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Characteristics of the Photocatalytic Oxidation of Methane into Methanol on V-Containing MCM-41 Catalysts

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Abstract V-containing MCM-41 catalysts were prepared by a direct synthesis method under acidic and basic conditions and impregnation. Their photocatalytic reactivity was evaluated for the selective photocatalytic oxidation of methane with NO under UV irradiation at 295 K. Selective methanol formation was observed on V-MCM-41 prepared in acidic solution and imp-V/MCM-41, while only coupling reaction products were obtained on V-MCM-41 prepared in basic solution. The photocatalytic reactivity of the catalysts for the partial oxidation of methane was found to strongly depend on the local structure of the V-oxide species including the coordination and loading sites, i.e., the charge transfer excited states of the isolated tetrahedral V^{5+}-oxide species supported on the catalyst surface act as the active sites for the selective photocatalytic oxidation of methane into methanol.

Keywords Photocatalyst · V-oxide · MCM-41 · Selective oxidation of methane

1 Introduction

The partial oxidation of methane into useful oxygenates such as methanol and formaldehyde through a single catalytic step is a great challenge in catalytic research [1–5]. Various attempts have been made to obtain C_1-oxygenates, however, it has been difficult to achieve yields beyond 4%. Among the various catalysts studied for the partial oxidation of methane into methanol and formaldehyde, supported vanadium oxide catalysts have exhibited the most promising results [6–10]. In most of these studies, high temperatures are required even for low conversion levels. Conversion increases with the temperature, however, the selectivity of the C_1-oxygenates drastically decreases due to the over-oxidation of the obtained C_1-oxygenates into carbon oxides at higher reaction temperatures. Thus, the selective activation of methane at low temperatures via new routes such as the use of photocatalysts need to be investigated. So far, few studies on the selective photooxidation of methane into useful compounds such as formaldehyde and methanol have been successful [11–15].

Previously, we have reported on the photoinduced formation of methanol from methane using nitric oxide (NO) as an oxidant on highly dispersed vanadium oxides supported on Vycor glass at 275 K [15] and supported on MCM-41 mesoporous molecular sieves at 295 K [16]. In this work, we report on the selective photocatalytic oxidation of methane on V-containing MCM-41 catalysts prepared by different synthesis methods. The influence of the local structure of the V-oxide species on the catalytic reactivity is also investigated.

2 Experimental

2.1 Preparation of Catalysts

V-MCM-41 gels were synthesized under both acidic and basic conditions. Under both pathways, cetyltrimethylammonium

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bromide (CTMABr) and NH_4VO_3 served as the template and vanadium ion precursor, respectively. For the acidic pathway, tetraethyl orthosilicate (TEOS) was used as the silicon source and the molar composition of the reaction mixture was 1.0 Si:0.0125 $\sim$ 0.5 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 and the mixture was vigorously stirred at 295 K for 5 days. For the basic condition pathway, silica (Aerosil) as well as sodium silicate was used as the Si source 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. The gel was stirred at 295 K for 24 h. After the as-synthesized products were recovered by filtration, washed thoroughly with deionized water and dried at 373 K for 12 h, calcination of the samples was carried out in air at 773 K for 8 h. The samples prepared by acidic and basic methods were then denoted as V-MCM-41 (acid) and V-MCM-41 (base), respectively.

The imp-V/MCM-41 catalysts (0.6 wt% as V) were prepared by the impregnation of an aqueous solution of NH_4VO_3 into MCM-41 and synthesized by the acidic and basic methods. The samples were dried at 373 K for 12 h, followed by calcination under a dry flow of air at 773 K for 5 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 vanadium content in these materials was determined by 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 using Cu K_α radiation ($\lambda = 1.5417$ Å). Diffuse reflectance UV–vis spectroscopic measurements were carried out on a Shimadzu UV–vis recording spectrophotometer, Model UV-2200A. The photoluminescence spectra were measured at 295 K with a Spex Fluorog-3 spectrophotometer.

2.3 Photocatalytic Reactions

The photocatalytic partial oxidation of methane with O_2 or NO was carried out with the catalysts in a quartz cell under UV light irradiation ($\lambda > 270$ nm) by a 100 W high pressure mercury lamp at 295 K. A water bath was employed to keep the cell at a constant temperature, thus, the influence of heat on the reaction could be excluded. After each run, the catalyst bed was heated to 573 K to collect the products that 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 the hydrocarbons and a thermal conductivity detector (TCD) for analysis of O_2, N_2, N_2O, CO, CO_2, etc.

3 Results and Discussion

XRD investigations showed that all of the prepared V-MCM-41 catalysts have a siliceous MCM-41 mesoporous structure. Figure 1 shows the UV–vis absorption spectra of the catalysts prepared by different synthesis methods and varying V content. The samples exhibited absorption bands at around 245 and 280 nm which could 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 [17, 18].

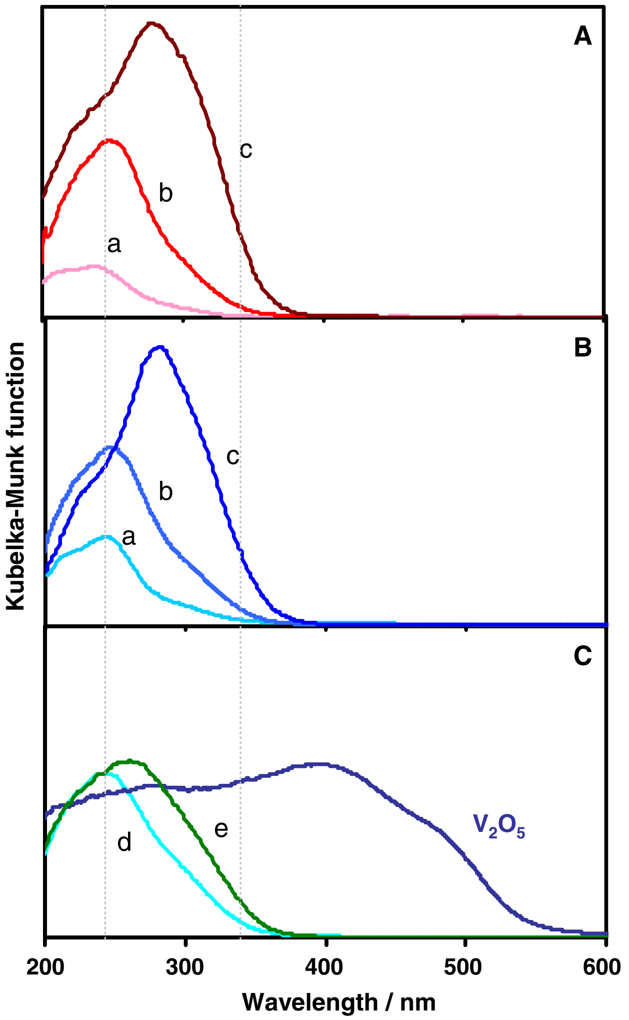

Fig. 1 Diffuse reflectance UV–vis spectra of: (**A**) V-MCM-41 (acid); (**B**) V-MCM-41 (base); and (**C**) imp-V/MCM-41 of varying V content. That is, (a) 0.15; (b) 0.6; (c) 3.6; (d) imp-(base) 0.6; and (e) imp-(acid) 0.6 wt%

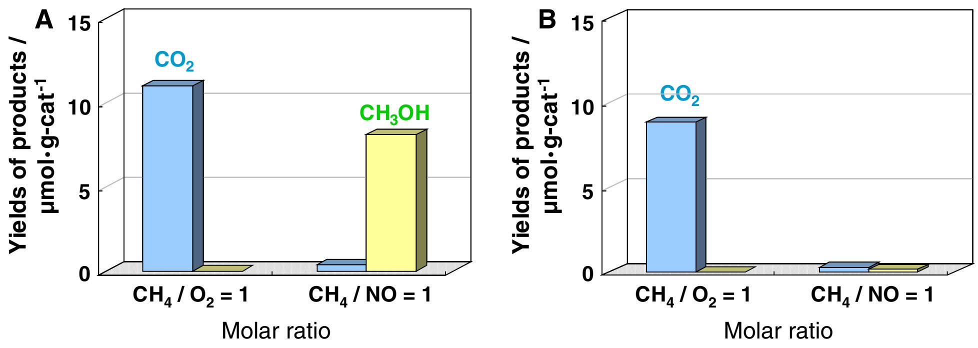

Fig. 2 Yields of methanol and CO_2 in the photocatalytic oxidation of CH_4 with NO or O_2 on: (**a**) V-MCM-41 (acid); and (**b**) V-MCM-41 (base), with 0.6 V wt% at 295 K. Amounts of reactant: 4 Torr; Reaction time: 3 h

When the V content increased to 3.6 wt%, a shoulder absorption at around 350 nm was also observed, suggesting the existence of some polymeric vanadium species (V–O–V) at higher V loadings. No absorption band could be observed in wavelength regions longer than 400 nm, indicating that the V-oxide species is present in a highly dispersed state and an aggregated V-oxide species such as V_2O_5 is not involved [18].

Figure 2 shows the results of the photocatalytic oxidation of methane with O_2 and NO at 295 K over the V-MCM-41 (0.6 wt%) catalysts prepared under acidic and basic conditions. No products could be detected without the catalysts or UV light irradiation either in the presence of methane and O_2 or methane and NO mixture. Siliceous MCM-41 itself did not exhibit any reactivity for the photocatalytic oxidation of methane with O_2 or NO under UV light irradiation, indicating that the presence of vanadium in the catalyst was essential in inducing the photocatalytic activity. In the presence of O_2, only the complete oxidation of methane into CO_2 and H_2O proceeded under UV light irradiation on both catalysts. However, the photocatalytic oxidation of methane with NO on the V-MCM-41 (acid) catalyst prepared under acidic conditions resulted in the selective formation of methanol, accompanied by the formation of trace amounts of CO_2 and acetaldehyde. Methane conversion and methanol selectivity reached 6 and 88%, respectively, after UV irradiation for 3 h. Interestingly, the selective formation of methanol from methane either in the existence of O_2 or NO could not be obtained on the V-MCM-41 (base) catalyst synthesized under basic conditions.

Figure 3 shows the effect of the V content of V-MCM-41 (acid) on the reactivity for the selective photocatalytic oxidation of methane with NO. The yield of methanol was found to increase with an increase in the V content up to 1.2 wt%, and then to sharply decrease with a further increase in the V content. V-MCM-41 was also observed to exhibit photoluminescence at around 500 nm under UV light excitation at 300 nm measured at 295 K, coinciding with the photoluminescence spectra of the tetrahedral V-oxide species highly dispersed on SiO_2 and HMS [19, 20], as shown in Fig. 4. The excitation and emission spectra are attributed to the following electron transfer process from the O^{2-} to V^{5+} ions of the tetrahedral vanadate (VO_4^{3-}) and its radiative decay from the charge transfer excited triplet state to the ground state (Eq. 1) [19–21].

$$\begin{tikzcd}[column sep=large]
{[\,V^{5+}=O^{2-}\,]} \arrow[r, "\text{UV excitation}"] & {[\,V^{4+}-O^{-}\,]^{*}} \arrow[r, "\text{photoluminescence}"] \arrow[dr, "\text{quenching}"] & {[\,V^{5+}=O^{2-}\,]} \\
\left(\begin{array}{l}\text{Ground state}\\ \text{of tetrahedral}\\ \text{V-oxides}\end{array}\right) & \left(\begin{array}{l}\text{Charge transfer}\\ \text{excited triplet}\\ \text{state}\end{array}\right) & {[\,V^{4+}-O^{-}\cdots Q\,]}
\end{tikzcd} \qquad (1)$$

Q: quencher molecules

The addition of quencher molecules (Q), such as CH_4 or NO, onto the catalyst led to an efficient quenching of the photoluminescence, the extent depending on the amount of Q, indicating that the CH_4 or NO molecules interacted with the photoexcited V-oxide species. A good correspondence between the yield of methanol and the intensity of the photoluminescence was observed, indicating that the isolated tetrahedral V-oxide species plays an important role in the partial photocatalytic oxidation of methane with NO into methanol.

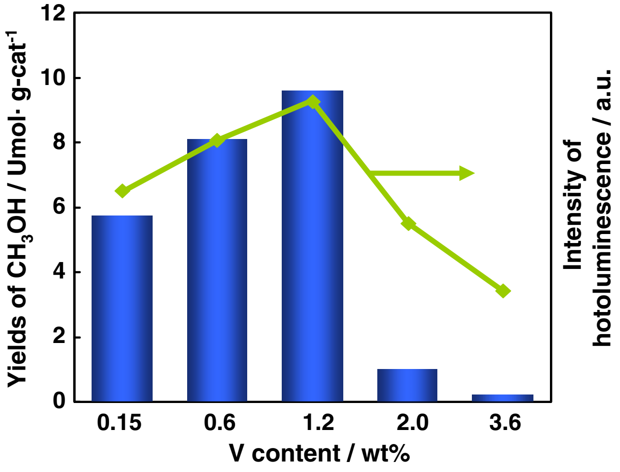

Fig. 3 Relationship between the yields of CH_3OH on V-MCM-41 (acid) and the relative intensity of the photoluminescence of the catalysts with varying V content at 295 K

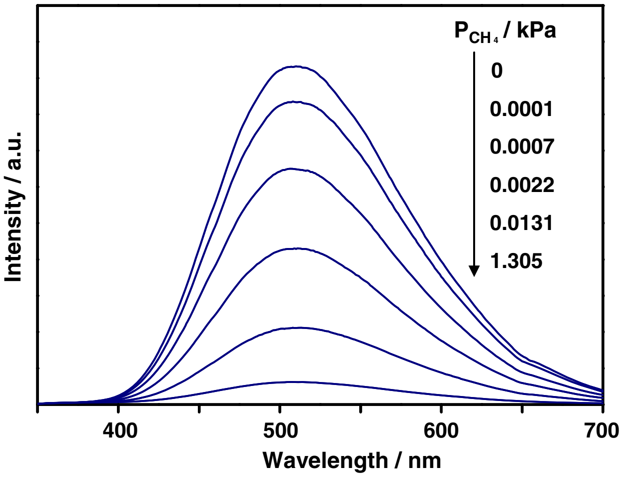

Fig. 4 Effect of the addition of CH_4 on the photoluminescence spectrum of V-MCM-41 (acid). Measured at 295 K, excitation beam is 300 nm

The effect of the preparation method of the catalysts, such as the pH value of the starting solution and V doping method, on the reactivity of the catalysts for the photocatalytic oxidation of methane with NO was also investigated. As shown in Table 1, a high conversion of methane and selectivity for the formation of methanol could be obtained on V-MCM-41 prepared in acidic solution. However, in the case of V-MCM-41 prepared in basic solution, methane conversion was quite low and methanol formation was replaced by C_2 production such as C_2H_x and acetaldehyde. On the other hand, the selective formation of methanol could be observed on both the imp-V/MCM-41 catalysts in which the V-oxide species is supported on the surface of siliceous MCM-41 synthesized by acidic and basic methods. Furthermore, it was found that the conversion of methane and the selectivity of the products on V-MCM-41 (acid) was quite similar to that on imp-V/MCM-41 (acid), suggesting that the V-oxide species in V-MCM-41 (acid) is loaded on the surface of the catalyst while the surface isolated tetrahedral V-oxide species act as the active sites in the selective photocatalytic oxidation of methane with NO into methanol. The low reactivity of V-MCM-41 (base) can be ascribed to the efficient incorporation of the V^{5+}-oxide species within the framework of MCM-41 due to its highly ordered framework [22], thus, inhibiting the efficient interaction of the V^{5+}-oxide species with any gaseous reactants.

4 Conclusions

The photocatalytic partial oxidation of methane with NO led to selective methanol formation under UV light irradiation at 295 K on the V-MCM-41 catalyst prepared in an acidic solution of pH 1 and imp-V/MCM-41. However, only coupling reaction products instead of methanol could be obtained on V-MCM-41 prepared in a basic solution of pH 11. The photocatalytic reactivity of V-MCM-41 for the selective oxidation of methane with NO was found to depend on the local structure of the V-oxide species including not only the coordination but also the loading sites, i.e., the charge transfer excited states of the isolated tetrahedral V-oxide species supported on the surface of the catalysts acted as the active sites for the photocatalytic partial oxidation of methane into methanol.

Table 1 The conversion of CH_4 and selectivity of the products in the selective photocatalytic oxidation of CH_4 with NO on the various V-MCM-41 and imp-V/MCM-41 catalysts

Catalyst	CH_4 conversion (%)	Selectivity (%)				
		CH_3OH	CO_2	C_2H_x	CH_3CHO	Other
V-MCM-41 (acid)	6.0	87.6	4.2	0.6	2.6	5.0
V-MCM-41 (base)	0.7	–	10.2	22.3	66.5	–
imp-V/MCM-41 (acid)	7.1	88.4	9.1	0.4	2.1	–
imp-V/MCM-41 (base)	2.2	74.7	2.4	5.9	17.0	–

Reactants: CH_4, 4 Torr (16 μmol); NO, 4 Torr (16 μmol). Reaction time: 3 h

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