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Photo-assisted synthesis of V-MCM-41 under UV light irradiation

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Vanadium ion-containing mesoporous molecular sieves V-MCM-41 were successfully prepared using a photo-assisted synthesis method with UV irradiation of the starting solutions at room temperature. Important advantages such as a shortened synthesis reaction time could be seen, leading to highly ordered regularly oriented pore structures for the V-MCM-41, when compared with synthesis using conventional method.

KEY WORDS: MCM-41; vanadium ion; photo-assisted synthesis; photocatalytic reduction of NO.

1. Introduction

Since its discovery in 1992, MCM-41 has become one of the most popular members of the M41S family of mesoporous silicate and aluminosilicate materials, particularly as a catalyst support due to its regularly oriented pore systems, large pore spaces as well as high surface area [1,2]. Along these lines, highly dispersed transition metal ions such as Ti, V, Mo, Cr incorporated within the framework of zeolites and such mesoporous molecular sieves have shown unique reactivities not only for catalytic [3–5] but also for photocatalytic reactions [6–10]. Until now, conventional methods of synthesizing MCM-41 required hydrothermal conditions and an extensive reaction time as well as the careful control of the reaction temperature and pH. Recently, a temperature-controlled microwave-assisted synthesis method of MCM-41 has been reported which can shorten crystallization time compared to conventional autoclave heating [11]. However, there are only few reports of synthesis under ambient atmospheric conditions [12]. Also, in 1989, the preparation of vanadium oxides supported on porous Vycor glass by a photochemical anchoring method was reported to produce a highly dispersed vanadium oxide species at room temperature [13]. In the present work, we report on a novel photo-assisted synthesis method of V ion-containing MCM-41 under UV light irradiation of the starting solutions at 295 K. Various spectroscopic methods were applied for characterization studies of the synthesized materials while their photocatalytic reactivities were investigated for the decomposition of NO in the presence of propane at 295 K.

2. Experimental

MCM-41 and V-MCM-41 gels were synthesized under acidic and basic conditions, respectively. 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, 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, 40 wt% tetramethylammonium hydroxide (TMAOH) combined with sodium silicate solution were added to a silica-included solution of the template under stirring. A vanadyl sulfate trihydrate solution was then added to the silica gel under stirring and the pH of the reaction mixture was adjusted to 11.0 with a NaOH solution or a dilute sulfuric acid. The molar composition of the gel mixture was 1.0 Si : 0.0125 V : 0.27 CTMABr : 0.13 Na_2O : 0.26 TMAOH : 60 H_2O. 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 while 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. The samples prepared with and without UV light irradiation were denoted as (V-)MCM-41(UV) and (V-)MCM-41(non-UV), respectively. The metal content of these materials were determined by atomic absorption analysis.

Prior to the 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. The photocatalytic reactions of NO in the presence of propane were carried out on V-MCM-41 using a 100 W Hg lamp ($\lambda > 270$ nm) at 295 K and the products were analyzed

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by gas chromatography. The powder X-ray diffractions of the samples were recorded on a Shimadzu XRD-6100 with Cu K_α radiation. UV-vis spectroscopic measurements were carried out on a Shimadzu UV-vis recording spectrophotometer, model UV-2200A.

3. Results and discussion

The XRD patterns of the calcined siliceous MCM-41 and V-MCM-41 prepared under pH1.0 conditions are shown in figure 1. Figure 1a shows the XRD patterns of the siliceous MCM-41 prepared under UV light irradiation and without UV light irradiation at 295 K for 24 h and 120 h (5 days), respectively. The XRD patterns of the sample prepared under UV light irradiation for 24 h is characteristic of a hexagonal arrangement of pores with a unit cell size (a_0) of 4.0 nm, showing a sharp (100) plane peak and small but clear (110) plane peak compared with that of MCM-41(non-UV) for 24 h. This indicates that the former sample has a higher crystallinity than the latter sample. Moreover, the effect of UV light irradiation on the crystallization becomes more significant for MCM-41 incorporated with vanadium ions (figure 1b). V-MCM-41 (UV) prepared for 24 h shows a MCM-41 pattern similar to that of the product prepared without UV irradiation for 5 days, as can be seen in figure 1b. However, for V-MCM-41 (non-UV) synthesized without UV irradiation for 24 h, the (100) peak is very broad. These results coincide with the TEM images, which show that V-MCM-41 (UV) has a higher ordered mesoporous structure and crystallinity than V-MCM-41(non-UV). It is thus clear that UV light irradiation during synthesis can accelerate the crystallization. Although the details 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 plays a significant role in 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.

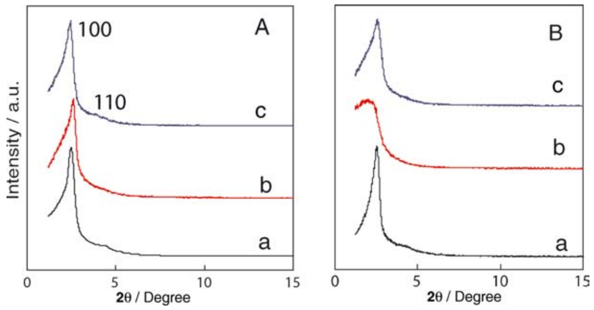

Figure 1. The XRD patterns of MCM-41 (a) and V-MCM-41 (b) prepared under pH1.0 conditions by stirring for 24 h at 295 K under UV light irradiation (a) and without UV light irradiation for 24 h (b) and 5 days (c).

The effect of UV light irradiation of the starting solution on the crystallization is more remarkable for V-MCM-41 synthesis in the basic than acidic solution. Figure 2 shows the XRD patterns of V-MCM-41 prepared in basic solutions (pH11.0) by constant stirring for 24 h at room temperature with and without UV irradiation. Compared to the broad (100) peak pattern of the sample prepared in the absence of UV light, a sharp (100) peak and small (110), (200) peaks were observed on V-MCM-41(UV) prepared under UV irradiation. These results indicate that the transition metal ions containing highly ordered MCM-41 can be synthesized in relatively short times using UV light starting at room temperature and confirmed that the excitation of the OH^- ions leads to the promotion of the crystallization of the mesoporous structure, since there are more OH^- ions in basic solution than in an acidic one. The basic chemicophysical properties of the prepared V-MCM-41 samples are shown in table 1. Interestedly, UV light irradiation during the stirring in the synthesis may increase the solubility of V under strongly acidic conditions, however, it may promote the incorporation of V into the MCM-41 framework under basic conditions.

Figure 3 shows the UV-Vis absorption spectra of the V-MCM-41 samples prepared in the pH1.0 and pH11.0 starting solutions. The two samples exhibit the same absorption band at 220 and 240 nm, 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+}) ion of the distorted tetrahedrally coordinated V-oxide species [16]. No absorption band could be observed in the wavelength regions longer than

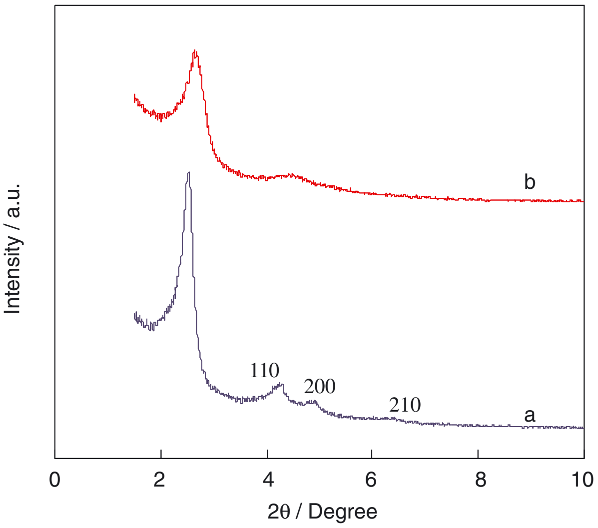

Figure 2. The XRD patterns of V-MCM-41 prepared under pH11.0 conditions by stirring for 24 h at 295 K under UV light irradiation (a) and without UV irradiation (b).

Table 1
The basic physicochemical properties of V-containing MCM-41 samples prepared at 295 K for 24 h

V-MCM-41	PH	Si/V (gel)	Wt% (solid)	a_0/Å	BET surface area/m^2 g^{-1}
Non-UV	1	80	0.25	44.9	914
UV	1	80	0.17	41.9	1136
Non-UV	11	80	0.38	40.3	1014
UV	11	80	0.60	42.1	1147

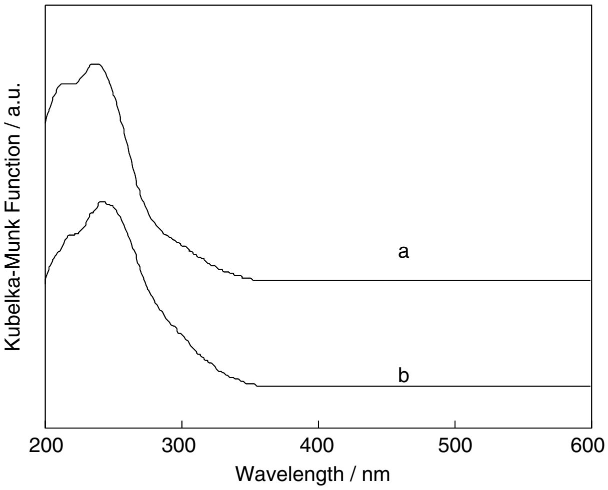

Figure 3. The UV–Vis diffuse reflectance spectra of V-MCM-41 (0.2 V wt%) prepared under UV light irradiation in pH 1.0 conditions (a) and pH 11.0 conditions (b).

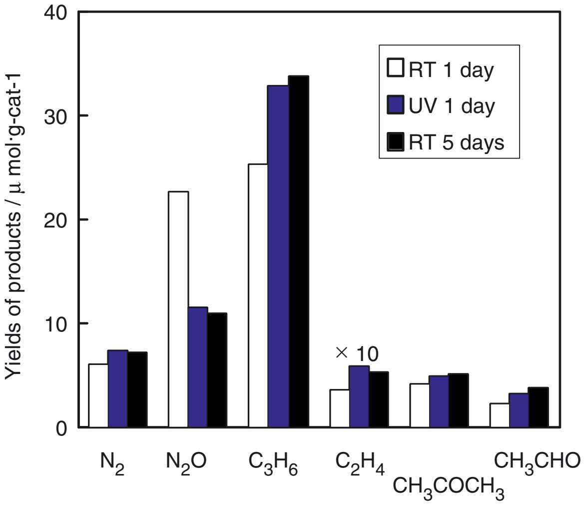

Figure 4. Yields of products in the photocatalytic decomposition of NO in the presence of propane on the V-MCM-41(0.2 V wt%) catalysts prepared in pH1.0 conditions at 295 K under UV light irradiation (λ > 270 nm) for 3 h.

400 nm, indicating that the V-oxide species are present in a highly dispersed state and an aggregated V-oxide species such as V_2O_5 is not involved. These observations show that photo-assisted synthesis has no detrimental effect when V ions are incorporated into the MCM-41 frameworks in tetrahedral coordination.

Highly dispersed V ions incorporated in zeolites and silicates were reported to exhibit high photocatalytic reactivity for the decomposition of NO in presence of propane under UV light irradiation [17,18]. The photocatalytic performance of the photo-assisted synthesis of V-MCM-41 was investigated by the reduction of NO in the presence of propane at 295 K. The reactions proceeded under UV light irradiation of V-MCM-41 prepared in the pH1.0 starting solution, leading to the formation of N_2, propylene and oxygen-containing compounds such as acetone and small amount of CO_2, etc. as shown in figure 4. It was found that the activity and selectivity of the photocatalytic reduction of NO into N_2 on V-MCM-41 prepared under UV light irradiation for 24 h are the same as those prepared in the absence of UV light for 5 days, of which two of the samples have similar XRD patterns, higher than those prepared without UV light for 24 h. Moreover, it was found that for photo-assisted synthesis, the reactivity of V-MCM-41 synthesized under pH11.0 conditions is higher than that of the catalysts synthesized under pH1.0 conditions, and especially, the yields of C_3 H_6 and acetone on the former catalyst are much higher that on the latter (figure 5).

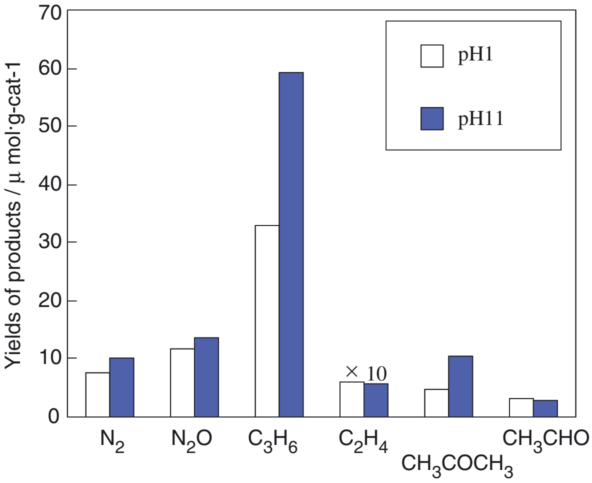

Figure 5. Yields of products in the photocatalytic decomposition of NO in the presence of propane on the V-MCM-41 (0.2 V wt%) catalysts prepared in pH1.0 and pH11.0 conditions at 295 K under UV light irradiation (λ > 270 nm) for 3 h. Amounts of added NO, 4 Torr; propane, 4 Torr.

4. Conclusions

These results clearly show that this novel photo-assisted synthesis method for V-MCM-41 under UV light irradiation of the starting solutions at room temperature exhibits significant advantages such as a shortening of the synthesis reaction time while achieving a highly ordered regular pore mesostructure in the preparation of transition metal ion-containing MCM-41, especially when compared with conventional synthesis methods. The effect of UV light irradiation on the crystallization of V-MCM-41 is more remarkable in basic rather than acidic synthesis conditions.

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