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The role of nanosize particles of uranium oxide in the adsorption/reaction of methanol over U_3O_8/MCM-48: FTIR study

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The surface species formed over MCM-48, U_3O_8 and U_3O_8/ MCM48 catalysts during the adsorption/reaction of methanol were monitored using FTIR spectroscopy, in order to get an insight into the high catalytic activity exhibited by the nanosize crystallites of uranium oxide dispersed in MCM-48. The results of this *in situ* study revealed that the title catalysts exhibited a distinct behavior for adsorption and subsequent reaction of methanol. Thus, while the room temperature adsorption over bulk U_3O_8 resulted in the formation of formate complex and oxymethylene species, the interaction over MCM-48 resulted in simultaneous and instant formation of surface methoxy groups and dimethyl ether. On the other hand, the exposure of methanol over U_3O_8/MCM-48 under similar conditions resulted in the appearance of intense IR bands due to surface-adsorbed $(\text{–OCH}_2)_n$ species, where $n \geq 1$, in addition to those of formate complexes, oxymethylene and methoxy groups. The role of the above-mentioned intermediate species in the formation of different reaction products is discussed in brief.

KEY WORDS: uranium oxide; nanocrystallites of; dispersed in MCM-48; methanol adsorption in; IR study of.

1. Introduction

The oxides of uranium have received much attention during recent years as prospective catalysts, and are found to exhibit excellent activity for oxidation of CO and NO and also for the oxidation and dehydration of various hydrocarbons such as alcohols, aldehydes, ketones, aromatics, chloro organic compounds, *etc.* [1–10]. The use of U_3O_8 as a redox catalyst is advocated particularly, because of its thermal stability in addition to the availability of two distinct oxidation states of U that undergo a low energy transition between themselves and facilitate the Mars and van Krevelen type reaction mechanism [11]. With this existing information, we have attempted to disperse U_3O_8 over large area supports of MCM-41 and MCM-48 type so as to increase the exposed area of oxide surface and hence the catalytic activity. We demonstrated recently that the dispersion of nanosize crystallites of U_3O_8 is facilitated by the exchange of templating molecules in the mesopores of these materials [12,13]. The highly dispersed crystallites of U_3O_8 are not only found to show many fold increase in the catalytic activity for methanol decomposition/oxidation reaction, but also give rise to selective formation of reaction products such as CO, CO_2, H_2 and CH_4 [14]. In the present communication, we employed FTIR spectroscopy in order to identify the transient species formed over MCM-48, U_3O_8, and U_3O_8 dispersed over MCM-48 during their exposure to methanol. An attempt is made in this study to address the role of nanocrystallites of U_3O_8 in the surface processes involved during the reactions of CH_3OH and to elucidate the overall impact on the reaction mechanism.

2. Experimental

2.1. Sample preparation, characterization and catalytic activity studies

The method used for the preparation of uranyl-exchanged mesoporous materials has been described elsewhere in detail [12,13]. In brief, 80 ml of 0.035 molar uranyl acetate ($UO_2(CH_3COO)_2 \cdot 2H_2O$) solution was contacted under continuous stirring with 1 g of as-synthesized siliceous MCM-48 at a constant temperature of 323 K. The samples were then washed several times with distilled water, followed by filtration and drying at 353 K. The uranyl-exchanged samples were calcined in a tubular furnace at 820 K, first in a flow (50 ml min^{-1}) of N_2 for 2 h and then in air for 8 h. The uranium metal content of the final sample, as estimated by spectrophotometry, was found to be around 26 wt%. The samples thus obtained after calcination are referred to as U/MCM-48 in the text for the sake of brevity.

The samples were characterized by powder XRD, FTIR spectroscopy, DR UV-Visible spectroscopy, N_2 sorption, TEM and XRF techniques, and the findings have been described elsewhere in detail [12–14]. The TEM pictures were taken on a Jeol, model 2000 FX instrument, operating at 155 kV. The samples were

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prepared by ultrasonicating 300 mesh size material in ethanol and then dispersing on a carbon film supported on a copper grid.

The activity of the catalyst was evaluated for methanol oxidation/decomposition reaction using a fixed bed, vertically mounted, flow-through microcatalytic reactor, the details of which are given elsewhere [13,14].

2.2. *IR studies*

IR spectra of the U/MCM-48, U_3O_8, and siliceous MCM-48 samples were recorded in transmission mode using a high-temperature and high-pressure stainless-steel cell, prior to and after dosing of methanol at room temperature. A self-supported sample wafer weighing ~ 90 mg was heated *in situ* for 24 h at 623 K and under a vacuum of 10^{-3} torr, prior to its exposure to methanol +argon (1:16 mol ratio) mixture. In most of the reported experiments, the amount of methanol thus dosed over a sample was around 54 μmol. A JASCO FTIR-610 spectrometer equipped with a DTGS detector was employed and 300 scans were collected at a resolution of 4 cm^{-1} for recording each spectrum. IR bands due to gaseous methanol were compensated appropriately before recording the final spectral plots. The values given in parentheses in some of the figures represent the absorbance values of particular IR bands and serve as an estimate of the relative intensity.

Methanol of Analytical reagent grade (SISCO Research Laboratories, Mumbai, India) was purified by distillation before use. The vapors of pure formaldehyde were generated from paraformaldehyde on heating at 500 K after appropriate degassing.

3. Results and discussion

3.1. *Sample characteristics and catalytic activity*

When MCM-48 sample exchanged with uranyl groups was calcined at 820 K, XRD reflection at {211} decreased in intensity and shifted to a higher 2θ value, indicating a decrease in the unit cell parameter and filling of the pores of host MCM-48 with the particles of uranium oxide, as also seen by N_2 sorption data [14]. The XRD pattern in the higher 2θ-region shows some weak reflections which are attributed to the presence of α-U_3O_8 (JCPDS card no. 24-1172). The size of these U_3O_8 crystallites, as estimated from the line width of the most intense XRD line, was found to be around 8 nm. These observations were in tune with the findings of TEM experiments. A typical TEM image of U/MCM-48 is presented in figure 1. This picture reveals that while the pore structure of the host material is retained to some extent after U-loading, a distortion is seen in the pore structure in certain areas. The dark features (marked by arrows) of size ~ 2 to 6 nm observed in figure 1 are due to dispersed nanocrystallites of U_3O_8, the presence of which is also substantiated by XRD data [14].

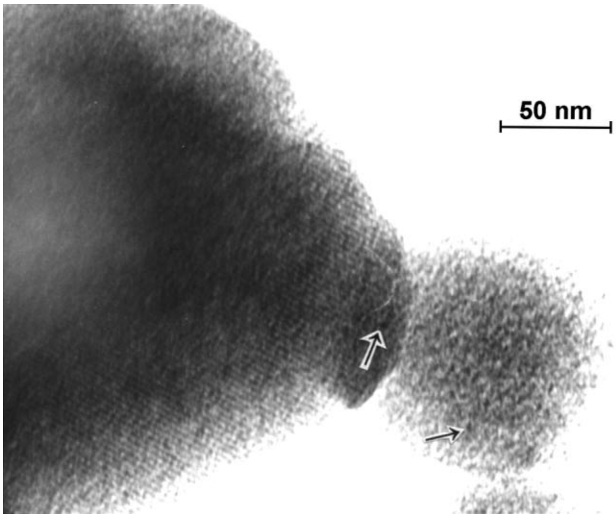

Figure 1. TEM picture of U/MCM-48.

The catalytic behavior of MCM-48, with and without uranium has been discussed elsewhere in detail [13,14]. In brief, the U/MCM-48 sample exhibited about eight times higher activity for methanol oxidation/decomposition reaction as compared to bulk oxide. Dimethyl ether was the main product formed on the host MCM-48 along with small amounts of oxides of carbon at temperatures above 700 K. The onset temperature decreased to 450 K in the case of U/MCM-48 and the main reaction products were CO, CO_2 and H_2. Formation of CH_4 was also observed on U/MCM-48.

3.2. *IR study of surface adsorbed species*

Figure 2 shows the prominent IR bands in the stretching and deformation modes, when U_3O_8 (curve [a]), MCM-48 (curve [b]) and U/MCM-48 (curve [c]) samples were pretreated at 650 K in vacuum and then exposed to 54 μmoles of methanol at room temperature. These data reveal that the surface species and the reaction products were different when methanol reacted at room temperature over MCM-48, U_3O_8 and the corresponding dispersed U_3O_8 sample. In order to identify the primary species formed at the catalyst surface and to enable us to make a comparison, the IR bands recorded in these regions for unadsorbed methanol (vapor and liquid), dimethyl ether and formaldehyde are compiled in figure 3. Based on the data in figure 3 and in cognizance of the literature reported for adsorption of methanol and formaldehyde over different

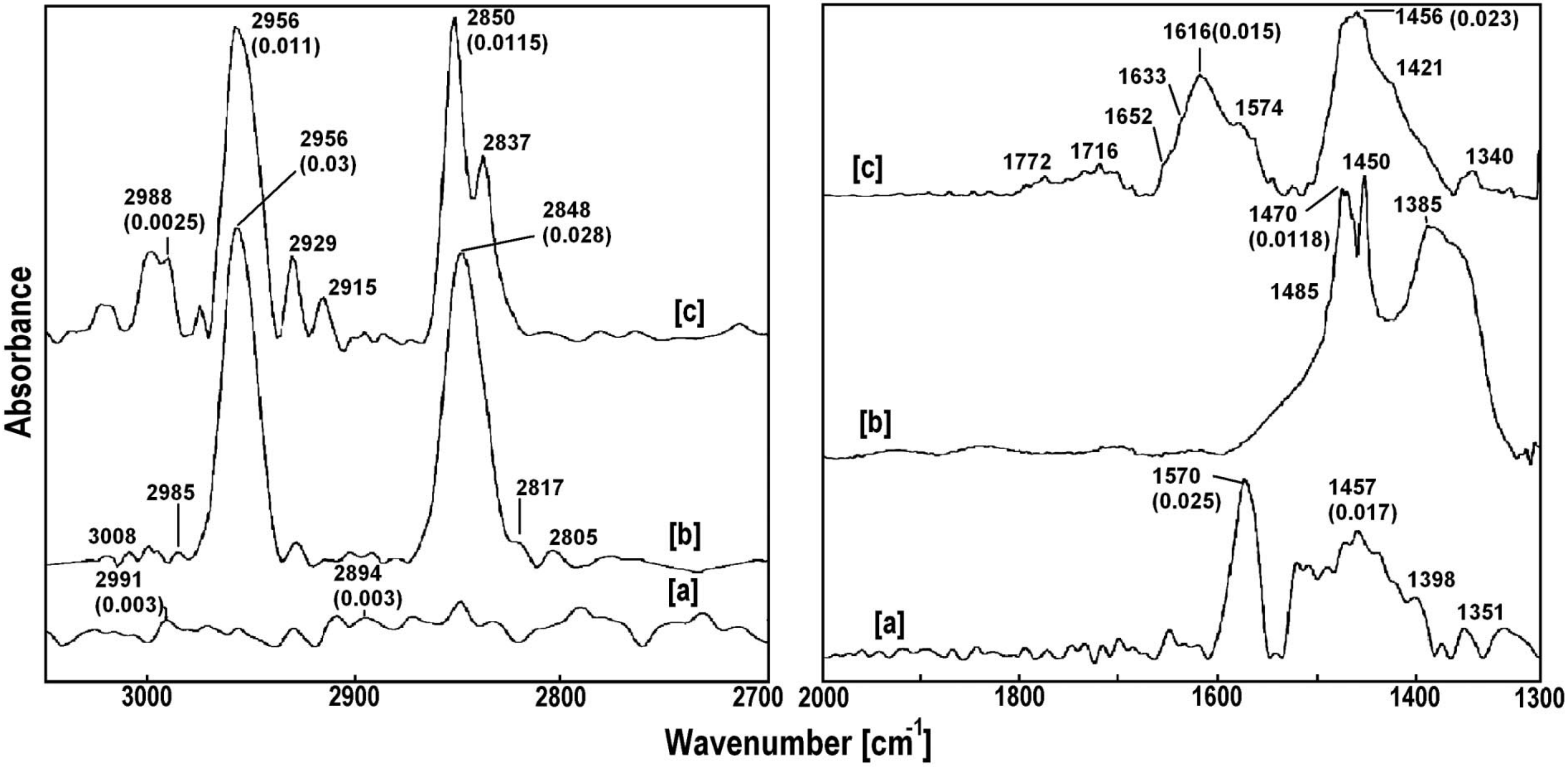

Figure 2. IR spectra of [a] U_3O_8, [b] Si-MCM-48, [c] U/MCM-48, after contacting with 54 μmol of methanol at room temperature.

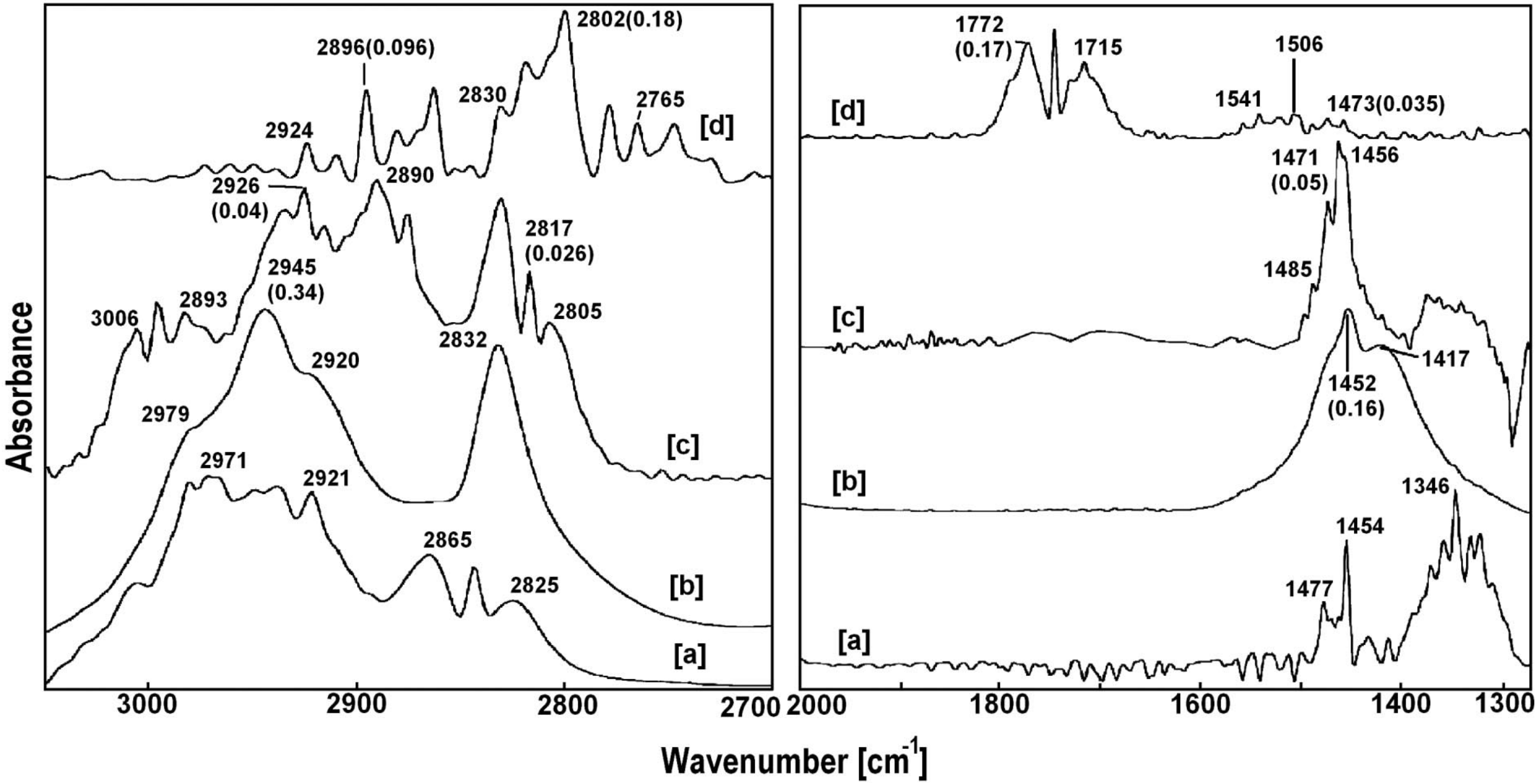

Figure 3. Typical IR spectra of [a] methanol vapor, [b] liquid methanol, [c] dimethyl ether and [d] formaldehyde.

oxides [15–25], the following picture emerges from our data:

(i) Only a small amount of methanol was adsorbed over U_3O_8 as seen from very weak bands in the ν(C–H) region in figure 2[a]. A comparatively strong band at $1570\,cm^{-1}$ and a group of overlapping bands in the $1550–1300\,cm^{-1}$ region may also be observed in figure 2[a]. The IR band at $1570\,cm^{-1}$ along with the bands in the $1360–1340\,cm^{-1}$ region are the features associated with the formate 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 and Sn-Mo oxide systems at elevated temperatures [15,16,25].

The overlapping group of bands in the lower frequency region of $1550–1370\,cm^{-1}$ in figure 2[a] match with the bands in this region of formaldehyde (figure 3[d]). However, since very weak bands in the corresponding carbonyl region ($1800–1650\,cm^{-1}$, figure 3[d]) are seen in figure 2[a], it is apparent that the group of bands mentioned above arise due to certain adsorbed species that may be identified with the oxymethylene ($-OCH_2$) groups, reported earlier for the adsorption of methanol over metal oxides [17].

Furthermore, since no IR bands due to adsorbed methanol are observed in figure 2[a] (cf. figure 3[a]), it is apparent that the methanol dehydrogenates over U_3O_8 even at room temperature to give rise to formaldehyde as a primary product.

(ii) The interaction of methanol over MCM-48 resulted in the evolution of prominent bands at 2956 and $2848\,cm^{-1}$ (figure 2[b]). These IR bands correspond to asymmetric and symmetric C–H stretching vibrations of the widely reported methoxy groups. The $1465\,cm^{-1}$ band in this figure may also be identified with the corresponding C–H bending vibrations of these methoxy groups. The growth of these IR bands in the aliphatic stretching region as a result of methanol loading is accompanied with the progressive disappearance of IR bands in the ν(OH) region, the effect being more pronounced on the vibrational band of external silanols, appearing at $3740\,cm^{-1}$ [26]. The intensity of the other hydroxy region bands with maxima at 3714 and $3702\,cm^{-1}$ was also found to decrease to some extent. Such observations have been reported earlier for both the mesoporous and the microporous molecular sieves [21,24], and are attributed to the binding of the methoxy groups to the silica sites ($Si-OCH_3$). In addition, the weak ν(C–H) bands at 3008, 2996, 2985, 2927, 2914, 2903, 2890, 2879, 2817, $2805\,cm^{-1}$ and the δ(C–H) bands at 1485, 1470, $1460\,cm^{-1}$ all match with the IR bands of dimethyl ether (figure 3[c]). The broad and the overlapping bands in $1390–1300\,cm^{-1}$ region in addition to a sharp band at $1450\,cm^{-1}$ in figure 2[b] may be attributed to methanol in a condensed form (cf. figure 3[b]).

(iii) In contrast to the IR data for bulk U_3O_8 (figure 2[a]), a number of additional bands are observed for the adsorption of methanol over U/MCM-48. These vibrational bands in figure 2[c] may be divided into the following groups, indicating the simultaneous evolution of various species.

(a) ν(C–H) bands at 2956 and $2850\,cm^{-1}$ are due to methoxy group vibrations as seen in figure 2[b]. The corresponding deformation region bands overlap with the absorption envelope in the 1500 to $1300\,cm^{-1}$ region in figure 2[c].

(b) A set of bands appearing at 2929 and $2837\,cm^{-1}$ in figure 2[c] is 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.*, $U-OCH_3$.

(c) The absorption bands appearing at 1574 to 1560, 1352 and $1340\,cm^{-1}$ are characteristic of the group of vibrations arising due to $\nu_{as}(COO^-)$, $\delta(CH_2)$ and $\nu_s(COO^-)$ of the formate complex [15,20,25].

(d) A group of overlapping δ(C–H) bands in the 1550 to $1370\,cm^{-1}$ region (1540, 1521, 1506, 1471, 1457, 1436, 1419, 1398 and $1375\,cm^{-1}$) are analogous to the IR bands seen in this region in figure 2[a]. As discussed earlier, these IR bands may be identified with the adsorbed oxymethylene species.

(e) Absorption bands in the ν(C–H) region at 3028, 3016, 2995, 2988, 2975, $2915\,cm^{-1}$ and the corresponding δ(C–H) bands at 1652, 1644, 1633, $1616\,cm^{-1}$, seen exclusively in U/MCM-48, are similar to those formed during exposure of formaldehyde over this sample at room temperature. The presence of only weak IR bands in the carbonyl stretch region of formaldehyde ($1800–1700\,cm^{-1}$, figure 2[d]) is also to be noticed in figure 2[c]. Similar features have been reported earlier for the polymerized/condensed form of formaldehyde over metal oxides dispersed on silica [15,17,20] and the set of IR bands mentioned above is therefore assigned to the formation of polyoxymethylene groups, *i.e.*, $(-OCH_2)_n$ where $n > 1$. It is also worth noting that the high intensities of δ(C–H) bands compared to those of corresponding ν(C–H) vibrational bands, as revealed by the absorbance values given in figures 2[a] and 2[c], are also the features reported earlier for methoxy and oxymethylene species bonded in polymerized form over vanadium oxide–titanium oxide catalysts [17].

With a view to further confirm the identity of IR bands in figure 2[c], varying amounts of formaldehyde were dosed at room temperature over U/MCM-48. A typical spectrum in ν(C–H) region for the exposure of $\sim$5 mmol formaldehyde is given in figure 4[a]. In addition to vapor phase IR bands of HCHO (cf. figure 3[d]), we observe here a group of rather strong bands in the 3050–2900 $\mathrm{cm^{-1}}$ region. The intensity of these bands increased progressively with the increase in the formaldehyde dose. On subsequent evacuation of the sample, the IR bands due to unadsorbed formaldehyde in the IR cell were removed quickly, leaving behind the IR bands due exclusively to adsorbed species and these results are shown in figure 4[b]. The effect of outgassing on the species developed on U/MCM-48 after the adsorption of methanol under similar conditions is shown in spectrum [c] of figure 4. Spectra [d] and [e] in figure 4 were obtained when the temperature of the samples in spectra [b] and [c] was raised to 520 K. It is important to note that in addition to prominent IR bands due to Si–OCH_3 (2956–2950 $\mathrm{cm^{-1}}$) and U–OCH_3 (2929 and 2937 $\mathrm{cm^{-1}}$) as mentioned above, all the bands in figure 4[b] are also seen in spectrum [c] of figure 4 (marked with *). The rise in sample temperature to 520 K gave rise to the transformation of 3050–2900 $\mathrm{cm^{-1}}$ bands in figure 4[b] to the bands arising from the formaldehyde vapor (figure 4[d]). The spectrum in figure 4[e] reveals a similar formation of formaldehyde, and at the same time the intensity of the IR bands due to methoxy species decreased only marginally. These results thus confirm that the methanol molecules interact independently with the uranium oxide crystallites and with the hydroxy groups of the support in U/MCM-48. The former process leads to dehydrogenation of methanol to produce formaldehyde, which on subsequent adsorption gives rise to the formate and oxymethylene species. We may thus infer that the later species polymerize at dispersed uranium oxide sites to give rise to the formation of polyoxymethylene (POM) groups. The interaction with the silanol groups, on the other hand, gave rise to methoxy groups as seen in figures 2[b] and [c]. The spectra in figures 4[a] and [b] show that the POM species are also formed during the direct exposure of the sample to formaldehyde. Also, they are stable to evacuation and transform to monomers of formaldehyde (figures 4[d] and [e]) and subsequently to CO and CO_2 on raising the sample temperature [14,25]. On the contrary, the methoxy species are fairly stable under evacuation and also at elevated temperatures (figure 4[e]).

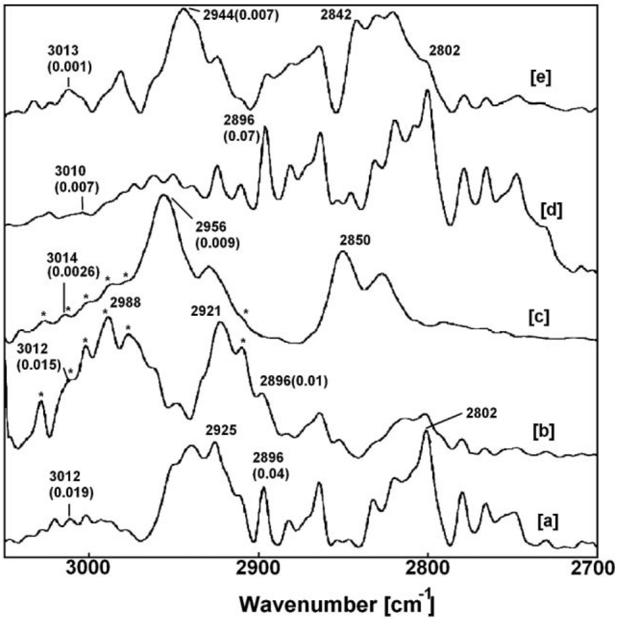

Figure 4. IR bands evolved on U/MCM-48 after room temperature exposure to 5 mmol formaldehyde prior to [a] and after pumping [b] of the exposed sample. Spectrum [c] shows similar results for a sample exposed to methanol followed by evacuation. Spectra [d] and [e] show IR bands developed after heating of samples [b] and [c], respectively, at 520 K.

The reaction steps that may occur on U_3O_8/MCM-48 during the interaction of methanol at room temperature and above may thus be identified as follows:

Reactions at U_3O_8 sites

$$CH_3OH \xrightarrow{298\,K} HCHO, H_2$$

$$HCHO \xrightarrow{298\,K} (\text{–}OCH_2)_{ad} \xrightarrow[(O_2)_{ad}]{(O_2^-)\text{ or}} (HCOO^-)_{ad} \xrightarrow{>450\,K} CO, CO_2, H_2$$

$$(\text{–}OCH_2)_{ad} \xrightarrow[U_3O_8]{\text{Dispersed}} (\text{–}OCH_2)_n \xrightarrow[(O_2^-)\text{ or }(O_2)_{ad}]{>450\,K} CO, CO_2, H_2O, H_2$$

Reactions at Silanol groups of molecular sieves

$$CH_3OH \xrightarrow{298\,K} Si\text{–}(OCH_3), H_2O$$

$$Si\text{–}(OCH_3) \xrightarrow{CH_3OH} CH_3OCH_3, Si\text{–}OH$$

$$Si\text{–}(OCH_3) \xrightarrow[(O_2)_{ad}]{>650\,K} CO_2, CO, H_2O, Si\text{–}OH$$

$$Si\text{–}(OCH_3) \xrightarrow[(H_2)]{>650\,K} CH_4, Si\text{–}OH$$

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. Summary

Our study reveals that the well-dispersed (nanosize) crystallites of U_3O_8 not only facilitate the adsorption of a 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 oxidize further to give rise to formation of CO, CO_2 and water as end products at the temperatures in the range 450 to 700 K [14,26]. 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 the case of bulk oxide and the oxymethylene species in the case of a well-dispersed sample. The methoxy species formed over MCM-48 under identical conditions are reactive only at temperatures above 650 K. Since the oxides of carbon are formed even when methanol was exposed over U_3O_8 or U/MCM-48 in the absence of O_2 [14,26], 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 the oxidation of VOC's is due to the facile uranium couple and the nonstoichiometric 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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