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Photo-assisted synthesis of V and Ti-containing MCM-41 under UV light irradiation and their reactivity for the photooxidation of propane

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Abstract

V and Ti-containing mesoporous molecular sieves MCM-41 were prepared using a photo-assisted synthesis method with UV light irradiation of the starting solutions at room temperature within a short synthesis time. The prepared V-MCM-41 showed high reactivity for the photocatalytic partial oxidation of propane into acetone. This reaction was enhanced on the V–Ti-MCM-41 catalyst with a higher acetone yield and selectivity than for V-MCM-41. After quenching, the recovery of the photoluminescence of V–Ti-MCM-41 proceeded more efficiently than that of V-MCM-41 by evacuation at 295 K. These results suggest that the excited state of the V-oxide moieties in V–Ti-MCM-41 interacts more weakly with the O_2 molecules, leading to the suppression of further oxidation of the photo-formed acetone into CO_2.

Keywords: Photo-assisted synthesis; Photocatalytic oxidation of propane; V-MCM-41; V–Ti-MCM-41

1. Introduction

Silica as well as zeolites and mesoporous molecular sieves supported vanadium and titanium oxide catalysts are known to be active and selective in various catalytic and photocatalytic reactions, e.g., in the selective oxidation of methane to methanol and formaldehyde [1–3], ethanol to acetaldehyde [4] and the selective catalytic reduction (SCR) of NO_x [5,6]. In line with such work, MCM-41 has attracted much attention as a catalyst support since its discovery in 1992, due to its regularly oriented pore systems, large pore spaces and high surface area [7,8]. However, conventional methods of synthesizing MCM-41 require hydrothermal conditions and an extended reaction time as well as careful control of the reaction temperature and pH, although a temperature-controlled microwave-assisted synthesis method for MCM-41 which could shorten the crystallization time compared to conventional autoclave heating has been reported [9].

Recently, we have reported on a novel photo-assisted synthesis method for MCM-41 under UV light irradiation of the starting solutions at 295 K, which has exhibited significant advantages such as a shortening of the synthesis reaction time while achieving a highly ordered mesoporous structure under ambient atmospheric conditions [10]. The selective conversion of light alkanes into more valuable compounds is also of great interest from both a scientific and industrial viewpoint [11–13].

In the present work, we have reported on the photo-assisted synthesis of V, Ti and V–Ti-containing MCM-41 under UV light irradiation of the starting solutions at 295 K along with an investigation of their photocatalytic reactivities for the partial oxidation of propane in the presence of O_2 at 295 K.

2. Experimental

2.1. Preparation of the catalysts

V-MCM-41 gels were synthesized under both acidic and basic conditions. Under both pathways, cetyltrimethylammonium bromide (CTMABr) served as the template. For the acidic pathway, tetraethyl orthosilicate (TEOS) and NH_4VO_3 were used as the silicon source and the vanadium ion precursor,

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respectively. The molar composition of the reaction mixture was 1.0 Si:0.0125 V:0.2 [$C_{16}H_{33}N(CH_3)_3$]Br:160 H_2O. The pH of the solution was adjusted to 1.0 by HCl solution. For the basic condition pathway, silica as well as sodium silicate and vanadyl sulfate trihydrate solution were used as the Si and the V ion source, respectively, and the pH of the reaction mixture was adjusted to 11.0 with dilute sulfuric acid. The molar composition of the gel was 1.0 Si:0.0125 V:0.27 CTMABr:0.13 Na_2O:0.26 tetramethylammonium hydroxide:60 H_2O. Ti-MCM-41 and V–Ti-MCM-41 were synthesized through a basic pathway and tetraisopropyl orthotitanate was used as the Ti source. For both pathways, the reaction mixtures were stirred under UV light irradiation. A 100 W high-pressure Hg lamp was used as the UV light source and a water bath was used to keep the synthesis system at room temperature. The crystalline products were filtered, washed with deionised water, dried overnight at 373 K and calcined in air at 773 K for 8 h.

Prior to photocatalytic reactions and spectroscopic measurements, the catalysts were degassed at 773 K for 1 h, heated in O_2 at the same temperature for 2 h, and finally degassed at 473 K for 2 h.

2.2. Catalyst characterizations

The metal content of these materials were determined with a Shimadzu atomic absorption flame emission spectrophotometer, model AA-6400F. The powder X-ray diffraction (XRD) patterns of the samples were recorded on a Shimadzu XRD-6100 with Cu Kα radiation (λ = 1.5417 Å). Transmission electron microscope (TEM) measurements were performed with a JEOL 2000 instruments. Diffuse reflectance UV–vis spectroscopic measurements were carried out on a Shimadzu UV–vis recording spectrophotometer, model UV-2200A. The photoluminescence was measured at 295 K with a Spex Fluorog-3 spectrophotometer.

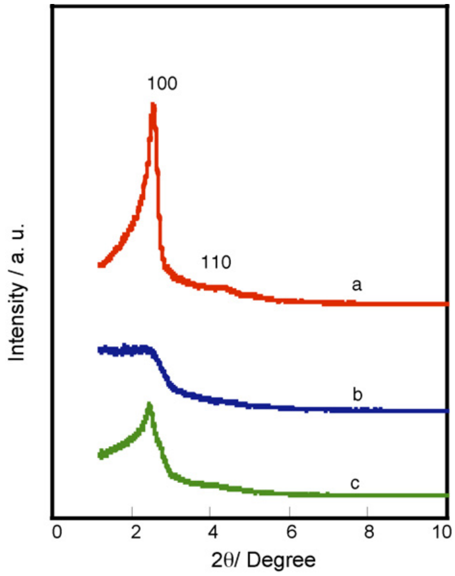

Fig. 1. XRD patterns of V-MCM-41 (2 wt.%) prepared in acidic solutions: (a) under UV light irradiation for 24 h; (b) in the dark for 24 h; (c) for 5 days.

2.3. Photocatalytic reactions

The photocatalytic partial oxidation of propane with O_2 was carried out in a closed reaction system. The catalyst (80 mg) was loaded in a quartz cell with a flat bottom connected to a vacuum system. After pretreatment, propane and O_2 (180 μmol g cat^{-1}) were introduced into the quartz cell. UV irradiation was carried out using a 100 W mercury lamp through a UV cut filter ($\lambda > 270$ nm) at 295 K and a water bath was employed to keep the flat bottom at a constant temperature. After each run, the catalyst bed was heated up to 573 K to collect the products that were adsorbed tightly onto the catalyst at room temperature. The products were analyzed with an on-line gas chromatographer equipped with a flame ionization detector (FID) for analysis of such hydrocarbons as CH_4, C_2H_4, C_3H_6, CH_3CHO, acetone, etc., and a thermal conductivity detector (TCD) for analysis of CO and CO_2, etc.

3. Results and discussions

The XRD patterns of the calcined V-MCM-41 prepared under pH 1.0 conditions are shown in Fig. 1. The sample prepared under UV irradiation for 24 h (Fig. 1a) shows a typical MCM-41 pattern with a hexagonal arrangement of pores having a unit cell size (a_0) of 4.0 nm. Moreover, this sample shows a sharper 1 0 0 plane peak than that prepared under dark conditions for 5 days, indicating that the former sample has a higher ordered mesopore structure and crystallinity. However, for the sample synthesized without UV light for 24 h, the (1 0 0) peak is very broad. It is, thus, clear that UV light irradiation of the starting solution can shorten the crystallization time.

Fig. 2 shows the XRD patterns of V-MCM-41 prepared in basic solutions. Compared to the broad (1 0 0) peak pattern of the sample prepared in the absence of UV light, a sharp (1 0 0) peak and small (1 1 0), (2 0 0) peaks were observed on V-MCM-41 prepared under UV light irradiation. The TEM images confirmed that this catalyst has a higher ordered hexagonal pore structure than that prepared without UV

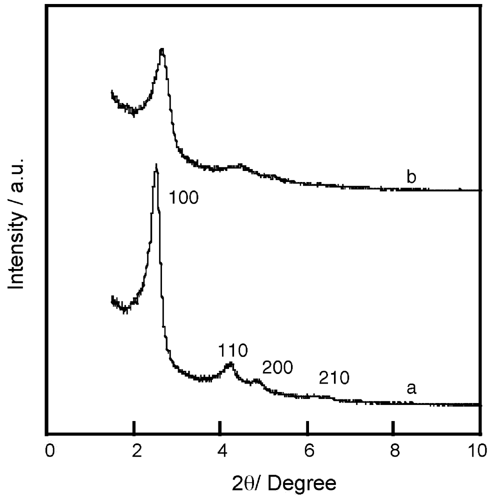

Fig. 2. XRD patterns of V-MCM-41 prepared for 24 h in basic solutions: (a) under UV light irradiation; (b) under dark conditions.

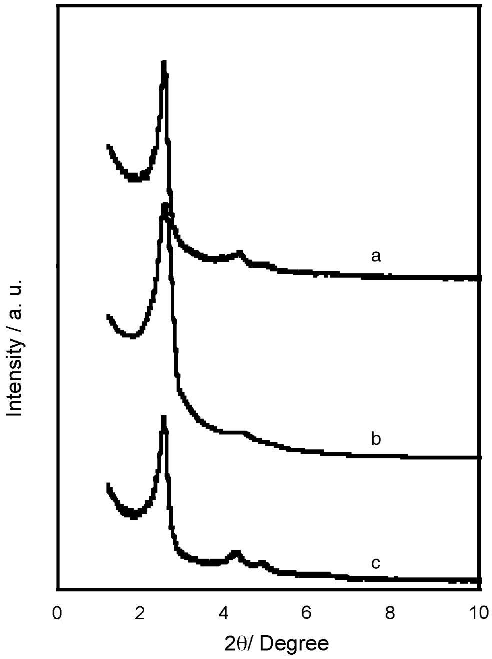

Fig. 3. XRD patterns of: (a) V–Ti-MCM-41; (b) Ti-MCM-41; (c) V-MCM-41 prepared under UV light irradiation for 24 h in basic solution.

irradiation. These results indicate that highly ordered V ion-containing MCM-41 can be synthesized in a relatively short time using UV light at initial room temperature. The effect of UV light irradiation of the starting solution on the crystallization is more remarkable for V-MCM-41 synthesis in basic than in acidic solution. Similar results were observed for the synthesis of MCM-41 and Ti-MCM-41.

The XRD patterns and TEM images of V and Ti, i.e., two kinds of ions incorporated MCM-41 photo-synthesized under basic conditions are shown in Figs. 3 and 4. It was observed that incorporating two different transition metal ions into the framework caused no damage to the mesopore structure. Although the detailed mechanisms are not yet clear, UV light irradiation of the starting mixture solutions may lead to the excitation of OH^- ions to form OH radicals [14] and/or the excited triplet state of the OH^- ion [15] which may play a significant role in the polymerization to form mesoporous MCM-41 network structures since the only common species excited under UV light for both MCM-41 and V-MCM-41 is the OH^- ions.

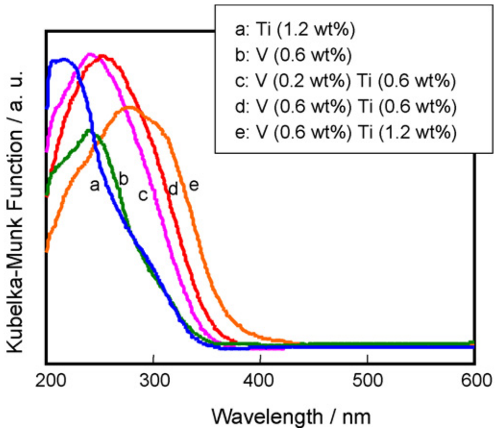

Fig. 5. Diffuse reflectance UV–vis spectra of Ti-MCM-41, V-MCM-41, and V–Ti-MCM-41 prepared under UV light irradiation for 24 h in basic solution.

Fig. 5 shows the UV–vis absorption spectra of the photo-synthesized V and Ti-containing MCM-41 samples prepared in the pH 11.0 starting solutions. V-MCM-41 and Ti-MCM-41 exhibited absorption bands which can be assigned to the charge transfer transition involving an electron transfer from the lattice oxygen $(O^{2-})_L$ to the vanadium (V^{5+}) and titanium (Ti^{4+}) ions of the highly dispersed tetrahedrally coordinated V- and Ti-oxide species, respectively [16,17]. The absorption of V–Ti-MCM-41 was found to exhibit a red shift compared to V-MCM-41 or Ti-MCM-41 and this shift increased with an increase in the content of V and Ti. No absorption band could be observed in wavelength regions longer than 400 nm, indicating that aggregated species such as V_2O_5 was not involved [3,16].

V-MCM-41 prepared by the photo-assisted synthesis method showed high activity for the photocatalytic partial oxidation of propane with oxygen into acetone. Ti-MCM-41 exhibited very low conversion of propane but high selectivity for the formation of acetone, as shown in Table 1. This reaction was enhanced on the V–Ti-MCM-41 catalyst and the propane conversion and selectivity for the formation of acetone was higher than on V-MCM-41 or Ti-MCM-41. The yield and

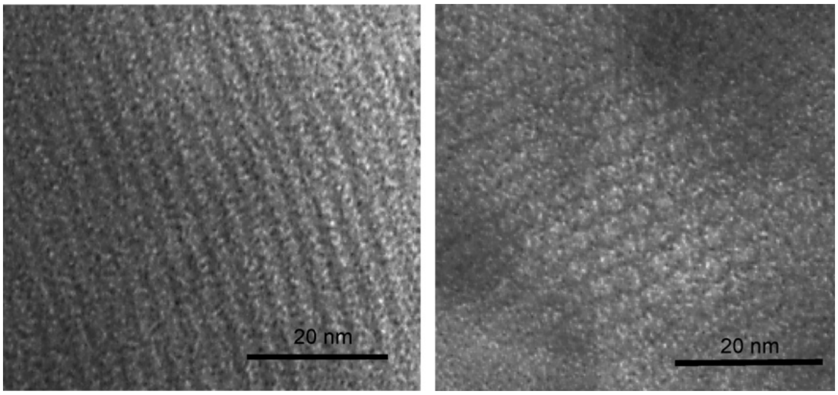

Fig. 4. TEM images with different orientations of V–Ti-MCM-41 prepared under UV light irradiation for 24 h in basic solutions.

Table 1
Conversion and selectivity in the photocatalytic oxidation of propane on V-MCM-41, Ti-MCM-41, and V–Ti-MCM-41 prepared under UV light irradiation for 24 h in basic solutions

Catalysts	C_3H_8 conversion (%)	Selectivity (%)					
		CH_3COCH_3	C_3H_6	C_2H_4	CH_3CHO	CH_4	CO_2
V (0.2)	22.5	56.9	13.4	2.0	4.9	2.8	20.1
Ti (0.6)	4.5	72.4	9.9	1.0	11.6	0	5.1
V (0.2), Ti (0.6)	28.6	73.9	9.9	1.5	7.4	1.5	5.2
V (0.2), Ti (0.6)[a]	28.8	63.8	18.2	1.8	7.3	1.8	7.1

Amounts of added: C_3H_8, 4 Torr; O_2, 4 Torr; irradiation time, 3 h; $\lambda > 270$ nm.

[a] The catalyst prepared without UV light irradiation.

Table 2
Photocatalytic oxidation of propane on V–Ti-MCM-41 having different V/Ti ratios

Catalysts	V:Ti	C_3H_8 conversion (%)	CH_3COCH_3 selectivity (%)
V (0.6), Ti (0.6)	1:1	31.3	66.2
V (0.6), Ti (1.2)	1/2:1	36.7	72.0
V (0.6), Ti (0.2)	3:1	24.6	59.2
V (0.2), Ti (0.6)	1/3:1	28.6	73.9
V (0.05), Ti (0.6)	1/10:1	16.6	65.4
V (0.2), Ti (1.2)	1/6:1	26.6	67.3

Amounts of added: C_3H_8, 4 Torr; O_2, 4 Torr; irradiation time, 3 h; $\lambda > 270$ nm.

selectivity of CO_2 on V-MCM-41 was also much higher than on the other catalysts, suggesting that full oxidation occurs more easily on V-MCM-41. Moreover, V–Ti-MCM-41 prepared under UV light irradiation exhibited higher selectivity to acetone than that prepared without UV light irradiation which may be related to the high dispersion of V and Ti oxides on the large surface of MCM-41 with a well-ordered hexagonal pore structure.

The optimal V/Ti ratio of the catalyst for photocatalytic reactivity in the partial oxidation of propane was also investigated. The results of the reaction on V–Ti-MCM-41 of different V/Ti ratios are shown in Table 2. When the amount of V is half or a third of Ti, propane conversion and acetone selectivity were found to be higher than with other ratios.

The catalysts exhibited a photoluminescence spectrum at around 400–600 nm upon excitation at around 250–300 nm and this can be attributed to the radiative decay process from the charge transfer excited state to the ground state of the isolated Ti- and V-oxides in tetrahedral coordination [18–21], as shown in Figs. 6 and 7. The addition of propane or O_2 onto these catalysts led to a quenching of the photoluminescence with different efficiencies without any changes in the shape of the spectra. Fig. 8 shows the Stern–Volmer plots:

$$\frac{\Phi_0}{\Phi} = 1 + \tau k_q[Q]$$

which can be obtained by applying a steady-state treatment during the primary processes [18]. The photoluminescence yields in the absence and presence of the quencher molecules are Φ_0 and Φ, respectively. The τ, k_q, and $[Q]$ are the lifetime of the charge transfer excited state of the tetrahedrally coordinated V or Ti oxide species in vacuum, the quenching rate constant, and the concentration of the added quencher molecules, respectively. The plots for Φ_0/Φ versus $[Q]$ formed a straight line with an interception equal to 1 and a slope equal to τk_q, indicating that the quenching of the photoluminescence occurs dynamically by the interaction of the charge transfer excited state of the V or Ti oxide species with the added molecules, leading to a nonradiative deactivation pathway. The quenching efficiencies were determined from the slope of the Stern–Volmer plots. As shown in Figs. 6 and 8A, the quenching efficiency of propane on V-MCM-41 and V–Ti-MCM-41 was found to be much higher than that on Ti-MCM-41, indicating that propane can react more easily and efficiently with the excited state of the V-oxides than Ti-oxides. Moreover, compared to the easy recovery of the photoluminescence of Ti-MCM-41 to its initial

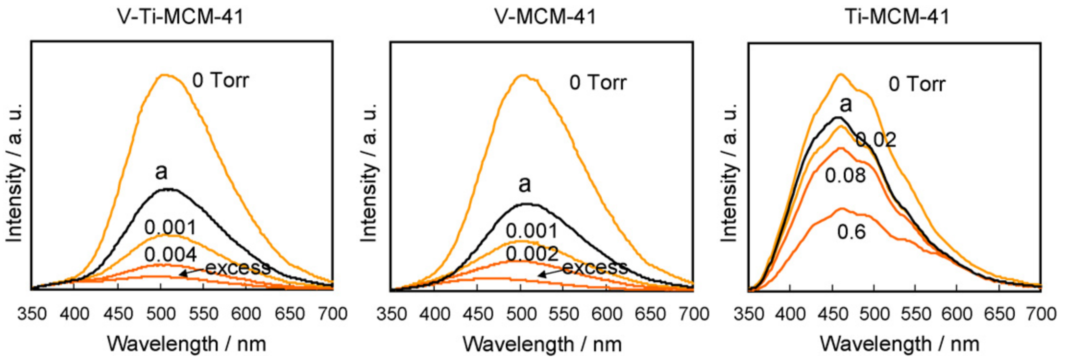

Fig. 6. Effect of the addition of propane on the photoluminescence spectra of V–Ti-MCM-41 (V, 0.2 wt.%; Ti, 0.6 wt.%), V-MCM-41 (0.2 wt.%), and Ti-MCM-41 (0.6 wt.%); (a) after degassing at 295 K for 30 min.

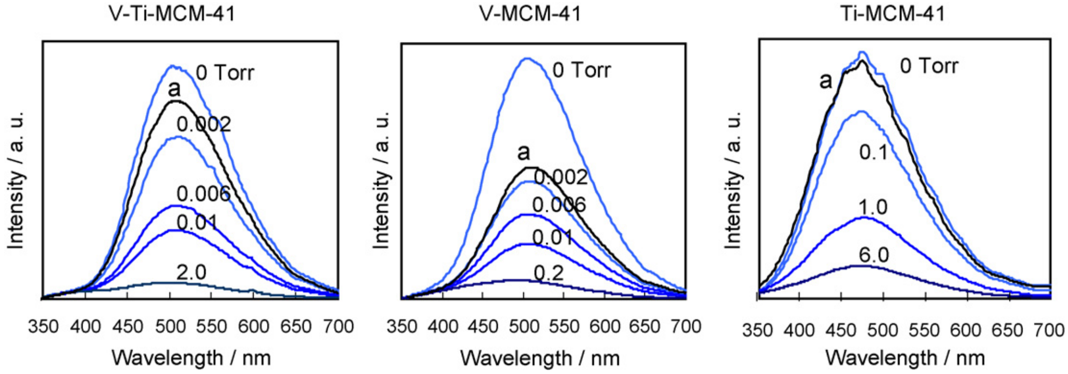

Fig. 7. Effect of the addition of O_2 on the photoluminescence spectra of V–Ti-MCM-41 (V, 0.2 wt.%; Ti, 0.6 wt.%), V-MCM-41 (0.2 wt.%), and Ti-MCM-41 (0.6 wt.%); (a) after degassing at 295 K for 30 min.

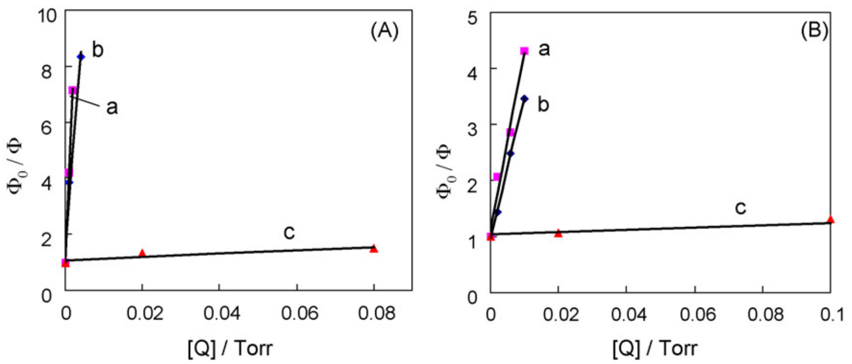

Fig. 8. Stern–Volmer plots of Φ_0/Φ values vs. $[Q]$ for the quenching of photoluminescence of various catalysts by (A) propane and (B) O_2 molecules; (a) V-MCM-41, (b) V–Ti-MCM-41, and (c) Ti-MCM-41.

intensity level, for V-MCM-41 and V–Ti-MCM-41, subsequent evacuation of propane at 295 K did not lead to the recovery of the photoluminescence intensity to their original levels. From these results, it could be concluded that a stably adsorbed species for propane was formed through the strong interaction between propane and the excited state of the V-oxide species on the V-MCM-41 and V–Ti-MCM-41 catalysts which may be the intermediate species of the photocatalytic and selective oxidation of propane.

In the case of O_2 (Figs. 7 and 8B), V–Ti-MCM-41 and V-MCM-41 showed a similar high quenching efficiency of O_2. However, after quenching of the photoluminescence by O_2 and subsequent evacuation at 295 K, the recovery of the photoluminescence of V–Ti-MCM-41 proceeded more efficiently than that of V-MCM-41, indicating that the excited state of the V-oxides in V–Ti-MCM-41 interact more weakly with the O_2 molecules. Such an interaction of O_2 with the charge transfer excited state of the V-oxide moieties was shown to play a major role in the further oxidation of the formed acetone into CO_2 on V-MCM-41.

It was also found that the quenching efficiency of both O_2 and propane on Ti-MCM-41 was very low and the photoluminescence recovered to its original intensity after degassing at 295 K, suggesting that the interaction of these additives with the excited Ti-oxides is weak, leading to a low reactivity of the photooxidation of propane on Ti-MCM-41.

4. Conclusions

V and Ti-containing MCM-41 were prepared using a photo-assisted synthesis method under UV light irradiation of the starting solutions at room temperature. Important advantages such as a shortened synthesis reaction time could be achieved, leading to an ordered, regularly oriented pore structure for the V and Ti-MCM-41 catalysts when compared with conventional synthesis methods. V-MCM-41 prepared by the photo-assisted synthesis method showed high reactivity for the photocatalytic partial oxidation of propane into acetone. This reaction was enhanced on V–Ti-MCM-41 with a higher yield and selectivity for the formation of acetone than for V-MCM-41. The excited state of the V-oxide moieties in V–Ti-MCM-41 interacted more weakly with the O_2 molecules than those of V-MCM-41. Such interactions of O_2 with the charge transfer excited state of the V-oxide moieties was shown to play an important role in the efficient oxidation of acetone into CO_2 on the V-MCM-41 catalyst.

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