

V-MCM-41 for Selective Oxidation of Propane to Propene and Acrolein

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The V-MCM-41 with lower V content catalyzes the oxidation of propane to acrolein with a yield of 3.3% and selectivity of 20%, while that with higher V content mainly produces propene.

V-containing mesoporous materials such as V-MCM-41 have received much attention since they can provide high concentration of isolated vanadium species, which are desirable for many partial oxidation reactions. Although many publications have contributed to the syntheses and characterizations of V-MCM-41,¹⁻³ the reports on the use of it as catalyst are still scarce and mainly limited to liquid phase oxidation reactions using H₂O₂ or *tert*-butyl hydroperoxide.^{4,5} On the other hand, vanadium-substituted zeolites such as V-silicates⁶ and VAPO-5⁷ have shown good performances in the oxidative dehydrogenation of lower alkanes. Recently, we found that V-MCM-41 showed unique catalytic properties in partial oxidation of lower alkanes such as C₃H₈. Not only alkene but also oxygenate could be obtained with moderate selectivity depending on Si/V ratio. This communication is the first report on the partial oxidation of C₃H₈ to C₃H₆ and acrolein using V-MCM-41.

V-MCM-41 was prepared by hydrothermal synthesis at 120 °C for 96 h. Sodium silicate, vanadyl oxalate and cetyltrimethylammonium bromide were used as silicon, vanadium sources and surfactant template, respectively. The resultant solid after hydrothermal synthesis was recovered by filtration, washed thoroughly with deionized water, dried in vacuum at 40 °C for 24 h, and finally calcined at 550 °C for 6 h. V content in each sample was determined by ICP spectrometry. ICP measurements also showed that nearly no Na⁺ remained in the sample. Catalytic reactions were performed using a U-typed fixed-bed flow reactor. Standard reaction conditions were as follows: *T* = 400–550 °C, *P*(C₃H₈) = 12.2 kPa, *P*(O₂) = 6.1 kPa, *W* = 0.2 g, *F* = 50 mL/min.

Figure 1 shows the XRD patterns of V-MCM-41 samples with different Si/V ratios. The peaks (100), (110) and (200) indexed to hexagonal regularity of MCM-41 were clearly observed for all samples except the one with the highest V content. The peak of (210) was not clearly observed for the V-MCM-41 and similar phenomenon has been reported by Kevan and coworkers.² Table 1 shows the results obtained from N₂ adsorption measurements. BET surface area was ca. 1000 m² g⁻¹ for MCM-41 and the samples with low V content and the value decreased for the samples with high V content. Pore size distribution determined by DH method showed a sharp peak at 2.3–2.7 nm depending on Si/V ratio.

UV-vis spectroscopic measurements exhibited a main peak at 275 nm for all samples, indicating that vanadium was in tetrahedral coordination environment. H₂-TPR showed one reduction peak at 550–580 °C, and Laser-Raman spectroscopy

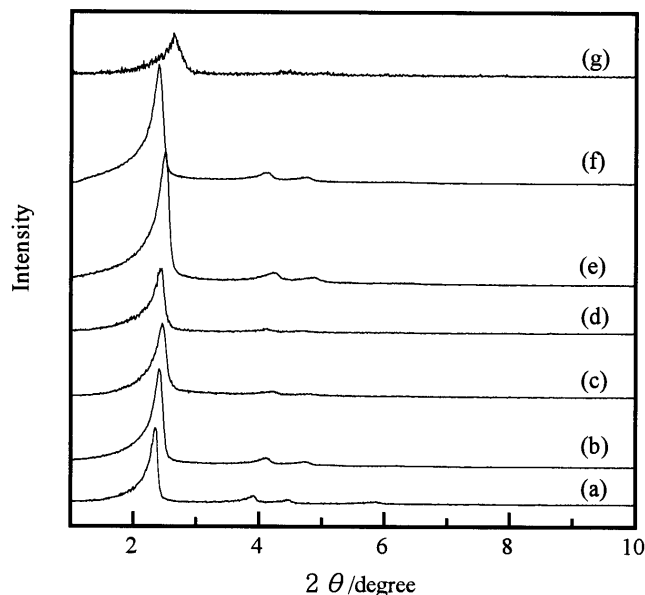


Figure 1. XRD patterns of V-MCM-41 with different Si/V ratio. (a) MCM-41, (b) Si/V= 543, (c) Si/V= 210, (d) Si/V=120, (e) Si/V= 87, (f) Si/V= 40, (g) Si/V= 23.

Table 1. Results obtained from N₂ adsorption measurements

Sample	S _{BET} /m ² g ⁻¹	Pore volume /cm ³ g ⁻¹	Pore diameter /nm
MCM-41	1025	0.89	2.7
V-MCM-41 (543) ^a	1030	0.90	2.5
V-MCM-41 (210)	1086	0.92	2.5
V-MCM-41 (120)	998	0.85	2.7
V-MCM-41 (87)	883	0.74	2.5
V-MCM-41 (40)	890	0.85	2.5
V-MCM-41 (23)	660	0.34	2.3

^aThe number in the parenthesis is the Si/V atomic ratio.

gave a band at 956 cm⁻¹ probably ascribed to framework Si–O–V stretching. These features resemble those observed for V-silicate zeolite,⁸ suggesting that vanadium was mainly incorporated into the framework of MCM-41.

Table 2 shows the catalytic results for C₃H₈ oxidation at 550 °C. No reaction occurred without catalyst under the reaction conditions used here. C₃H₈ was also converted over MCM-41. The incorporation of V remarkably increased C₃H₈ conversion and the selectivity for partial oxidation products. C₃H₆ was formed with high selectivity over the catalysts with high V content and the C₃H₆ yield was comparable with that obtained over V-containing zeolites. It should be noted that not only C₃H₆ but

acrolein was also obtained over V-MCM-41. The selectivity and yield of acrolein were the highest over the sample with Si/V ratio of 120. Further increase in V content decreased selectivity to acrolein and increased that to C_3H_6 . C_3H_8 conversion and C_3H_6 selectivity decreased over the catalyst with Si/V ratio of 23, probably due to the decrease in BET surface area of this sample.

Table 2. Catalytic properties of V-MCM-41 for C_3H_8 oxidation

Catalyst	C_3H_8 conv. /%	Selectivity /%		
		C_3H_6	$CH_2=CHCHO$	CO_x
MCM-41	6.4	22.1	10.1	67.8
V-MCM-41 (543)	11.1	20.7	11.4	67.9
V-MCM-41 (210)	11.9	29.2	14.0	56.8
V-MCM-41 (120)	16.3	42.8	20.0	37.2
V-MCM-41 (87)	16.2	54.4	7.6	38.0
V-MCM-41 (40)	14.2	63.5	8.0	28.5
V-MCM-41 (23)	13.7	57.9	3.3	38.8

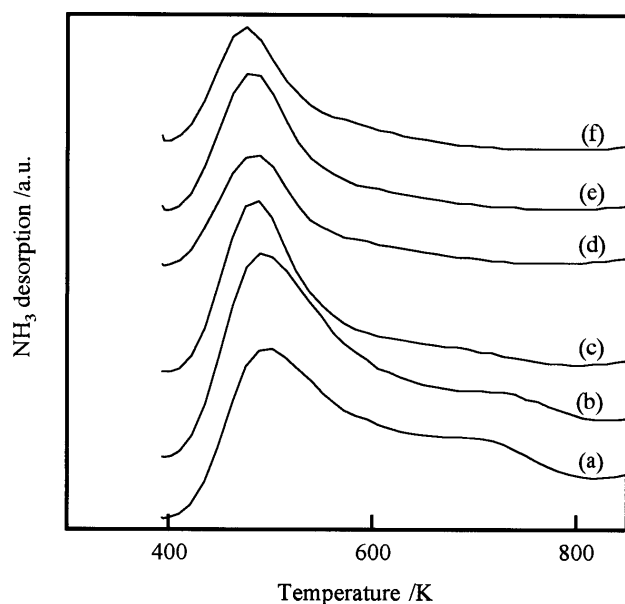


Figure 2. NH_3 -TPD profiles of V-MCM-41 samples with different Si/V ratios. (a) MCM-41, (b) Si/V= 210, (c) Si/V= 120, (d) Si/V= 87, (e) Si/V= 40, (f) Si/V= 23.

The oxidation of C_3H_8 to acrolein has been reported over complex metal oxide catalysts containing Bi, Mo, Ni and many other components and a good catalyst generally gives yield of ca. 3%.⁹ No report has shown the production of acrolein over V-containing silica or zeolite catalysts. Thus, V-MCM-41 is very unique for the selective oxidation of C_3H_8 .

To investigate the influence of acidity on the catalytic reaction, NH_3 -TPD was performed and the results are shown in Figure 2. For MCM-41 and the samples with low V content, a shoulder at 700–730 K corresponding to acid sites with medium strength was observed along with the main peak at 490–500 K ascribed to weak acid sites. The medium acid sites disappeared for the sample with high vanadium content. Such change in acidity corresponds well with the shift of partial oxidation product from acrolein to C_3H_6 with the increase in V content. Thus, it is likely that C_3H_6 or allylic intermediate produced on the catalysts with low V content may interact strongly with the medium acid sites and be further oxidized into acrolein. On the other hand, the desorption of C_3H_6 must be facile over the catalysts without such acid sites. The elucidation of the nature of acid sites and their influences on adsorption and conversion of C_3H_6 is underway.

References and Notes

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