

Sunlight-assisted photocatalytic oxidation of methane over uranyl-anchored MCM-41

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Uranyl ions anchored within the mesopores of MCM-41 silicate host matrix served as highly efficient heterogeneous catalysts for sunlight-assisted room-temperature photooxidation of methane in the presence of air to selectively form carbon dioxide. The extent of conversion depended upon the methane content; lower the concentration, faster was the completion of reaction. It was also confirmed that no thermocatalytic reaction occurred below 200 °C in the absence of radiation, other test conditions remaining the same. These results are of relevance from the point of view of abatement of VOCs in the environment.

KEY WORDS: uranyl ion; MCM-41; photocatalysis; sunlight; methane decomposition; VOCs.

1. Introduction

As methane is one of the greenhouse gases, its abatement is vital for the maintenance of a cleaner environment. The oxidation of methane to carbon dioxide is one possible path to achieve this objective. In addition, the oxidative transformation of methane either to its oxygenates or to the oxides of carbon opens a viable route for the synthesis of various value-added products utilizing natural gas as a feedstock. Nevertheless, the stability of methane molecules because of a high C–H bond energy (104 kcal/mole) makes the oxidation of methane an energy intensive process. With these aspects in view, some efforts have been devoted in recent years to investigate the photo-assisted catalytic oxidation of methane and other alkanes [1–5]. In these experiments, supported metal oxides and *n*-type solid oxide semiconductors were employed for the oxidation of methane in presence of UV irradiation. However, only small amounts of partial or deep oxidation products were obtained at elevated temperatures of ~500 K. Therefore, the development of photocatalysts that exhibit high activity under the ambient conditions of sunlight ($\lambda > 380$ nm) may offer a practical and economic means for applications, such as the cleaning of air.

The ability of the uranyl ion (UO_2^{2+}) to photocatalytically oxidize a wide range of organic substrates has received much attention, owing to its long lived and strongly oxidizing excited state [6]. In particular, the photocatalytic oxidation of hydrocarbons has been studied in the liquid phase using aqueous uranyl ions,

resulting in the formation of partial oxidation products [7–10]. In our earlier investigations, we have described the methodology for anchoring of uranyl ions onto the silicate matrix of mesoporous MCM-41/ MCM-48 and the simultaneous dispersion of nanosize crystallites of $\alpha\text{-U}_3\text{O}_8$ inside their pore system [11–15]. The presence of these two uranium moieties and the size of the entrapped U_3O_8 crystallites could be controlled by adopting appropriate synthesis and subsequent calcination conditions. We also demonstrated that these samples exhibited excellent catalytic activity for the oxidation of carbon monoxide, methanol etc. [13–15]. More recently, we successfully demonstrated that isolated uranyl ions anchored strongly within the mesopores of MCM-41 molecular sieves, referred to as $\text{UO}_2^{2+}/\text{MCM-41}$, behave as highly efficient heterogeneous photocatalysts in the complete degradation of methanol, under ambient conditions of solar radiation [16]. In continuation, in the present study, we have now successfully exploited the absorbance of the uranyl ions anchored in these materials in the UV–visible region for various photocatalytic reactions, in the presence of sunlight. In the present letter, we describe for the first time the heterogeneous photocatalytic oxidation of methane using $\text{UO}_2^{2+}/\text{MCM-41}$, where complete conversion of methane into carbon dioxide could be achieved at room temperature and in the presence of sunlight and air. Further, the objective of the present study was to demonstrate the effectiveness of $\text{UO}_2^{2+}/\text{MCM-41}$ as an efficient catalyst for the complete destruction of typical volatile organic compounds (VOCs), such as methane, in the presence of solar radiation. For comparison, the results of identical experiments performed in the absence of

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sunlight but at elevated reaction temperatures are also included.

2. Experimental

2.1. Catalyst preparation and characterization

The catalyst was prepared as described earlier [11,12], where the precursor uranyl nitrate solution (0.005 M) was exchanged under an optimized pH of 5.0 with the surfactant cations in as-synthesized MCM-41 [17]. The uranyl-anchored MCM-41 sample, after drying at $\sim 70^\circ\text{C}$ and calcination at 550°C for 2 h in N_2 and then 6 h in air, was found to contain 9.8 wt% of uranium by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) measurements. The surface area and pore diameter of this sample were found to be $\sim 600\text{ m}^2\text{ g}^{-1}$ and 28 \AA respectively; the corresponding values in the case of the parent MCM-41 subjected to similar pretreatments being $1000\text{ m}^2\text{ g}^{-1}$ and 30 \AA . The low angle X-ray diffraction (XRD) patterns of the $\text{UO}_2^{2+}/\text{MCM-41}$ catalysts exhibited the reflections characteristic of hexagonal MCM-41 structure [12]. At higher 2θ values, weak reflections appearing at 21.35 , 26.03 , 34.03 , 45.83 and 51.38° indicated the presence of $\alpha\text{-U}_3\text{O}_8$ crystallites encapsulated in the mesopores of MCM-41 [12–15]. The intensity of the diffuse reflectance ultraviolet-visible (DRUV–VIS) spectra of these samples, recorded prior to and after calcination, revealed that the anchored uranyl groups were fairly stable and only $\sim 10\text{--}15\%$ of the uranyl ions were transformed into $\alpha\text{-U}_3\text{O}_8$ crystallites. FT-IR study similarly provided evidence for the strong binding of the uranyl group, $[\text{O}=\text{U}=\text{O}]^{2+}$ at the Si-O^- sites of the MCM-41 matrix. The details have been given in our earlier publications [11–15].

2.2. Photocatalytic activity measurements

The photooxidation of methane was carried out in the concentration range of 0.15 to 2.3% volume/volume methane in air. For this purpose, about 100 mg of catalyst sample was dispersed in a quartz reaction cell of 15 mm diameter, 150 mm length and sealed with a silicon rubber septum. The reactants were introduced into the cell without any pretreatment of the catalyst and the final pressure in the cell was kept at around 1.2 bar. The reaction products sampled at ~ 30 min interval were analyzed on a Chemito model-8510 gas chromatograph, equipped with thermal conductivity detector (120°C), and Porapak-Q (30°C) or Spercocarb (50°C) column. The photocatalytic activity was evaluated under the sunlight and the average photon flux of sunlight, as measured by uranyl oxalate actinometer, was $\sim 2.1 \times 10^{14}$ photons $\text{s}^{-1}\text{ cm}^{-2}$. Parallel experiments were carried out in the absence of sunlight using identical quartz cells at various isothermal temperatures.

3. Results and discussion

3.1. DRUV–VIS studies

Figure 1 depicts the DRUV–VIS spectra of uranyl-anchored MCM-41. The inset shows the DRUV–VIS spectrum of uranyl nitrate dihydrate, $\text{UO}_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$. It can be seen from this figure that the absorbance region of 200–500 nm exhibited by uranyl-anchored MCM-41 samples matches with that of parent uranyl nitrate (inset) as well as the isolated uranyl groups in aqueous medium [6]. Nevertheless, in contrast to the absorbance spectrum of parent uranyl nitrate (inset), the uranyl-anchored MCM-41 shows broad and overlapping bands along with a considerable change in their relative intensity, which provide clear evidence that these groups are in a constrained environment as a consequence of immobilization and binding to the defect silica sites. The strong band observed in the UV region (200–330 nm) is attributed to intra-ligand electron cloud excitation or charge transfer bands corresponding to electronic transitions from the equatorial ligands to uranyl groups [6]. On the other hand, the weak visible band (330–500 nm) is attributed to transitions within the uranyl groups from highest filled π -orbitals to non-bonding orbitals of uranium [6]. It can also be seen from this figure that as compared to as-exchanged sample (figure 1a), the calcined sample (figure 1b) shows a slight decrease in absorbance in the visible region. This could be attributed to a partial conversion of the uranyl ions into U_3O_8 clusters, as the latter does not exhibit absorbance in this region. This clearly indicates that UO_2^{2+} ions are tightly bound to the silicate matrix. Thus, the prominent absorbance component of $\text{UO}_2^{2+}/\text{MCM-41}$ in the visible region ($\lambda > 380\text{ nm}$) would offer a far superior photocatalytic activity for applications in sunlight, compared to commonly used UV–region photocatalysts such as TiO_2 .

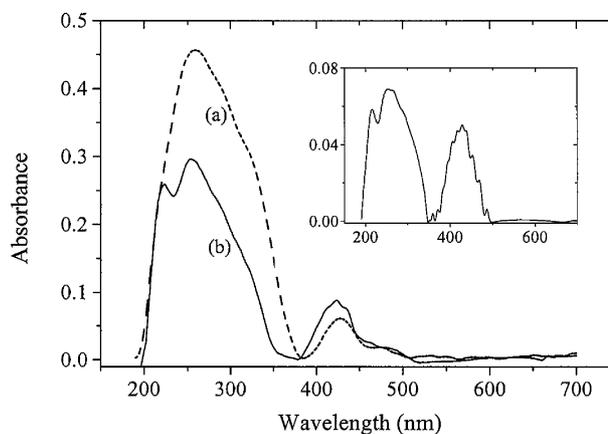


Figure 1. The DRUV–VIS spectra of: (a) uranyl-exchanged MCM-41, (b) uranyl-exchanged and calcined MCM-41 ($\text{UO}_2^{2+}/\text{MCM-41}$). Inset: DRUV–VIS spectrum of uranyl nitrate dihydrate.

3.2. Catalytic activity under sunlight

The sunlight-assisted room temperature reaction of methane + air over $\text{UO}_2^{2+}/\text{MCM-41}$ gave rise to the formation of carbon dioxide only; no partial oxidation products such as carbon monoxide, methanol, formaldehyde, and formic acid were formed. Figure 2 exhibits the photocatalytic activity of $\text{UO}_2^{2+}/\text{MCM-41}$ for varying concentrations of methane in air. As seen in data of figure 2, the extent of conversion depended upon the initial concentration of methane in air. The conversion (%) is expressed in this figure as $[1-(C_t-C_o)]$, where C_o is the initial concentration of methane and C_t is the concentration of methane remaining at time t . The completion of the reaction was faster for the low concentrations of methane in air. Thus, $\sim 100\%$ CH_4 CO_2 conversion was achieved within about two and a half hours time when 0.15 volume% of methane in air was exposed over $\text{UO}_2^{2+}/\text{MCM-41}$ at room temperature (figure 2, curve a). The required exposure time for reaching equilibrium increased progressively with the increasing concentration of methane in air, as seen in curves (c) and (d) of figure 2. These results indicate that the product yield is controlled by the number of uranyl sites available for the reaction and not the methane concentration. We may also mention that no formation of carbon dioxide was detected in parallel experiments conducted on the uranyl-free MCM-41 sample. Similarly, no reaction occurred during the room temperature exposure of methane and air over $\text{UO}_2^{2+}/\text{MCM-41}$ under the identical test conditions, but in the absence of sunlight. We also confirmed that the photolysis of methane did not occur in the gas phase, i.e., in the absence of a catalyst. In addition, experiments carried out using bulk $\alpha\text{-U}_3\text{O}_8$ as a catalyst under identical conditions resulted in no carbon dioxide formation.

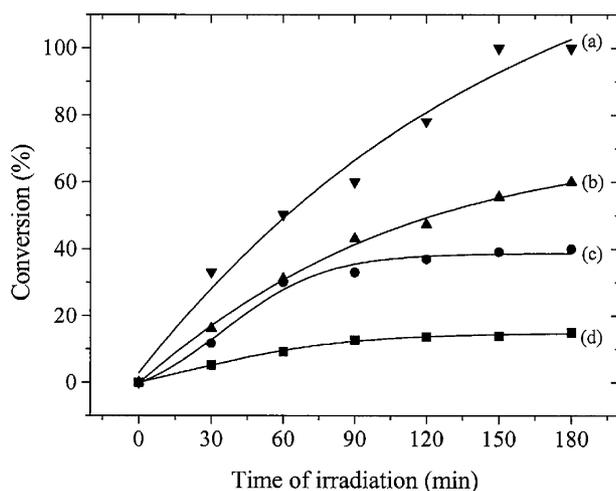


Figure 2. Time dependent variation in CO_2 yield during oxidation of methane in air over $\text{UO}_2^{2+}/\text{MCM-41}$ under sunlight irradiation. Curves (a) to (d) represent methane concentrations in air varying at 0.15, 0.5, 1.25, and 2.3 volume %, respectively.

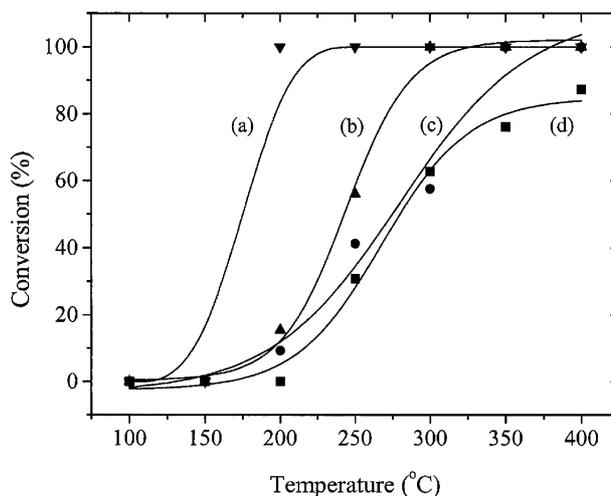


Figure 3. Temperature dependent variations in CO_2 yield during oxidation of methane in air over $\text{UO}_2^{2+}/\text{MCM-41}$ in the absence of sunlight. Curves (a) to (d) represent methane concentrations in air varying at 0.15, 0.5, 1.25, and 2.3 volume %, respectively.

These results thus demonstrate the involvement of highly dispersed uranyl ions in the heterogeneous photocatalytic process followed in this study.

3.3. Thermal catalytic activity

For comparison, the temperature dependent catalytic oxidation of methane over $\text{UO}_2^{2+}/\text{MCM-41}$ was monitored in the absence of sunlight, and the results are included in figure 3. A measurable formation of carbon dioxide commenced only at temperatures above 150°C in case of lower concentrations of methane (figure 3a) and above 200°C for the higher concentrations (figure 3c,d). In our previous studies [12–15], we have highlighted the role played by bulk oxygen of uranium oxide species encapsulated in the pores of MCM-41 in such thermal-catalytic reactions involving the oxidation of carbon monoxide and methanol. These results thus substantiate the role of uranyl species in the results presented in figure 2, where the absorbance in the visible region of solar spectrum and the strongly oxidizing nature of the uranyl ion in their excited state may play a crucial role in the activation of methane molecules, leading thereby to hydrogen abstraction and subsequent oxidation to form carbon dioxide.

4. Conclusions

In the present study, we have demonstrated the high activity of the uranyl-anchored MCM-41 as a heterogeneous photocatalyst for the total oxidation of methane at room temperature under ambient sunlight conditions. The present study has confirmed that the isolated uranyl groups anchored in the cavities of a

mesoporous matrix may behave like the uranyl ions in aqueous medium. At the same time, we believe that such confinement inside a silica host may help in minimizing the concerns related to the natural radioactivity of ^{238}U atoms, in case the depleted uranium is employed for such applications as a photocatalyst.

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