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Selective photooxidation of methane into methanol by nitric oxide over V-MCM-41 mesoporous molecular sieves

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The partial photooxidation of methane by nitric oxide selectively led to methanol formation over the V-MCM-41 catalysts under UV irradiation ($\lambda > 270$ nm) at room temperature, while only a complete oxidation of methane could occur in the presence of oxygen. The yield of methanol corresponds with the yield of the photoluminescence of the isolated tetrahedrally coordinated V-oxides species, indicating that the charge transfer excited triplet state of these species are active sites in this photooxidation reaction.

KEY WORDS: partial photooxidation of methane; methanol; NO; V-MCM-1.

1. Introduction

The selective conversion of methane to higher hydrocarbons and/or oxygen-containing compounds such as methanol and formaldehyde has attracted much attention in the last decade since there are still difficulties in activating C–H bonds of CH_4 and C_2H_6 [1–5]. In most of these studies, high temperatures are required even for low conversion levels. Previously, it has been reported that a silica-supported vanadium oxide catalyst exhibits relatively high reactivity for oxidation of methane into methanol and formaldehyde [6–9].

Recently, Yoshida *et al.* [10] have reported that the SiO_2–Al_2O_3–TiO_2 ternary oxide system exhibited high photocatalytic activity for photoinduced direct methane coupling at room temperature to produce H_2 and hydrocarbons such as ethane. However, few studies on the selective photooxidation of methane into valuable and 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 at 275 K on highly dispersed vanadium oxides supported on Vycor glass [15]. In this paper, we report on the photooxidation of methane on V-MCM-41 mesoporous molecular sieves since they can accommodate high concentrations of the isolated vanadium oxide species, significant for the successful partial oxidation of alkanes.

2. Experimental

The V-MCM-41(x), (x = 0.15, 0.28, 0.6, 1.2 V wt%), were synthesized in accordance with previous literature [16], using tetraethyl orthosilicate (TEOS) and NH_4VO_3 as the starting materials and cetyltrimethylammonium bromide (CTMABr) as the template. After the assynthesized 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 vanadium content in these materials was determined by atomic absorption analysis.

Prior to carrying out the photoinduced 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 photooxidations of methane with O_2 and NO were carried out on V-MCM-41 using a 100 W leg lamp ($\lambda >$ 270 nm) at room temperature. After each run, the catalyst bed was heated up to 573 K for the collection of the products that adsorbed tightly onto the catalyst at room temperature. The products were analyzed by online gas chromatography equipped with a flame ionization detector (F1D) for the analysis of the hydrocarbons and a thermal conductivity detector (TCD) for the analysis of O_2, N_2, N_2O, CO, CO_2, H_2O, etc. The photoluminescence spectra were measured at 77 K with a Shimadzu RF-501 spectrofluorophotometer.

3. Results and discussion

The XRD patterns 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 with different V contents. The samples exhibit absorption bands at around 245 and 300 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

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tetrahedrally coordinated V-oxide species [17,18]. No absorption band could be observed in wavelength regions longer than 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.

Figure 2 shows the results of the photooxidation of methane with O_2 and NO over the V-MCM-41 (0.6) catalyst. No products could be detected without the oxide catalysts or UV-light irradiation either in the presence of methane and O_2 or methane and NO mixture. In the presence of O_2, only the complete oxidation of methane into CO_2 and H_2O could occur under UV-light irradiation. However, the photooxidation of methane with NO over V-MCM-41 resulted in the formation of methanol with a high selectivity in addition to small amounts of CO_2 and traces of CO and C_2H_4. The methane conversion was 7% and the selectivity of methanol was 80%. The simultaneous photoreduction of NO led to the formation of N_2 and small amounts of N_2O. Figure 3 shows the reaction time profiles of the yields of the main products, CH_3OH and N_2, in the photoinduced reaction of CH_4 and NO on V-MCM-41. UV irradiation of V-MCM-41 in the presence of a mixture of CH_4 and NO led to the formation of CH_3OH and N_2 as major products together with CO_2 and N_2O as minor products. As shown in figure 3, the N_2 and CH_3OH yields increase in proportion to the UV-light irradiation time, while no products could be detected under dark conditions.

Figure 4 shows the effect of the V content of V-MCM-41 catalysts on the reactivity for the photooxidation of methane with NO. The yields of methanol and N_2 are shown to be the highest in the case of V-MCM-41 (0.6 V wt%), and an increase in V content led to a decrease in the reactivity, showing a good correspondence with the intensities of the photoluminescence spectra attributed to the isolated tetrahedrally

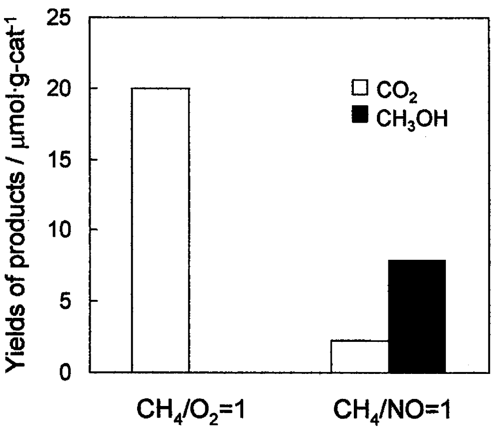

Figure 2. Yields of methanol and CO_2 in the photooxidation of methane with NO and O_2 on V-MCM-41 (0.6) at 295 K under UV light irradiation ($\lambda > 270$ nm) for 5 h. Amounts of added reactant: 150 μmol g cat^{-1}.

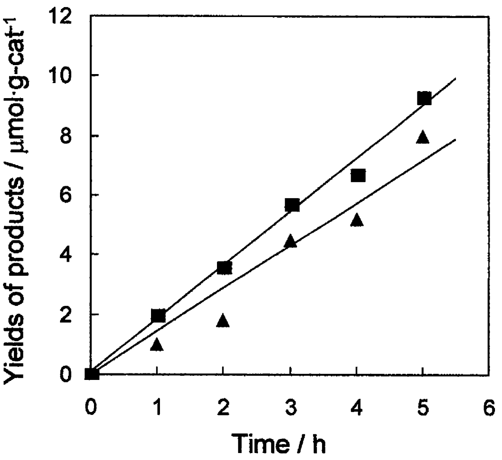

Figure 3. Reaction time profiles of the yields of CH_3OH (▲) and N_2 (■) in the photooxidation of methane with NO on V-MCM-41 (0.6) at 295 K under UV-light irradiation ($\lambda > 270$ nm).

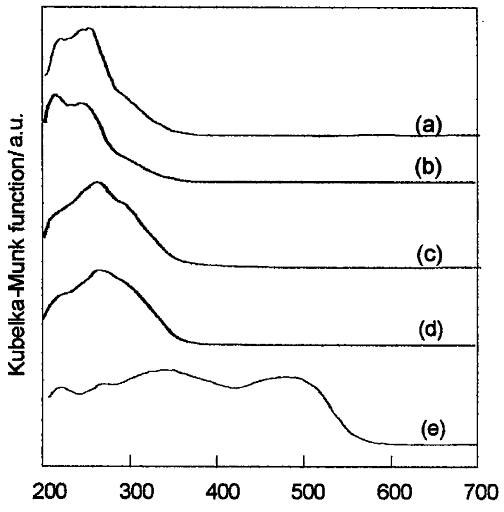

Figure 1. Diffuse reflectance UV–Vis, spectra of V-MCM-41 with various V contents: (a) 0.15, (b) 0.28, (c) 0.6, (d) 1.2 wt%, and (e) V_2O_5.

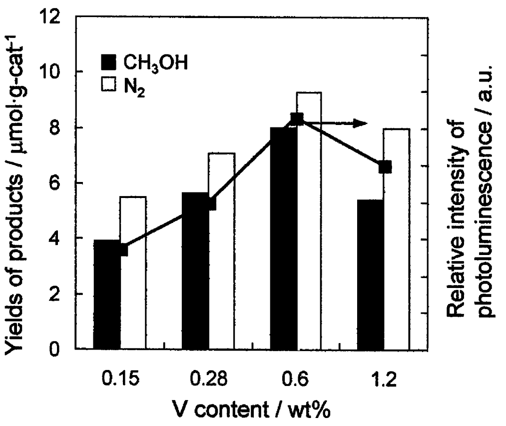

Figure 4. Relationship between the yields of CH_3OH, N_2 formation and the relative intensity of the photoluminescence spectra of V-MCM-41 having various V contents.

coordinated V-oxide species [19,20]. These results indicate that the charge transfer excited triplet state of the tetrahedrally coordinated V-oxide species acts as active sites in the photooxidation of methane in the presence of NO to form methanol and N_2.

4. Conclusions

The photoinduced partial oxidation of methane with NO selectively led to methanol formation over the V-MCM-41 catalyst under UV irradiation at room temperature, however, only the complete oxidation of methane into CO_2 and H_2O was able to occur with O_2. It was found that the photocatalytic reactivity of V-MCM-41 for the partial oxidation of methane with NO depends on the local structure of the V-oxide species. The yield of methanol corresponded to the yield of the photoluminescence of the isolated tetrahedrally coordinated V-oxides species, indicating that the charge transfer excited triplet state of these species plays an important role as the active sites in the partial photooxidation reaction of methane with NO.

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