i.e., by exchanging the surfactant template cations in the as-synthesized MCM-41 (with anionic silicate precursor and cationic quarternary ammonium surfactant) with VO^{2+} cations in the aqueous solution. The mesoporous structure and the location of vanadium are characterized by XRD, N_2 adsorption, and laser-Raman spectroscopy. The catalytic properties of thus prepared V-MCM-41 in the oxidative dehydrogenation of propane to propene are evaluated and compared with that prepared by the direct hydrothermal method.

2. Experimental

MCM-41 was prepared by a modified method of Beck and coworkers [11], in which sodium silicate and $C_{16}H_{33}(CH_3)_3NBr$ were used as silica source and surfactant template, respectively. The hydrothermal synthesis was carried out at 120 °C for 96 h with continuous stirring. The resultant was filtered and thoroughly washed with deionized water and then dried at 40 °C in vacuum. For introducing vanadium by TIE method, the as-synthesized (uncalcined) MCM-41 (2 g) containing ca. 50 wt% template was added to the aqueous solution of $VO(C_2O_4)$ (40 ml), stirred vigorously at room temperature for 1 h and then kept at 80 °C for 20 h to promote the exchange of VO^{2+} with the template cation in the as-synthesized MCM-41. The resultant was filtered, washed thoroughly with deionized water, dried at 40 °C in vacuum and finally calcined at 550 °C for 6 h. For the preparation of V-MCM-41 with the direct hydrothermal method, the aqueous solution of $VO(C_2O_4)$ was added to the synthesis gel prior to hydrothermal synthesis. After hydrothermal synthesis at 120 °C for 96 h, the product was filtered, washed, dried and calcined at 550 °C for 6 h.

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The content of vanadium was determined by ICP spectrometry after the sample was completely dissolved using diluted HCl and a small amount of HF. The mesoporous structure was characterized with XRD and N_2 adsorption (at 77 K) measurements. Diffuse reflectance UV-vis and laser-Raman spectroscopic measurements were used to evaluate the coordination environment of vanadium. An argon laser with 514.5 nm line was used for laser-Raman experiments.

The oxidative dehydrogenation of propane was carried out using a U-type fixed-bed flow reactor (quartz tube). The catalyst was pretreated in the reactor in a gas flow containing N_2 (10 ml/min) and O_2 (3 ml/min) at 550 °C before reaction. The standard reaction conditions were as follows: $P(C_3H_8) = 12.2$ kPa, $P(O_2) = 6.1$ kPa, $F = 50\ \mathrm{ml\,min^{-1}}$ and $W = 0.2$ g.

3. Results and discussion

Figure 1 shows XRD patterns of the calcined V-MCM-41 with different Si/V ratio prepared by the TIE method. All four XRD diffraction lines indexed to hexagonal regularity of MCM-41, i.e., (100), (110), (200), and (210), were observed and the peak intensity kept almost unchanged except for the sample with the highest vanadium content (Si/V = 12). The peak position of (100) slightly shifted to a lower value with increasing vanadium content up to Si/V ratio of 23, indicating the slight increase in d_{100} spacing, but further increase in V content shifted the peak to a higher value again. The results from ICP analysis and N_2 adsorption measurement are listed in table 1. No tendency was observed in the change of surface area with the introduction of V to MCM-41 by TIE method, and pore volume was not significantly altered at the same time. The pore diameter distribution determined from the N_2 adsorption isotherm using the DH method is shown in figure 2. A peak at 2.7 nm was observed for all the samples. These results indicate that no significant destruction of the structure of MCM-41 occurs during the TIE process. Further calculation by subtracting unit cell parameter ($a_0 = 2d_{100}/\sqrt{3}$) with pore diameter showed that the wall thickness was slightly increased with decreasing Si/V ratio to 23. Thus, a small part of vanadium may probably be incorporated into the siliceous wall of MCM-41 by the TIE method.

For comparison, the properties of the samples prepared by the direct hydrothermal method are also shown in table 1. It can be seen that the BET surface area and pore volume keep almost unchanged at lower V content, but drop remarkably as V content increases. The extent of such decrease with increasing V content was larger as compared with the samples prepared by the TIE method. Mesoporous structure was not formed for the sample with Si/V ratio of 12 prepared by the direct hydrothermal method.

The location of vanadium in the V-MCM-41 synthesized above was investigated by diffuse reflectance UV-vis spectroscopy. Figure 3 shows UV-vis spectra of the calcined samples synthesized by both TIE and direct hydrothermal methods. The band at 275 nm has been proposed to correspond to the tetrahedral vanadium incorporated inside the framework of MCM-41, while the band at 340 nm to that

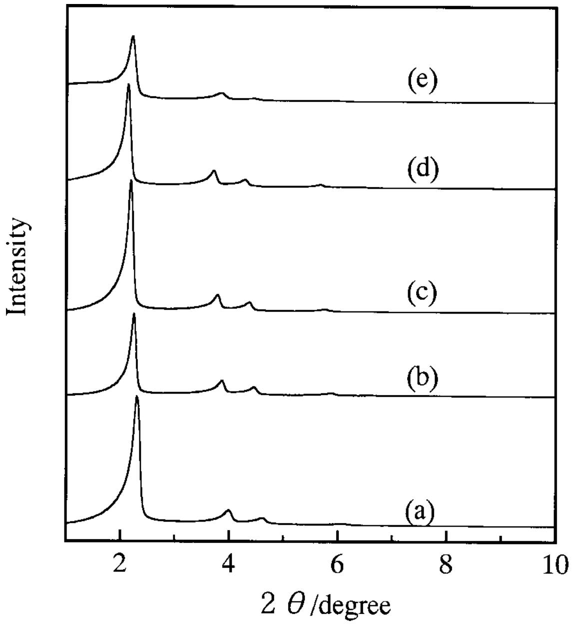

Figure 1. XRD patterns of V-MCM-41 prepared by the TIE method: (a) pure silica MCM-41, (b) Si/V = 83, (c) Si/V = 47, (d) Si/V = 23, and (e) Si/V = 12.

Table 1
Physical properties of V-MCM-41 prepared by TIE and DHT method.[a]

Si/V ratio in preparation	Method for introducing V	Si/V ratio by ICP	V content (wt%)	Surface area ($m^2\,g^{-1}$)	Pore volume ($cm^3\,g^{-1}$)	Pore diameter (nm)	Color of sample: As synthesized	Calcined	After 2 h in open air[b]
Pure MCM-41	–	–	0	1025	0.94	2.7	White	White	White
64	TIE	83	1.0	1010	0.94	2.7	Light green	White	Light orange
32	TIE	47	1.8	850	1.02	2.7	Light green	White	Orange
16	TIE	23	3.6	830	1.02	2.7	Green	White	Orange
8	TIE	12	6.6	962	0.96	2.7	Green	White	Orange
50	DHT	210	0.4	1086	0.92	2.5	White	White	White
32	DHT	87	1.0	883	0.74	2.5	White	White	White
16	DHT	23	3.6	660	0.34	2.3	Light green	White	Light orange
8	DHT	12	6.6	2	0	–	Green	Yellow	Yellow

[a] TIE and DHT represent the template-ion exchange and direct hydrothermal methods, respectively.

[b] The room humidity and temperature were ca. 40% and 20 °C, respectively.

on the wall surface [5]. It can be seen from figure 3 that, for TIE samples, the component at 275 nm decreases and that at 340 nm increases with V content, and the latter one becomes dominant as V content exceeds 1.8 wt% (Si/V = 47). On the other hand, the peak still centers at 275 nm for the samples by direct hydrothermal method with higher V content. These results suggest that the V species introduced by the TIE method mainly exist on the wall surface, while most of them are incorporated inside the framework of MCM-41 by direct hydrothermal method. Furthermore, the contribution of the square pyramidal (415 nm) and octahedral (450 nm) type V species became considerable for the samples by TIE method as V content became high. These two kinds of species were probably formed due to the hydration of the surface tetrahedral V under ambient circumstance during UV-vis measurements. Actually, the color change was observed during UV-vis measurements particularly for the samples by TIE method. As can be seen in table 1, all calcined samples except the one not forming mesoporous structure were white in color, but many of them, particularly those by TIE method changed to orange after 2 h exposure in open circumstance. This corresponds to the change of environment of vanadium from tetrahedral to pyramidal or octahedral coordination by hydration.

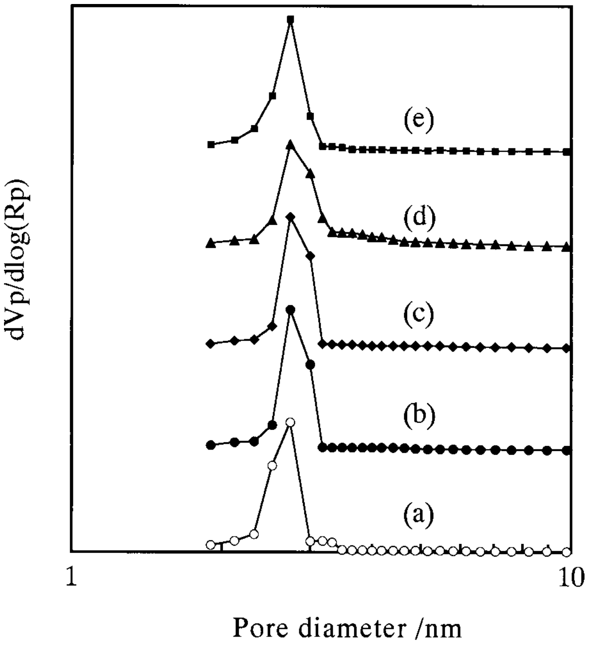

Figure 2. Pore distribution of V-MCM-41 prepared by the TIE method: (a) pure silica MCM-41, (b) Si/V = 83, (c) Si/V = 47, (d) Si/V = 23 and (e) Si/V = 12.

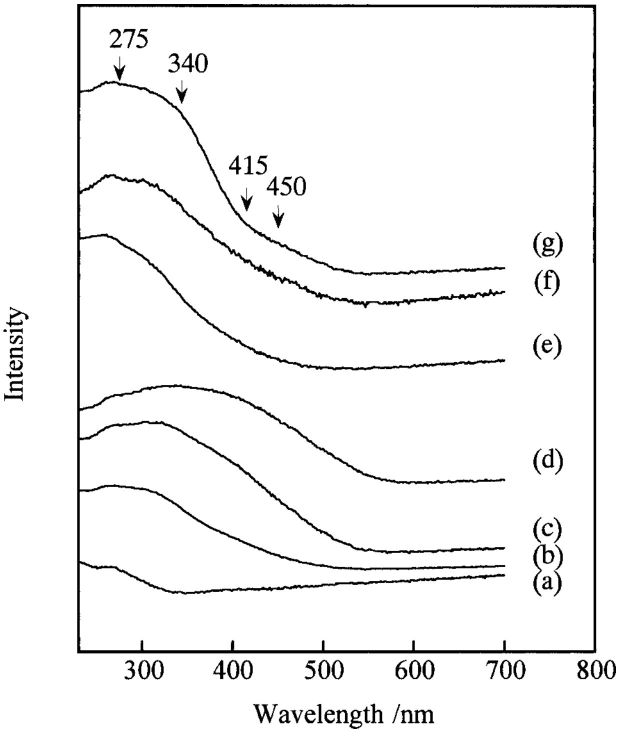

Figure 3. Diffuse reflectance UV-vis spectra of V-MCM-41 prepared by TIE and direct hydrothermal method: (a) pure silica MCM-41, (b) TIE Si/V = 83, (c) TIE Si/V= 47, (d) TIE Si/V= 23, (e) DHT Si/V= 210, (f) DHT Si/V= 87 and (g) DHT Si/V= 23.

Laser-Raman spectroscopy was also used to elucidate the environment of vanadium, since Raman spectroscopy provided direct information on the coordination environment in characterizing supported vanadium oxides with both tetrahedral and octahedral coordination structures [12–15]. Figure 4 shows Raman spectra of the V-MCM-41 by TIE method with different Si/V ratio. A peak at 1036 cm^{-1} began to be observed when the Si/V ratio reached 47 and the intensity of this peak increased with vanadium content. V=O stretching frequencies for VOF_3, $VOCl_3$, and $VOBr_3$ with tetrahedral structure occur at 1053, 1035, and 1028 cm^{-1}, respectively. A band at 1042 cm^{-1} has been assigned to the V=O stretching vibration of tetrahedral monomeric vanadyl

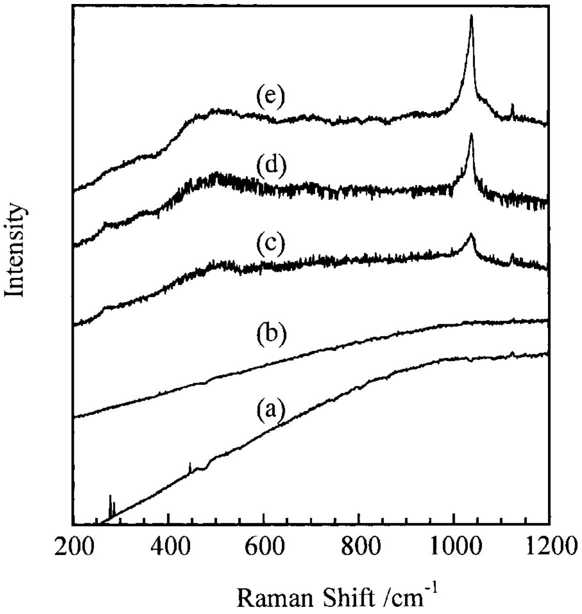

Figure 4. Laser-Raman spectra of V-MCM-41 prepared by the TIE method: (a) pure silica MCM-41, (b) Si/V = 83, (c) Si/V = 47, (d) Si/V = 23 and (e) Si/V = 12.

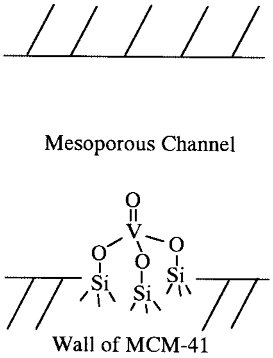

Figure 5. Coordination structure of vanadium in V-MCM-41 prepared by the TIE method.

species bound directly to the SiO_2 support [12,13]. Thus, the peak at 1036 cm^{-1} observed here could be assigned to the V=O stretching of tetrahedrally coordinated vanadyl species anchored on the surface of MCM-41 as shown in figure 5. The absence of the Raman band ascribed to V=O of the polymerized octahedral coordination in the region of 900–1000 cm^{-1} and that ascribed to the V–O–V stretching vibration in the region of 600–800 cm^{-1} supports that all the vanadium sites are in tetrahedral coordination environment.

It should be noted that the Raman peak at 1036 cm^{-1} was not observed for the samples by direct hydrothermal method. The Raman band ascribed to V = O stretching vibration was also not observed in V-silicalite whose V was in the framewok of silicalite zeolite [16]. Moreover, in a recent communication, it has been reported that the information about V species in V-MCM-41 by direct hydrothermal method cannot be obtained by visible Raman spectroscopy [17]. Probably, the environment of vanadium in the V-MCM-41 by direct hydrothermal method resembles that in vanadium isomorphously substituted zeolites.

The catalytic properties of the V-MCM-41 prepared by the TIE method for the oxidative dehydrogenation of C_3H_8 at 500 °C are shown in figure 6. The results of the samples prepared by the direct hydrothermal method are also plotted in the figure for comparison. No reaction occurred without catalyst under the conditions of figure 6. MCM-41 without vanadium also exhibited some activity for C_3H_8 conversion, but no C_3H_6 was formed under such conditions. It has been suggested that the silanol groups on silica freshly prepared by hydrolysis of silicon alkoxide would initiate the radical oxidation of butane [18]. Thus, similar reaction may occur for the oxidation of C_3H_8 on MCM-41, which is known to contain a large quantity of silanol groups in its structure. The introduction of vanadium to MCM-41 produced C_3H_6 as a main product. Both C_3H_8 conversion and C_3H_6 selectivity increased with increasing vanadium content up to Si/V ratio of 23. Further increase in vanadium content slightly decreased C_3H_6 selectivity due to consecutive oxidation.

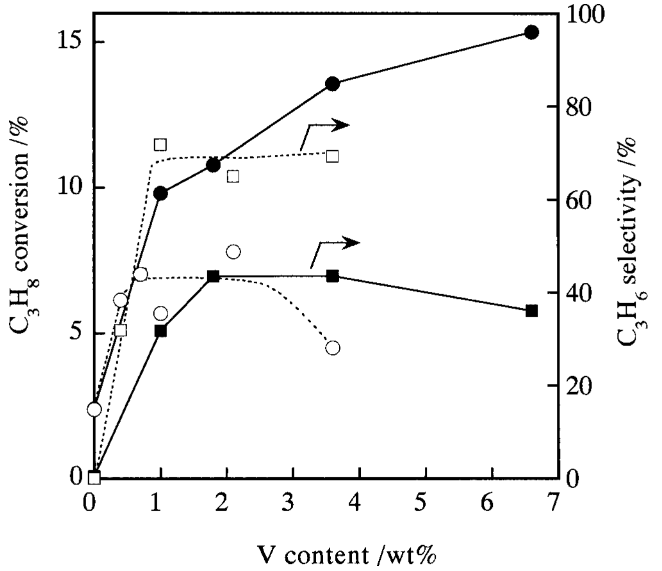

Figure 6. Comparison of catalytic properties of V-MCM-41 prepared by TIE with those by direct hydrothermal method: (•) C_3H_8 conversion (TIE), (○) C_3H_8 conversion (hydrothermal method), (•) C_3H_6 selectivity (TIE), and (□) C_3H_6 selectivity (hydrothermal method).

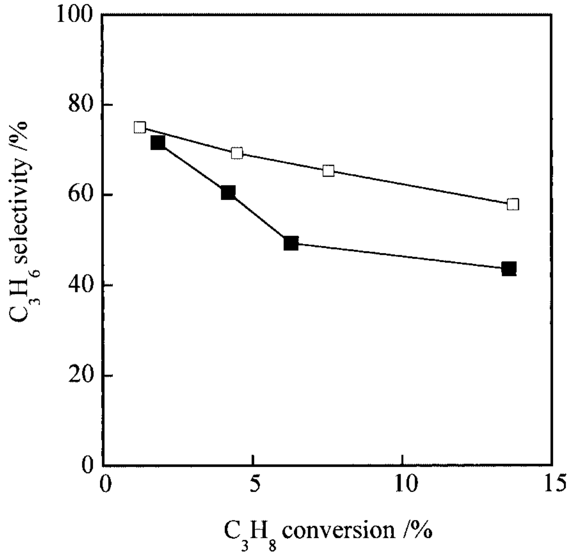

Figure 7. C_3H_6 selectivity versus C_3H_8 conversion over V-MCM-41 (Si/V = 23) prepared by TIE (■) and direct hydrothermal method (□).

On the other hand, the increase in V content did not significantly increase C_3H_8 conversion for the samples by direct hydrothermal method although the introduction of a small amount of vanadium (up to ca. 1 wt%) enhanced the reaction. C_3H_8 conversion rather decreased for the sample with the highest V content in figure 6. The decrease in BET surface area with increasing V content (table 1) and the inaccessibility of a large part of vanadium sites by this method are probably responsible for such a low activity. As can be seen from figure 6, with increasing V content, C_3H_6 selectivity increases very sharply in the region of low V content and then keeps at a high level of ca. 70%. This result also indicates that only a limited part of vanadium sites play roles in the reaction. The sample with Si/V ratio of 12 (V content, 6.6 wt%) prepared by direct hydrothermal method was inactive for the reaction (not shown in the figure) because the mesoporous structure was not formed and non-dispersed vanadium oxide mainly existed in this sample.

Figure 7 compares C_3H_6 selectivity over the samples (Si/V = 23) prepared by TIE and direct hydrothermal methods at different C_3H_8 conversions. C_3H_8 conversion was changed by varying reaction temperature in the figure, and higher temperature was needed for the sample by direct hydrothermal method to achieve the same conversion due to its lower activity. As shown in figure 7, the sample by direct hydrothermal method showed relatively higher C_3H_6 selectivity at the same C_3H_8 conversion level, particularly in the region of high C_3H_8 conversion. This suggests that the consecutive oxidation of C_3H_6 proceeds more easily over the sample prepared by the TIE method. Further detailed comparisons of the catalytic behaviors and kinetic features with these samples are underway.

4. Conclusions

The template-ion exchange method could introduce more vanadium species into MCM-41 by keeping its mesoporous structure than the direct hydrothermal method. The TIE method provided tetrahedrally coordinated vanadyl species highly dispersed in the channel of MCM-41. The vanadium species in such synthesized V-MCM-41 could easily be accessed by the reactant, and thus showed higher activity for the oxidative dehydrogenation of C_3H_8 than that prepared by the direct hydrothermal method. On the other hand, the vanadium sites introduced by the direct hydrothermal method gave higher C_3H_6 selectivity.

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