

# The selective adsorption/reaction of methanol over nanosize uranium oxide crystallites dispersed in MCM-48: FT-IR and TPD studies

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## Abstract

The techniques of in situ Fourier-transform infrared spectroscopy (FT-IR) and temperature-programmed desorption (TPD) were employed to discriminate between the surface species formed over  $U_3O_8$ /MCM-48, bulk  $U_3O_8$  and MCM-48 during the interaction of methanol at different temperatures. The  $U_3O_8$ /MCM-48 was found to exhibit a different behavior, as compared to the other two catalysts. Thus, methanol reacted over  $U_3O_8$ /MCM-48 to form methoxide, oxymethylene, polyoxymethylene (POM) and formate complex type species over catalyst surface. These species gave rise to formation of formic acid, formaldehyde, CO,  $CO_2$ ,  $H_2$  and methane at elevated temperatures, as revealed by TPD coupled with QMS and FT-IR results. The room temperature adsorption of  $CH_3OH$  over MCM-48, on other hand, resulted mainly in the development of methoxide species. Small amounts of dimethyl ether, CO and  $CO_2$  were the main reaction products formed during subsequent thermal activation, the yields depending upon temperature. Furthermore, a negligibly small amount of methanol was adsorbed over bulk  $U_3O_8$  during room temperature adsorption and no methoxy groups were formed in the process, surface formate and oxymethylene groups were observed at elevated temperatures. The results indicate that the presence of highly dispersed  $U_3O_8$  promoted the formation of certain polyoxymethylene  $[U(-OCH_2)_n]$  species that are responsible for the selective oxidation of methanol to formaldehyde and formic acid. The role of the particle size of  $U_3O_8$  crystallites and the transient surface species responsible for the selective catalytic behavior of  $U_3O_8$ /MCM-48 are discussed in the light of these results.

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**Keywords:** MCM-48; Dispersed uranium oxide; Methanol adsorption; TPD; In situ FT-IR

## 1. Introduction

The oxides of uranium are viewed as prospective catalysts for the oxidation and dehydration reactions of various organic compounds because of their better thermal stability and also because of the availability of two distinct oxidation states of U, which undergo a low energy transition between them and thus facilitate the Mars and van Krevelen type reaction mechanism [1–11]. In recent publications from our laboratories, we reported on dispersion of  $U_3O_8$  in mesoporous materials of MCM-41 and MCM-48 type that result in the increase of

exposed surface area and hence the catalytic activity of uranium oxide [12–14]. We demonstrated that the dispersion of nanosize crystallites of  $U_3O_8$  is facilitated by the exchange of template molecules in the mesopores of these materials [12–14]. The highly dispersed crystallites of  $U_3O_8$  gave rise to not only many fold increase in the catalytic activity for methanol decomposition/oxidation reactions, but also selectivity. Thus, while a considerable amount of  $CH_3OH$  was converted to organic compounds (dimethyl ether, formaldehyde, dimethoxy methane and methyl formate), on reaction over bulk  $U_3O_8$  and MCM-48 silica host, only CO,  $CO_2$ ,  $CH_4$  and  $H_2$  were the reaction products in case of  $U_3O_8$ /MCM-48. The detailed comparative study for the same were described elsewhere [14]. In the present communication, we employed temperature-programmed desorption (TPD) and

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Fourier-transform infrared (FT-IR) spectroscopy to identify the transient species formed over MCM-48,  $U_3O_8$  and  $U_3O_8$  dispersed over MCM-48 samples during their exposure to methanol at different temperatures. An attempt is made in this study to address the role of nanocrystallites of  $U_3O_8$  in the surface processes occurring in the reactions of  $CH_3OH$  and to elucidate the overall impact on the reaction mechanism.

## 2. Experimental

### 2.1. Sample preparation

The preparation and characterization of Si-MCM-48 and  $U_3O_8$ /MCM-48 catalysts used in this study has been described elsewhere [12–14]. In brief, about 1 g of as synthesized MCM-48 sample was stirred with 0.035 M uranyl acetate solution for about 12 h. The yellow colored mass obtained was filtered, washed thoroughly with distilled water, dried and finally calcined at 823 K for 2 h in  $N_2$  and 8 h in  $O_2$ . The uranium content of the loaded sample, as determined by spectrophotometry, was found to be about 26 wt.%. The samples were characterized using various techniques such as XRD, IR, UV–vis, TEM and  $N_2$  sorption, the studies of which have been reported in our earlier publications [12–14]. The TEM micrographs, were obtained on JEOL-2000 FX microscope operating at 120 kV. For this purpose, 300 mesh size sample was dispersed in ethanol by ultrasonication and then a drop of this suspension was placed on a copper grid covered with a carbon film. A sample of bulk  $U_3O_8$  was prepared by heating uranyl acetate monohydrate in air at 823 K. XRD patterns of the sample thus obtained matched with that of  $\alpha$ - $U_3O_8$ .

### 2.2. Temperature programmed desorption

The TPD of methanol was monitored under flow of purified helium using a TPDRO-1100 instrument (Thermoquest, Italy) equipped with a thermal conductivity detector and coupled to an on-line Quadrupole mass spectrometer (Omnistar 200, Pfeiffer Vacuum). The sample (50 mg in a quartz microreactor) was pretreated at 820 K in He ( $30 \text{ ml min}^{-1}$ ) for 24 h and then cooled to room temperature. It was then exposed to around forty pulses (10 ml each) of 5% methanol in argon under He flow ( $10 \text{ ml min}^{-1}$ ), so as to achieve saturation coverage. The catalyst was then purged with He ( $20 \text{ ml min}^{-1}$ ) at room temperature for 1 h in order to remove the physisorbed methanol. The TPD run was recorded in 25–550 °C temperature region at a ramping rate of  $10^\circ/\text{min}$ . The effluents from the reactor were continuously monitored by TCD and QMS as a function of temperature.

### 2.3. FT-IR studies

In situ infrared spectroscopy experiments were performed using a high-temperature, high-pressure, stainless steel cell

fitted with water-cooled  $CaF_2$  optical windows. A self supporting sample pellet (80 mg, 25 mm diameter) was mounted in IR cell and the spectra were recorded in transmission mode using JASCO 610 FT-IR Spectrophotometer equipped with a DTGS detector. In order to achieve good signal to noise ratio, 300 scans were collected for recording each spectrum at a resolution of  $4 \text{ cm}^{-1}$ . Prior to its exposure to methanol, the sample pellets were heated in a vacuum of about  $10^{-4}$  Torr for 24 h at a temperature of 300 °C. The experiments were carried out by exposing the sample wafers to methanol vapor in argon (1:16 mole ratio) while maintaining the sample at a temperature between 25 and 250 °C. The final spectra were recorded with unexposed sample wafer as a reference and the IR bands due to unadsorbed methanol were subtracted wherever applicable. The values given in the parentheses in some figures represent the absorbance values of individual IR bands so as to give an estimate of the relative intensity.

## 3. Result and discussion

Fig. 1a presents TEM micrographs of Si-MCM-48 sample taken along (1 1 1) direction, depicting an ordered cubic pore

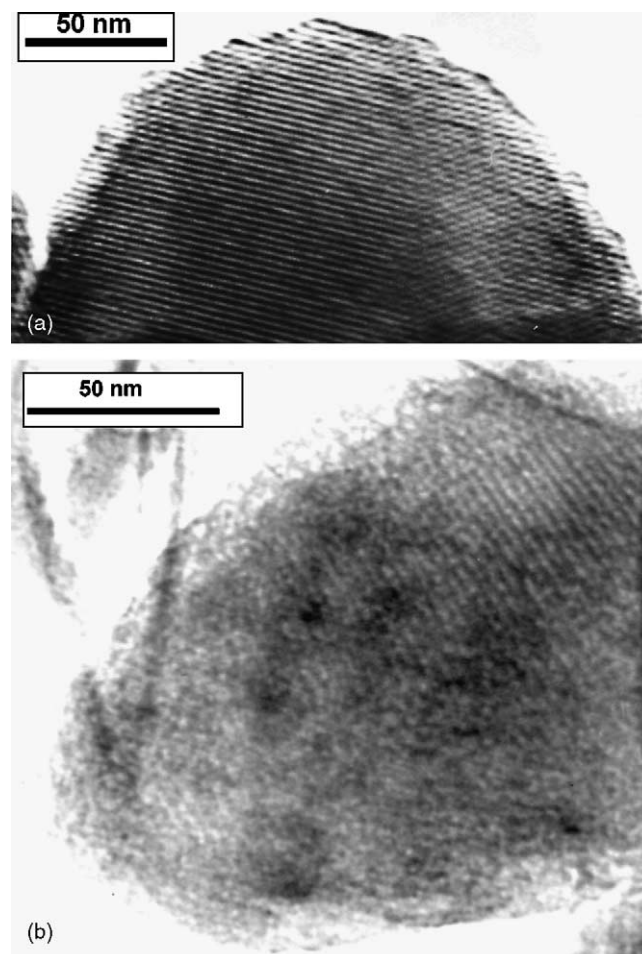


Fig. 1. TEM micrographs of (a) MCM-48 and (b)  $U_3O_8$ /MCM-48.

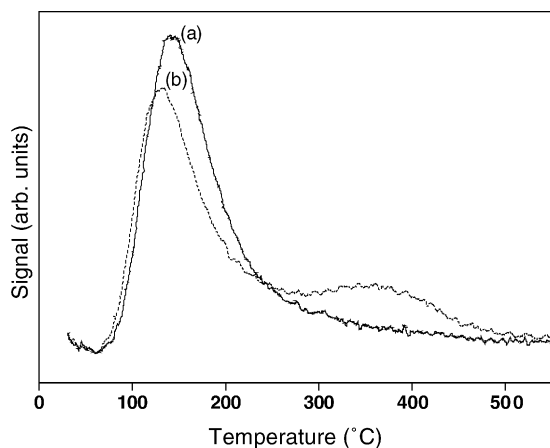


Fig. 2. TPD profiles obtained for methanol adsorption studies on (a) MCM-48 and (b)  $U_3O_8$ /MCM-48 samples.

structure typical of host material [15]. Fig. 1b shows TEM micrograph of  $U_3O_8$ /MCM-48 sample. As is seen clearly in this figure, the pore structure of the host MCM-48 is preserved to considerable extent in spite of high loading of uranium (26 wt.%). At the same time, some disordering in the cubic structure of the host is seen in certain regions of Fig. 1b. Also noticeable in Fig. 1b are some dark feature of size  $\sim 2$ –6 nm located near the mouth of the pores and to certain extent on the surface of the host matrix. These dark features are attributed to the presence of highly dispersed nanocrystallites of  $U_3O_8$ , the presence of which is substantiated by XRD results. We may mention here that, due to their higher mass number, the uranium moieties are likely to present strong contrast as compared to the host matrix thus justifying our inferences.

The surface area and pore volume of MCM-48,  $U_3O_8$ /MCM-48 and  $U_3O_8$  samples were evaluated from  $N_2$  sorption isotherms data using BET equation. The surface area and pore volume of MCM-48 sample were found to be  $1200 \text{ m}^2/\text{g}$  and  $0.98 \text{ cm}^3/\text{g}$ , respectively and these values decreased to  $400 \text{ m}^2/\text{g}$  and  $0.46 \text{ cm}^3/\text{g}$  in case of the samples having occluded uranium oxide. The pore size in the loaded samples was also found to decrease from 28 to 20 Å. Both the host and the uranium loaded MCM-48 samples showed type-IV isotherm, indicating that the mesoporosity of the host sample was preserved even after high loading of uranium oxide and the observed changes in above mentioned physical characteristics may therefore be attributed to filling of the pores of the host matrix by nanoparticles of uranium oxide. The surface area of  $\alpha$ - $U_3O_8$  was found to be  $\sim 6 \text{ m}^2/\text{g}$ .

Temperature programmed desorption profiles were obtained after adsorption of methanol on  $U_3O_8$ , MCM-48 and  $U_3O_8$ /MCM-48 samples at room temperature. Only a baseline signal was observed during desorption run carried out on  $U_3O_8$ , indicating little adsorption of methanol on low surface area oxide of uranium. Fig. 2a depicts a single broad desorption profile with a temperature maximum ( $T_{\text{max}}$ ) of  $\sim 150^\circ\text{C}$  for methanol adsorbed on siliceous MCM-48 sample. On the contrary, the TPD profile of methanol constituted of two well defined peaks in case of  $U_3O_8$ /MCM-48 sample

(Fig. 2b), one with temperature maximum ( $T_{\text{max}}$ ) of  $\sim 125^\circ\text{C}$  and the other broad band at  $\sim 350^\circ\text{C}$ . The QMS analysis of the species desorbed from MCM-48 and  $U_3O_8$ /MCM-48 samples are given in Figs. 3 and 4, respectively. It is evident from Fig. 3 that in case of MCM-48, adsorbed methanol ( $m/e = 31$ ) and water ( $m/e = 18, 16$ ) were released in the temperature range  $100$ – $200^\circ\text{C}$ , followed by hydrogen ( $m/e = 2$ ), methane ( $m/e = 16$ ) and carbon dioxide ( $m/e = 44$ ) desorption at higher temperatures ( $>375^\circ\text{C}$ ). This indicates that while most of the methanol adsorbed is loosely bound on the substrate, a small amount interacts with the host leading to the formation of water and methoxide groups (as seen by IR). The methoxide groups formed further undergoes oxidation and coupling reactions to form CO,  $\text{CO}_2$ ,  $\text{H}_2$  and  $\text{CH}_4$  at higher temperatures (Fig. 3). No desorption profile was obtained for dimethyl ether ( $m/e = 45, 15$ ) and formic acid ( $m/e = 45, 46$ ). Mass spectral analysis of desorption profile for  $U_3O_8$ /MCM-48 sample is shown in Fig. 4. The data in Fig. 4 reveals that while the species evolved in lower temperature region consisted mainly of methanol and  $\text{H}_2\text{O}$ , the TPD signal for the middle temperature region ( $T_{\text{max}}$  at  $\sim 270^\circ\text{C}$ ) corresponded primarily to formic acid ( $m/e = 45, 46$ ) and the subsequent desorption at higher temperatures ( $300$ – $500^\circ\text{C}$ ) comprised of CO ( $m/e = 28$ ),  $\text{CO}_2$  ( $m/e = 44$ ),  $\text{CH}_4$  ( $m/e = 16$ ),  $\text{H}_2$  ( $m/e = 2$ ), and  $\text{H}_2\text{O}$  ( $m/e = 18$ ). It may thus be inferred that even though the low temperature process occurring on  $U_3O_8$ /MCM-48 remains identical to that observed for MCM-48, a part of adsorbed methanol also interacts with the dispersed uranium oxides to form formic acid in middle temperature region ( $150$ – $350^\circ\text{C}$ ). The species (CO,  $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{H}_2$ ) obtained in higher temperature region may be due to decomposition of certain strongly held complex species.

Fig. 5 shows infrared absorption spectra in the stretching and deformation modes, when siliceous MCM-48 sample pellet was exposed to  $54 \mu\text{mol}$  of methanol at temperatures of  $25^\circ$  (room temperature),  $100$ ,  $200$  and  $250^\circ\text{C}$ . The IR spectrum recorded at  $25^\circ\text{C}$  (Fig. 5a) displays prominent bands at  $2956$  and  $2846 \text{ cm}^{-1}$  corresponding to asymmetric and symmetric stretching vibrations of widely reported methoxy groups. The  $1465 \text{ cm}^{-1}$  band may be identified with the C–H bending vibration of methoxy groups [16,17]. In addition, the weak  $\nu(\text{C–H})$  bands seen in the  $3100$ – $2800 \text{ cm}^{-1}$  region and the  $\delta(\text{C–H})$  bands at  $1473$ ,  $1463$  and  $1444 \text{ cm}^{-1}$  in Fig. 5a match with the IR bands of dimethyl ether [18]. The band at  $1632 \text{ cm}^{-1}$  may be attributed to water formed during the reaction, and since no associated rotational bands are observed it is surmised that the water is adsorbed on the catalyst surface.

Curves b, c, and d in Fig. 5 show IR spectra of methanol exposed on Si-MCM-48 at  $100$ ,  $200$  and  $250^\circ\text{C}$ , respectively. The intensity of  $2956$  and  $2848 \text{ cm}^{-1}$  bands due to methoxy species was found to decrease (as shown in bracket in figures) with the rise in temperature. At the same time, the  $\nu(\text{C–H})$  bands due to dimethyl ether at around  $3008$ ,  $2996$ ,  $2985$ ,  $2927$ ,  $2914$ ,  $2903$ ,  $2890$ ,  $2879$ ,  $2817$  and  $2805 \text{ cm}^{-1}$  and the  $\delta(\text{C–H})$  bands at around  $1473$ ,  $1463$  and  $1444 \text{ cm}^{-1}$  were found to grow progressively (Fig. 5(b–d)). It is envisaged that

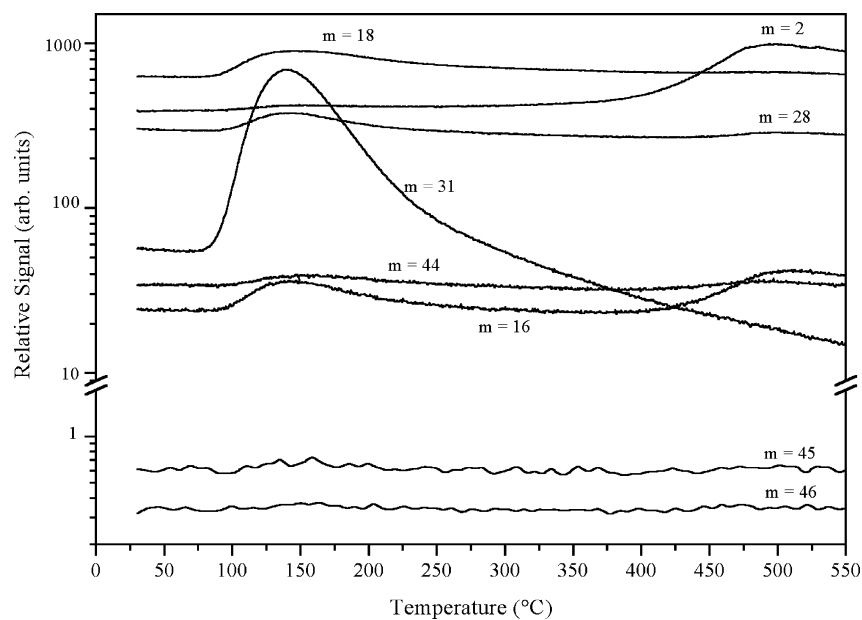


Fig. 3. Mass spectral data of various effluents for methanol TPD study on MCM-48.

the formation of dimethyl ether may occur during interaction of free methanol molecules with the existing methoxy groups [18]. Also observed are a number of rotational bands in the lower region and these bands are attributed to the presence of water formed during the reaction in the vapor form at higher temperatures.

Spectra a, b and c in Fig. 6 show IR bands arising due to exposure of methanol on bulk  $U_3O_8$  wafer at temperatures of 25, 200 and 250 °C, respectively. The IR spectrum at 25 °C (Fig. 6a) shows very weak bands in  $\nu(C-H)$  stretch region, but a comparatively strong band at  $\sim 1570\text{ cm}^{-1}$  and a group of overlapping bands in  $1550\text{--}1300\text{ cm}^{-1}$  region.

The IR band appearing at  $\sim 1570\text{ cm}^{-1}$  along with bands in  $1360\text{--}1300\text{ cm}^{-1}$  region are the features associated with  $\nu_{as}$  and  $\nu_s(COO^-)$  species bonded to metal sites, the formation of which has been reported earlier for the adsorption of methanol over  $Cu/ZrO_2$ ,  $Cu/SiO_2$ ,  $V_2O_5\text{--}TiO_2$  and  $Sn\text{--}Mo$  oxide systems at elevated temperatures [16,19–22]. The overlapping group of bands observed in the frequency region of  $1550\text{--}1370\text{ cm}^{-1}$  match with the bands in this region of formaldehyde. With weak bands seen in the corresponding carbonyl region ( $1750\text{--}1650\text{ cm}^{-1}$ ) of formaldehyde it can be inferred that the group of bands mentioned above may arise due to certain adsorbed species that may be identified

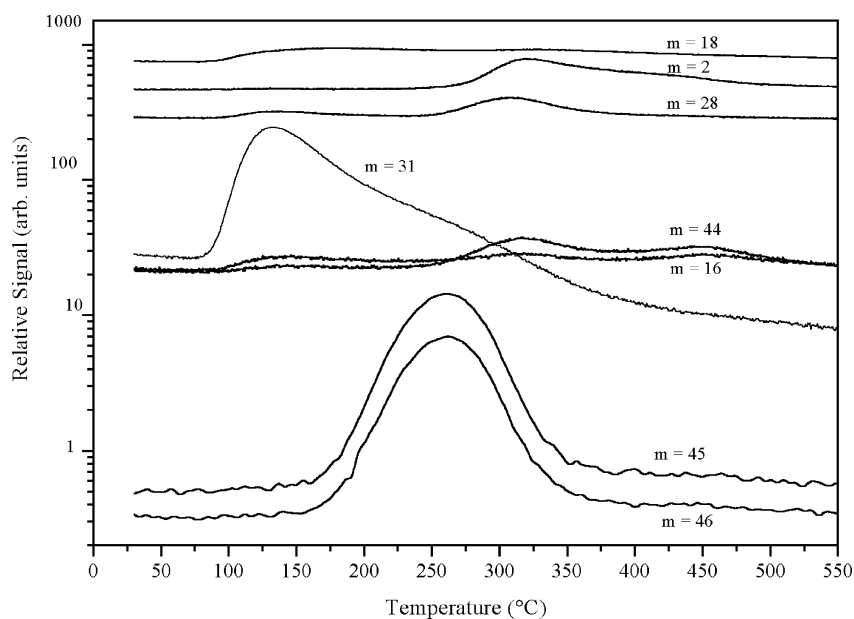


Fig. 4. Mass spectral data of various effluents for methanol TPD study on  $U_3O_8/MCM-48$ .

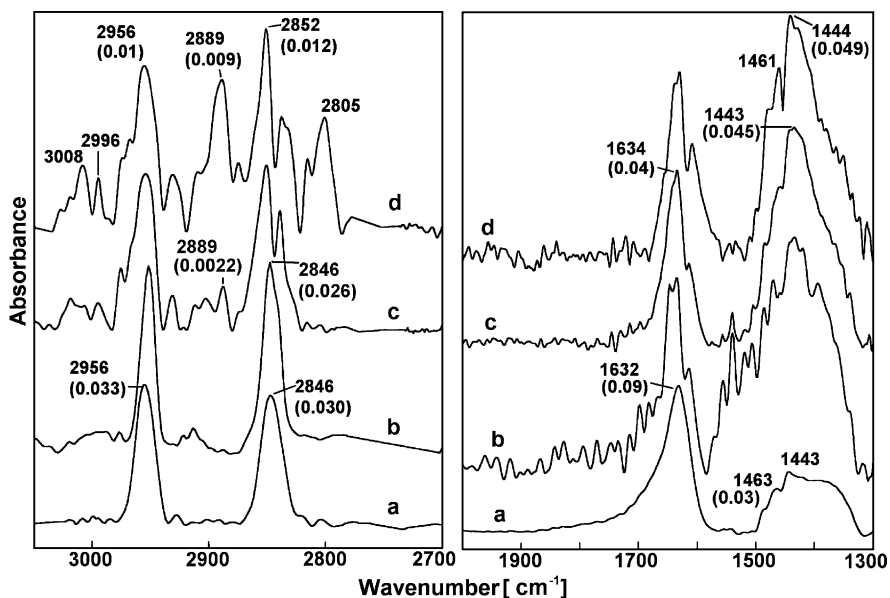


Fig. 5. IR spectra for methanol adsorption ( $54 \mu\text{mol g}^{-1}$ ) on MCM-48 at different temperatures: (a) RT; (b)  $100^\circ\text{C}$ ; (c)  $200^\circ\text{C}$ ; (d)  $250^\circ\text{C}$ .

with oxymethylene ( $-\text{OCH}_2$ ) groups, reported earlier for the adsorption of methanol over other metal oxides [19,20,22]. This indicates that methanol interacts with oxide and under goes dehydrogenation process to give formaldehyde in adsorbed form which is further oxidized to formate complex species.

When methanol was exposed to the bulk oxide at higher temperatures of 200 and  $250^\circ\text{C}$  (Fig. 6b and c), strong and prominent bands in the  $\nu(\text{C}-\text{H})$  stretching region at around 2950, 2942, 2923, 2911, 2896, 2881, 2863, 2846, 2832, 2817, 2802, 2779, 2765, 2748 and  $2730 \text{ cm}^{-1}$  were observed. These bands match with the C–H stretching bands of formalde-

hyde. In addition, the bands at 1771, 1745 and  $1716 \text{ cm}^{-1}$  along with shoulders at 1789, 1729, 1701, 1685, 1671 and  $1652 \text{ cm}^{-1}$  correspond to the PQR branching of the carbonyl group of formaldehyde [22,23]. Also observed were bands due to CO and  $\text{CO}_2$  in the  $2400\text{--}2000 \text{ cm}^{-1}$  region, not shown in the figure.

The overlapping bands in the region between  $1550\text{--}1370 \text{ cm}^{-1}$  were found to decrease in intensity with increasing temperature and simultaneous increase was observed in the intensity of carbonyl bands of formaldehyde indicating release of adsorbed formaldehyde. The decrease in intensity of the formate complex bands in  $\sim 1570 \text{ cm}^{-1}$

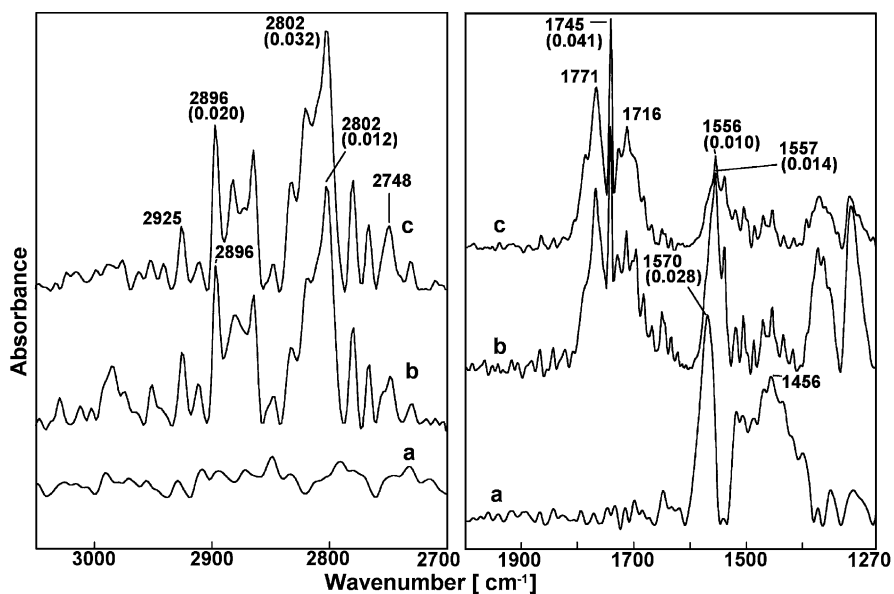


Fig. 6. IR spectra for methanol adsorption ( $54 \mu\text{mol g}^{-1}$ ) on bulk  $\text{U}_3\text{O}_8$  at different temperatures: (a) RT; (b)  $200^\circ\text{C}$ ; (c)  $250^\circ\text{C}$ .

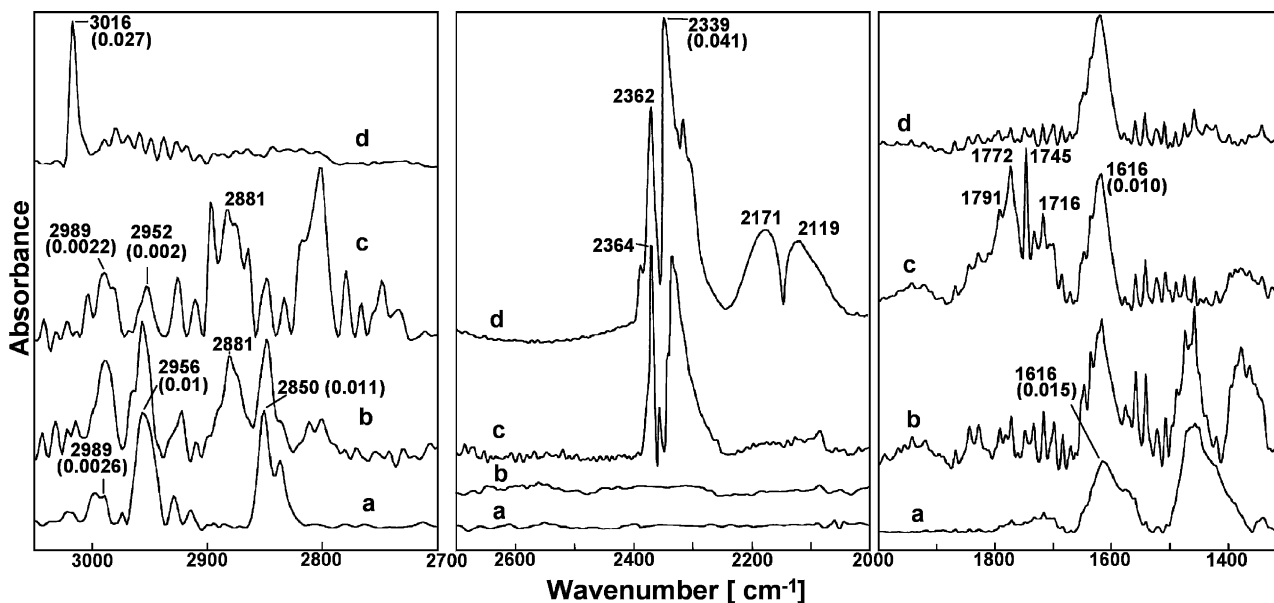


Fig. 7. IR absorption spectra for methanol adsorption ( $54 \mu\text{mol g}^{-1}$ ) on  $\text{U}_3\text{O}_8/\text{MCM-48}$  at different temperatures: (a) RT; (b)  $100^\circ\text{C}$ ; (c)  $200^\circ\text{C}$ ; (d)  $250^\circ\text{C}$ .

and  $1360\text{--}1300\text{ cm}^{-1}$  at  $250^\circ\text{C}$  and formation of CO and  $\text{CO}_2$  show decomposition of these species to give oxides of carbon.

Fig. 7 shows comparative IR spectra obtained upon exposure of methanol over  $\text{U}_3\text{O}_8/\text{MCM-48}$  at various temperatures. Fig. 7a shows the IR spectra at RT and the vibrational bands observed can be divided into the following groups indicating simultaneous evolution of various species:

- $\nu(\text{C-H})$  bands at  $2956$  and  $2850\text{ cm}^{-1}$  are due to methoxy group vibrations. The corresponding deformation region bands overlap with the absorption envelope in the  $1500\text{--}1300\text{ cm}^{-1}$  region.
- A set of bands appearing at  $2929$  and  $2837\text{ cm}^{-1}$  are seen only in the sample consisting of dispersed uranium oxide and may therefore be attributed to the methoxy groups bonded to uranium sites, e.g.  $\text{U-OCH}_3$ .
- The absorption bands appearing at  $1574\text{--}1560$ ,  $1352$  and  $1340\text{ cm}^{-1}$  are characteristic of the group of vibrations arising due to  $\nu_{\text{as}}(\text{COO}^-)$ ,  $\delta(\text{CH}_2)$  and  $\nu_{\text{s}}(\text{COO}^-)$  of formate complex [19–22].
- A group of overlapping  $\delta(\text{C-H})$  bands in the  $1550\text{--}1370\text{ cm}^{-1}$  region are analogous to the IR bands seen in this region in Fig. 5a and are identified with the adsorbed oxymethylene species [19,22].
- Absorption bands in the  $\nu(\text{C-H})$  region at  $3028$ ,  $3016$ ,  $2995$ ,  $2988$ ,  $2975$ ,  $2915\text{ cm}^{-1}$  and the corresponding  $\delta(\text{C-H})$  bands at  $1652$ ,  $1644$ ,  $1616\text{ cm}^{-1}$ , seen exclusively in  $\text{U}_3\text{O}_8/\text{MCM-48}$ , are similar to those formed during exposure of formaldehyde over this sample at room temperature [23]. Similar features have been reported earlier for polymerized/condensed form of formaldehyde over metal oxides dispersed on silica [19,20,22] and the set of IR bands mentioned above is therefore as-

signed to the formation of polyoxymethylene groups, i.e.  $(-\text{OCH}_2)_n$  where  $n > 1$ , dioxane, trioxane type species.

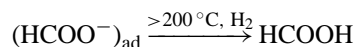
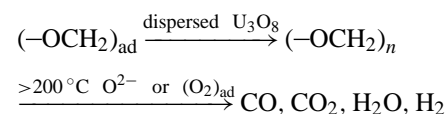
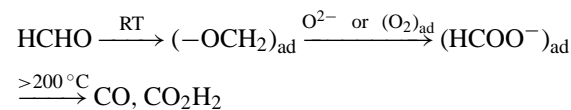
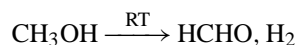
When  $\text{U}_3\text{O}_8/\text{MCM-48}$  was exposed to methanol at higher temperature at  $100$  and  $200^\circ\text{C}$  (Fig. 7b and c) bands due to formaldehyde were observed at around  $2925$ ,  $2910$ ,  $2896$ ,  $2881$ ,  $2875$ ,  $2863$ ,  $2832$ ,  $2817$ ,  $2802$ ,  $2779$ ,  $2765$ ,  $2775$ ,  $2748$ ,  $2732\text{ cm}^{-1}$  in the  $\nu(\text{C-H})$  region and  $1791$ ,  $1772$ ,  $1745$ ,  $1731$ ,  $1716$ ,  $1698\text{ cm}^{-1}$  corresponding to the PQR branching with shoulder for the carbonyl group of formaldehyde [22,23], the concentration of which was found to increase with increasing temperature. Bands due to CO and  $\text{CO}_2$  in the region were also observed at  $200^\circ\text{C}$ . The intensity of the bands due to adsorbed methoxide species, oxymethylene species, polyoxymethylene species and formate complex decreased as the temperature was raised, indicating their transformation to free formaldehyde and oxides of carbon. At  $250^\circ\text{C}$ , a strong band appeared at  $3014\text{ cm}^{-1}$  with a number of weak bands centered around it and this band is assigned to the methane. Also observed were strong bands due to formation of CO and  $\text{CO}_2$  with simultaneous decrease in the bands of formaldehyde, formate complex, polyoxymethylene and methoxide species.

Formation of methane is observed dominantly in case of  $\text{U}_3\text{O}_8/\text{MCM-48}$  as observed by the in situ FT-IR studies and this can be related to the interaction of  $\text{H}_2$  (formed on this sample as seen by TPD-MS study) with the methoxide species leading to the formation of methane. Increase in the intensity of CO and  $\text{CO}_2$  bands with simultaneous decrease of formaldehyde, oxymethylene, polymethylene and formate species indicates their decomposition at higher temperatures to give oxides of carbon.

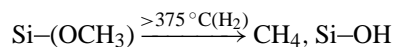
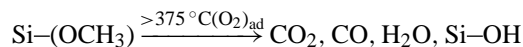
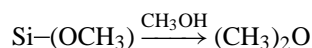
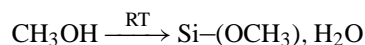
Based on the results described above, the reaction steps that may occur on  $\text{U}_3\text{O}_8\text{-MCM-48}$  during the interaction of

methanol may thus be identified as follows.

Reactions at  $U_3O_8$  sites



Reactions at silanol groups of molecular sieves



In these reaction schemes,  $O^{2-}$  represents the lattice oxide ion of uranium oxide and  $(O_2)_{ad}$  is the reactant molecular oxygen in its adsorbed state.

#### 4. Conclusion

Our study reveals that the well-dispersed (nanosize) crystallites of  $U_3O_8$  not only facilitate the adsorption of large quantity of methanol, they also serve as independent reaction sites for the formation of formate complexes and the polymerized oxymethylene species, i.e.  $(-OCH_2)_n$  at room temperature. These species get converted to free formaldehyde and formic acid at higher temperature and then ultimately to  $CO$ ,  $CO_2$ ,  $H_2$  and water as end products at the temperatures in range  $200$ – $550^\circ C$ , as revealed by IR, TPD and our earlier catalytic activity study [14]. The nature of the intermediate species and hence the relative yield of reaction products may depend upon the dispersion of uranium oxide; the formate species playing an important role in case of bulk oxide and the oxymethylene species in the case of a well dispersed sample. The methoxy species formed over MCM-48 under the identical conditions are reactive only at temperatures above  $375^\circ C$ . Since the oxides of carbon are formed even when methanol

was exposed over  $U_3O_8$  or  $U_3O_8$ /MCM-48 in the absence of  $O_2$  it can be concluded that the bulk oxygen of  $U_3O_8$  participates in the reaction following the Mars van Krevelen mechanism, where the reversible abstraction and bulk diffusion of the lattice oxide ions play an important role in the partial oxidation reactions [11]. The involvement of the lattice oxygen in oxidative destruction of volatile organic compounds has been demonstrated in the earlier study of Taylor et al. using  $U_3O_8$  dispersed over silica [7,8]. Heneghan et al. [3] similarly reported that the high activity shown by  $U_3O_8$  for oxidation of VOCs is due to the facile uranium couple and the non-stoichiometric nature of the oxides. Our results thus suggest that uranium oxides in their suitably dispersed form may serve as practical catalysts for the selective oxidation reactions, provided appropriate safety regulations are adopted.

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