An *in situ* Raman study of dimethyl carbonate synthesis from carbon dioxide and methanol over zirconia

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In situ Raman spectroscopy has been used to investigate the mechanism of dimethyl carbonate (DMC) synthesis via the reaction of methanol with carbon dioxide over zirconia. Methanol adsorption leads to the appearance of adsorbed methoxide groups, whereas CO_2 adsorption leads to the formation of carbonate species. Monomethyl carbonate species, $(CH_3O)COO(Zr)_2$, are formed by the reaction of methoxide and monodentate carbonate species and DMC is formed via the further reaction of monomethyl carbonate species with methanol. This sequence is supported by evidence that DMC decomposition on zirconia proceeds via the reverse of the proposed mechanism.

Keywords: dimethyl carbonate, zirconia, methanol, carbon dioxide, Raman spectroscopy

1. Introduction

Novel approaches to the synthesis of dimethyl carbonate (DMC) have been stimulated by the recognition that DMC is a non-toxic molecule having a diverse number of possible applications. Using DMC, non-phosgene based methods have been developed for the synthesis of polycarbonates and isocyanates [1]. DMC can also be used as a methylating agent in substitution for methyl halides and dimethyl sulfate, both of which are toxic and corrosive [1,2]. Yet another application for DMC is its use as a substitute for methyl tertiary butyl ether (MTBE) [3].

Several reports have recently appeared indicating that DMC can be synthesized directly by the reaction of methanol with carbon dioxide [4–6]:

$$2CH_3OH + CO_2 \rightarrow (CH_3O)_2CO + H_2O$$

Of the heterogeneous catalysts investigated thus far, only ZrO_2 exhibited any activity for DMC formation from methanol and carbon dioxide, and it is hypothesized that this is a consequence of the amphoteric character of the surface of ZrO_2 [5,6]. The present investigation was undertaken with the aim of identifying the elementary processes involved in the synthesis of DMC over ZrO_2. Raman spectroscopy was used to examine the species formed during the adsorption of methanol, carbon dioxide, and DMC, and during the reaction of methanol with carbon dioxide.

2. Experimental

Zirconia was prepared by precipitation from $ZrOCl_2$ with NH_4OH at a constant pH of 10. After filtration and washing, the product was calcined at 723 K in 20% O_2 in He for 2 h. XRD analysis showed that the calcined zirconia is present exclusively in the tetragonal phase. The BET surface area of the calcined zirconia was 140 m^2/g.

In situ Raman experiments were carried out in a quartz cell that could be heated up to 1023 K [7]. Approximately 50 mg of catalyst was placed in the sample holder. Since the sample is white, rotation of the sample to avoid heating by the laser beam was not necessary. Spectra were recorded with a HoloLab 5000 Raman spectrometer (Kaiser Optical). The stimulating light source is a Nd:YAG laser, the output of which is frequency doubled to 532 nm. Spectra were acquired using a power level of 45 mW measured at the sample with a laser power meter (Edmund Scientific).

Carbon dioxide (Coleman Instrument Grade, >99.99%, Matheson) was mixed with He (UHP, Airgas) to the desired ratio and supplied to the Raman cell at a total flow rate of 50 cm^3/min. Methanol and DMC were supplied by flowing He through a bubbler containing liquid methanol or DMC at 298 K. The vapor pressures of methanol and DMC in the saturated He stream were 16.1 and 2.4 kPa, respectively.

3. Results

Figure 1 shows the Raman spectrum of ZrO_2 at room temperature while a mixture of 80% CO_2 in He is passed over the catalyst. Also shown is a spectrum of ZrO_2, prior to CO_2 exposure. Upon adsorption of CO_2, the bands at 3757 and 3690 cm^{-1} due to isolated and bibridged Zr–OH groups [8–11] decrease in intensity and a new band appears at 3614 cm^{-1} attributable to the O–H stretching vibration of bidentate bicarbonate groups, HCO_3–Zr [12–21]. The broad band at 1637 cm^{-1} is also attributable to HCO_3–Zr. New bands are also observed at 1384, 1279, and

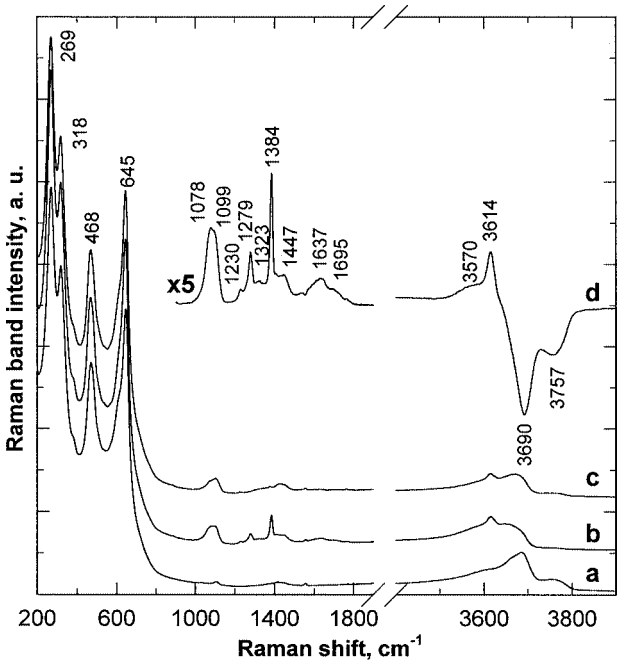
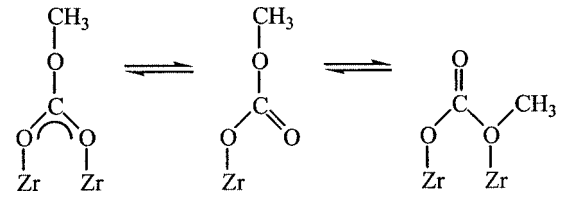


Figure 1. Raman spectra recorded at 303 K (a) after pretreatment in 20% O_2 at 773 K for 2 h, (b) after exposure to 80% CO_2 at 298 K, (c) after purging with He for 10 min, and (d) the difference between spectrum (a) and spectrum (b).

1078 cm^{-1} due to monodentate carbonate species, m-CO_3–Zr [15,17–22] and at 1447 and 1099 cm^{-1} due to ionic carbonate species, i-CO_3^{2-} [12,17–22].

Figure 2(A) shows Raman spectra recorded during the exposure of ZrO_2 to 3.2 kPa of methanol. The bands observed at 2937, 2828, and 1042 cm^{-1} in figure 2 are similar to those for liquid CH_3OH (2945, 2836, and 1036 cm^{-1}) and, hence, are assigned to physically adsorbed CH_3OH. The features observed at 2925, 2818, 2593 (not shown), 1462, 1450, 1162, 1102, and 1037 (see figure 2(B)) cm^{-1} are assigned to methoxide species associated with Zr cations, CH_3O–Zr [14,16,21–25]. When the cell is flushed with He, the bands associated with physically adsorbed CH_3OH disappear and only those associated with the methoxide species remain. This trend is clearly seen in figure 2(B). It is also noted that once the band at 1042 cm^{-1} has attenuated, a broad band at 1037 cm^{-1} can be seen, which is due to the methoxide species. Heating the catalyst to 423 K does not cause a significant change in the intensity of the methoxide bands, indicating that these species are stable up to this temperature, in good agreement with previous reports [21,25].

Raman spectra taken as a function of time after the exposure of ZrO_2 to 1.2 kPa of DMC in He are shown in figure 3. The bands observed at 3033, 3013, 2964, 2889, 2848, 2733, 1755, 1458, 1211, 1162, 1118, 1021, 916, 863, and 518 cm^{-1} can be assigned to physically adsorbed DMC by comparison with the positions of equivalent bands in the spectrum of liquid DMC [26]. The bands at 2929 and 2828 cm^{-1} are assigned to CH_3O–Zr species, whereas the band at 945 cm^{-1} is assigned to a product of DMC decomposition, as discussed below. As shown in figure 3(B), desorption of physically adsorbed DMC occurs when the Raman cell is flushed with He. Within 10 min, all of the bands associated with DMC disappear and the only bands remaining are those located at 3025, 2969, 2941, 2929, 2890, 2823, 1607, 1450, 1375, 1203, 1162, 1102, 1021, and 945 cm^{-1}. Based on the data given above, the bands at 2929, 2823, 1450, 1162, and 1102 cm^{-1} can be assigned to CH_3O–Zr. The features at 3025, 2969, 2941, 2889, 1607, 1203, 1021, and 945 cm^{-1} cannot be assigned definitively but are best ascribed to a bidentate-coordinated monomethyl carbonate (MMC), $(CH_3O)COO(Zr)_2$. For example, the infrared spectrum of crystalline $(CH_3O)COONa$ exhibits bands at 3016(w), 2985(m), 2951(m), 1631(vs), 1618(s), 1474(s), 1378(s), 1193(m), 1100(s), 1090(s), and 935(s) cm^{-1} [27]. The most intense band in this spectrum is that at 1631 cm^{-1} due to C=O vibrations. The absence of this feature in the spectrum of adsorbed DMC suggests that the adsorbed species does not contain a C=O group. Likewise, the absence of a strong feature near 1378 cm^{-1}, characteristic of O–(C=O)–O bending vibrations, suggests that the product of DMC decomposition does not contain a C=O bond. In view of these two observations, we propose that MMC may be bonded in a bidentate manner, as shown below,



The bridging chelating coordination proposed is consistent with that envisioned for MMC ligated to Mg and Ca complexes of the form $[Mg(O_2COMe)(OMe)(MeOH)_{1.5}]_n$ [28].

The reaction of CH_3OH and CO_2 was investigated in several ways. In the first case, ZrO_2 was first exposed to CH_3OH at 298 K for 10 min, purged with He for 10 min, and then exposed to a stream containing 80% CO_2. Figure 4(A) shows that prior to the introduction of CO_2, the spectrum is dominated by features at 2926, 2818, 2593, 1449, 1462, 1163, 1102, and 1037 cm^{-1}, all of which are characteristic of CH_3O–Zr. Upon introduction of CO_2, new features appear at 3024, 2958, 2832, 1607, 1386, 1285, 1203, and 946 cm^{-1} and the bands associated with CH_3O–Zr decrease in intensity. The bands at 1385 and 1285 cm^{-1} are characteristic of m-CO_3–Zr species, whereas the remainder are due to $(CH_3O)COO(Zr)_2$. Formation of the latter species occurs within 1–2 min, and the intensities of the bands for this species do not change significantly with time after their initial appearance. Flushing the cell with He at 298 K leads to the immediate decomposition of m-CO_3–Zr (1375 and 1285 cm^{-1}) and a slow loss in the intensity of the bands attributed to $(CH_3)COO(Zr)_2$. The latter species is stable up to 373 K, as can be seen

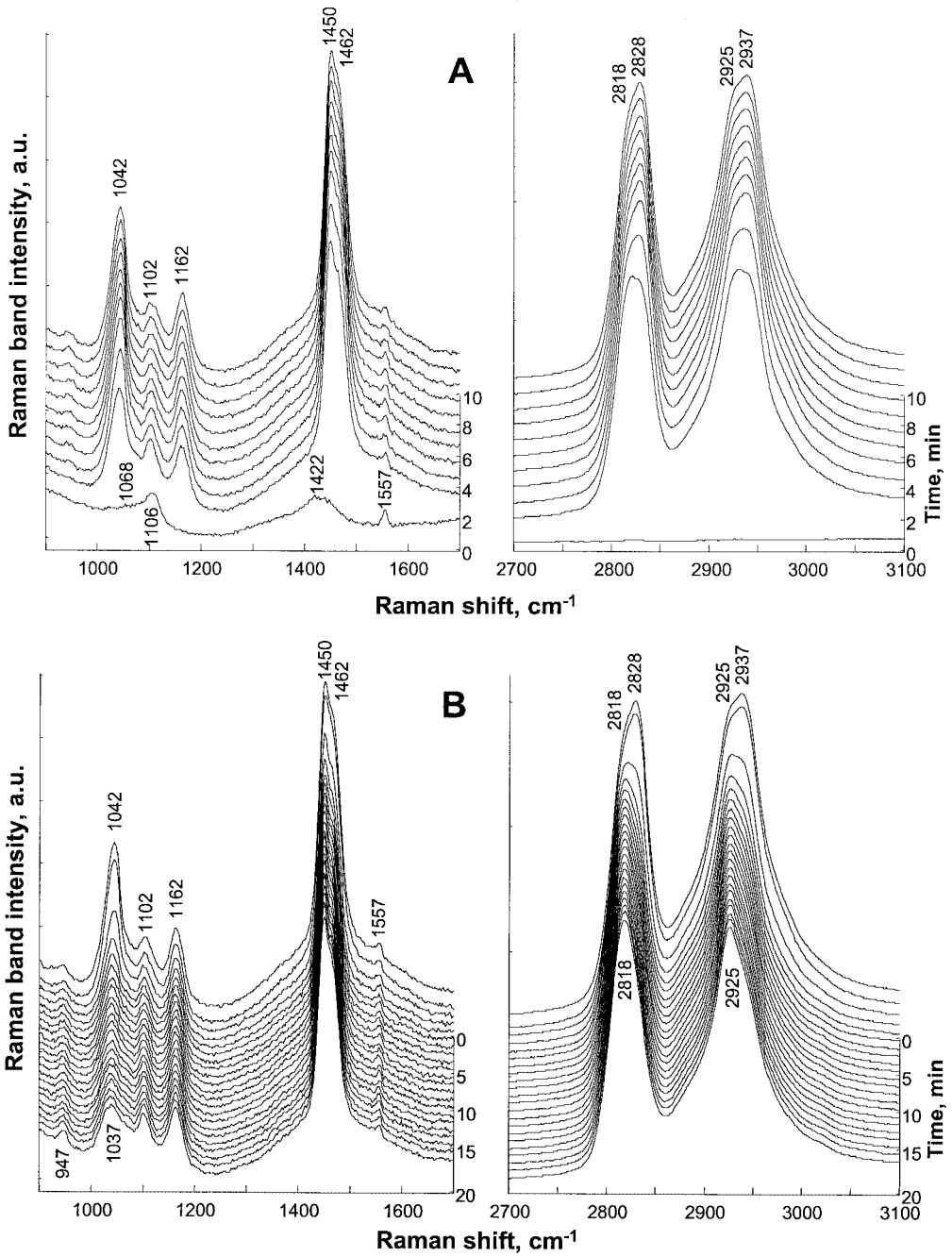


Figure 2. Raman spectra recorded during (A) exposure of ZrO_2 to 3.2 kPa of CH_3OH vapor and (B) subsequent purging with He. Spectra were recorded at intervals of 1 min.

by examination of the band at 945 cm^{-1} in the Raman spectrum shown in figure 5 taken during temperature-programmed desorption in flowing He. It is also evident that CH_3O–Zr species are stable up to 473 K, as judged by the lack of intensity loss in the bands at 2927 and 2822 cm^{-1}. These results suggest that at elevated temperatures, $CH_3COO(Zr)_2$ decomposes to form CH_3O–Zr and gas-phase CO_2.

Raman spectra taken during temperature-programmed reaction of a feed mixture containing 3.2 kPa CH_3OH and 80% CO_2 are shown in figure 6. These spectra are similar in appearance to those observed when CO_2 is contacted with preadsorbed methanol. The primary difference between these two sets of spectra is that when CH_3OH and CO_2 react concurrently the principal bands present in the C–H stretching region of the spectrum are those at 3020, 2948, and 2834 cm^{-1}, all of which have been assigned to $CH_3COO(Zr)_2$. As the reaction temperature rises, the first of these bands attenuates in intensity and the other two bands shift to 2927 and 2822 cm^{-1}, positions characteristic for CH_3O–Zr. This suggests that with increasing temperature, CH_3O–Zr groups occupy more of the ZrO_2 surface than $CH_3COO(Zr)_2$ groups. The reverse trend is seen, however, when preadsorbed CH_3O–Zr species react

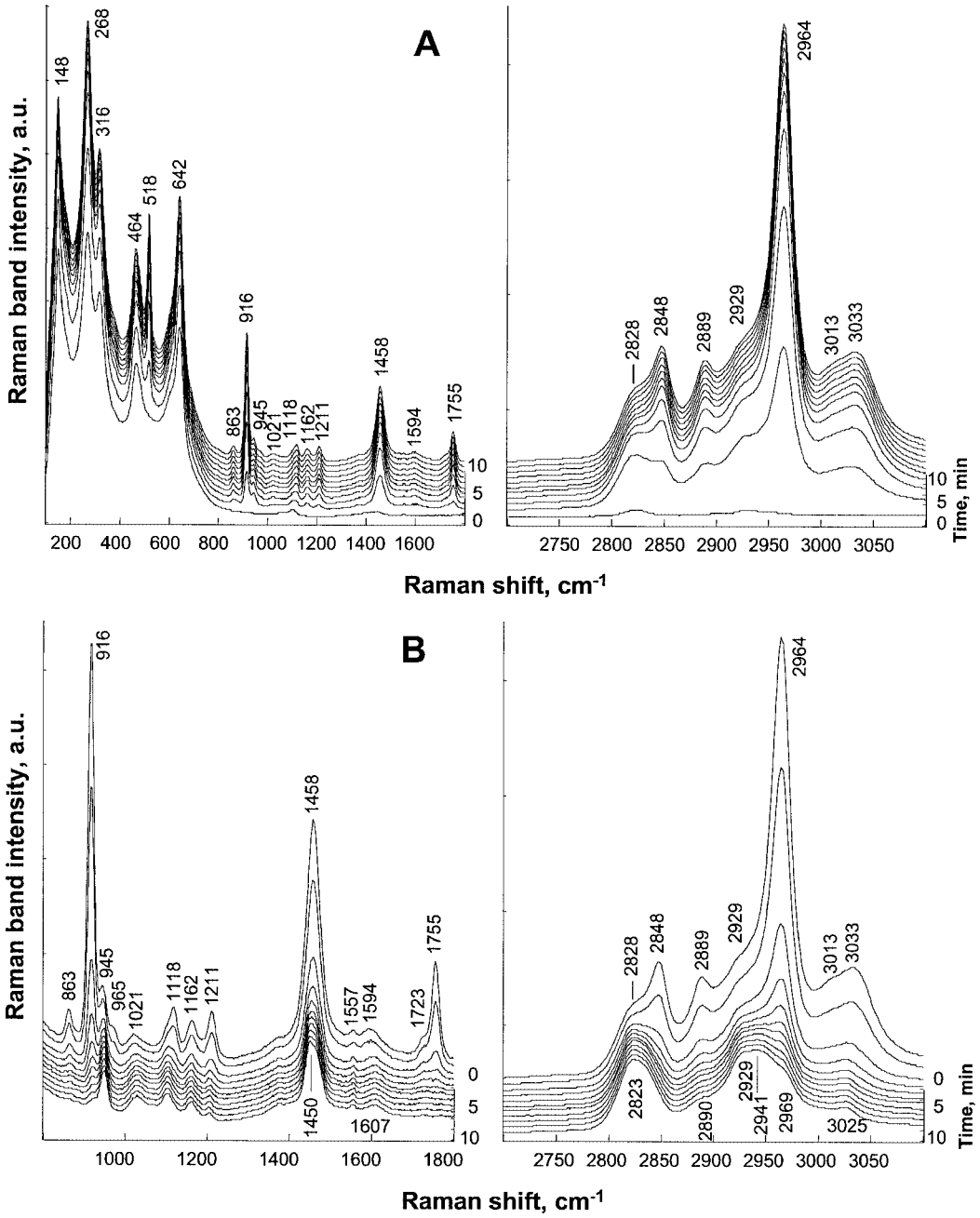


Figure 3. Raman spectra recorded at 298 K (A) during exposure of ZrO_2 to 1.2 kPa of DMC and (B) subsequent purging in He. Spectra were recorded at intervals of 1 min.

with CO_2 (see figure 4). In this case, the initially observed C–H stretching bands are those characteristic of adsorbed CH_3O–Zr (2926 and 2818 cm^{-1}) and those formed with time are characteristic of CH_3COO (3023, 2958, 2886, and 2832 cm^{-1}).

Temperature-programmed reaction of DMC was carried out by passing a stream of He containing 0.5 kPa of DMC over the catalyst. As illustrated in figure 7, the spectrum recorded at 298 K clearly shows evidence for adsorbed DMC, $(CH_3O)COO(Zr)_2$, and CH_3O–Zr. All of the bands for adsorbed DMC disappear by 353 K, whereas those for $(CH_3O)COO(Zr)_2$ decrease in intensity but are still visible at 393 K. In contrast, the bands at 2926 and 2823 cm^{-1} grow in intensity with increasing temperature, indicating a growth in the surface concentration of CH_3O–Zr.

4. Discussion

The results of the present investigation clearly show that similar Raman spectra are observed during the reaction of CO_2 with preadsorbed CH_3OH and during the decomposition of DMC. In both cases, the dominant adsorbed species present on the surface of ZrO_2 are CH_3OZr and $CH_3COO(Zr)_2$. At room temperature very small quantities of adsorbed CO_2, present as HCO_3–Zr and CO_3–Zr, can

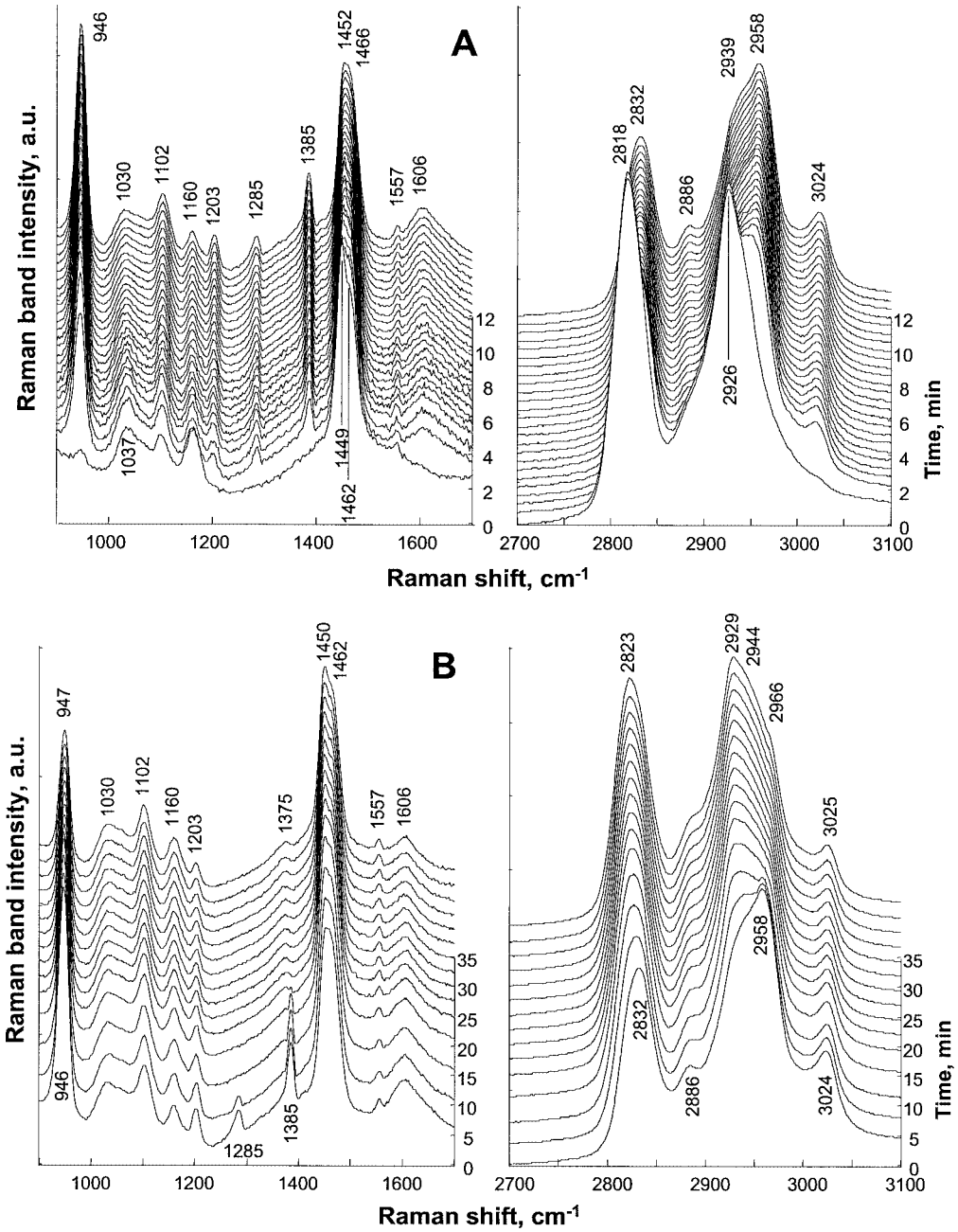


Figure 4. Raman spectra recorded at 298 K during the reaction (A) of adsorbed methoxide species with 80% CO_2 and (B) subsequent purging in He. Spectra were recorded at intervals of 0.5 min for spectrum (A) and 2.5 min for spectrum (B).

be seen, but at elevated temperatures, these species are not observable.

The following sequence of elementary processes can be proposed to explain the observations reported here:

$$CH_3OH_{(g)} + ZrOH \rightarrow CH_3O\text{–}Zr + H_2O_{(g)} \quad (1)$$

$$CO_2 + Zr\text{–}O\text{–}Zr \rightarrow m\text{-}CO_3(Zr)_2 \quad (2)$$

$$CH_3O\text{–}Zr + m\text{-}CO_3(Zr)_2 \rightarrow (CH_3O)COO(Zr)_2 + Zr\text{–}O \quad (3)$$

$$(CH_3O)COO(Zr)_2 + CH_3OH_{(g)} + Zr\text{–}O \rightarrow (CH_3O)_2CO_{(g)} + Zr\text{–}O\text{–}Zr + Zr\text{–}OH \quad (4)$$

This mechanism is similar to that previously proposed for the oxidative carbonylation of methanol over Cu-Y zeolite [5] and the direct synthesis of DMC from methanol and CO_2 [6]. Reaction (1) is the adsorption of CH_3OH to produce CH_3O–Zr and H_2O. This process has been previously reported in studies of methanol decomposition over ZrO_2 and was found to be readily reversible when water vapor is present [21]. The formation of carbonate species via reaction (2) is also well precedented and known to be reversible at temperatures above 523 K. Reaction (3) envisions the formation of $(CH_3O)COO(Zr)_2$ via the reaction of CH_3O–Zr and m-$CO_3(Zr)_2$. A good precedent for this reaction is given by Mingos and co-workers [28], who have shown that CO_2 will insert into the M–OCH_3 bond in Mg and Ca methoxide complexes to form com-

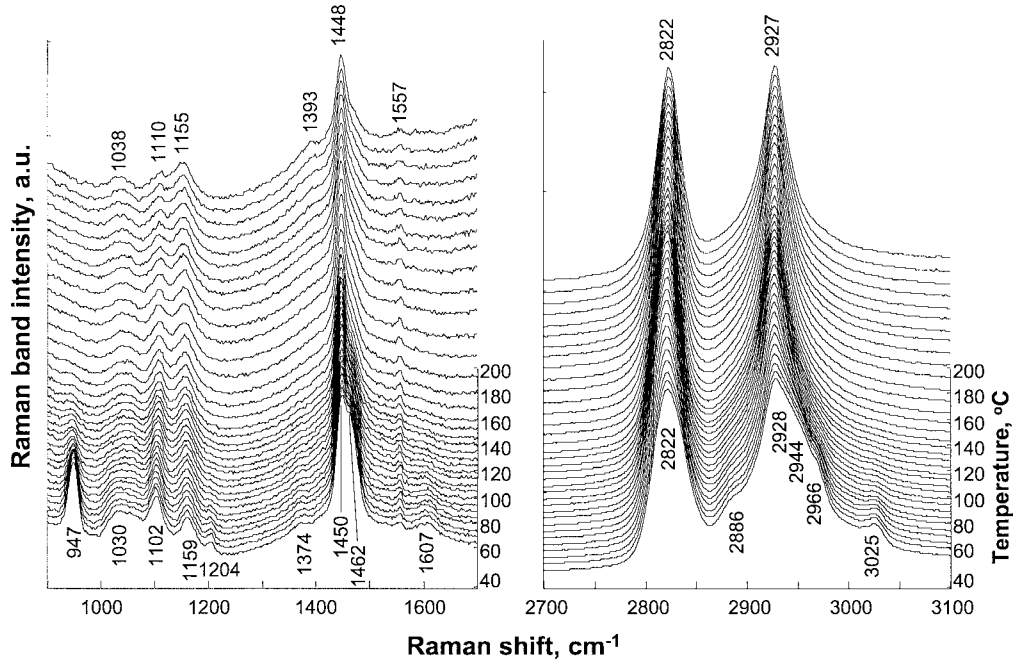


Figure 5. Raman spectra recorded during heating from 303 to 423 K in He at 5 K/min after pretreatment of the sample in the manner described for figure 4(B). Spectra recorded at intervals of 1 min.

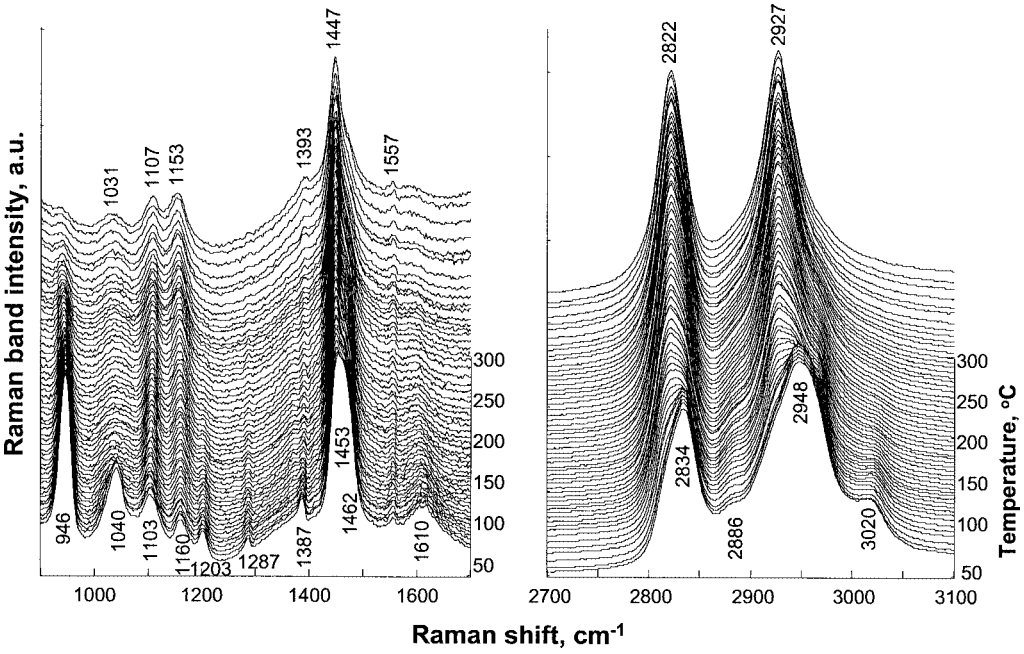


Figure 6. Raman spectra recorded as the sample temperature is raised at 5 K/min from 303 to 423 K in He at 5/min in a gas stream containing 80% CO_2 and 3.2 kPa of CH_3OH vapor, with the balance being He. All spectra were recorded at 298 K at intervals of 1 min.

plexes such as $[Mg(O_2COMe)(OMe)(MeOH)_{1.5}]_n$. Several different structures are proposed for coordination of the MMC ligand, but all involve either chelating or bridging chelating coordination of two O atoms to one or two metal atoms. Further supporting the proposed formation of $(CH_3O)COO(Zr)_2$ is the observation that this structure and CH_3O–Zr are formed when DMC decomposes on the surface of ZrO_2. Reaction (4) is without precedent, but is strongly supported by our observations of the species formed upon DMC decomposition.

5. Conclusions

The synthesis of DMC from CH_3OH and CO_2 is envisioned to proceed via a simple mechanism. Gas-phase CH_3OH reacts with OH groups on the surface of ZrO_2

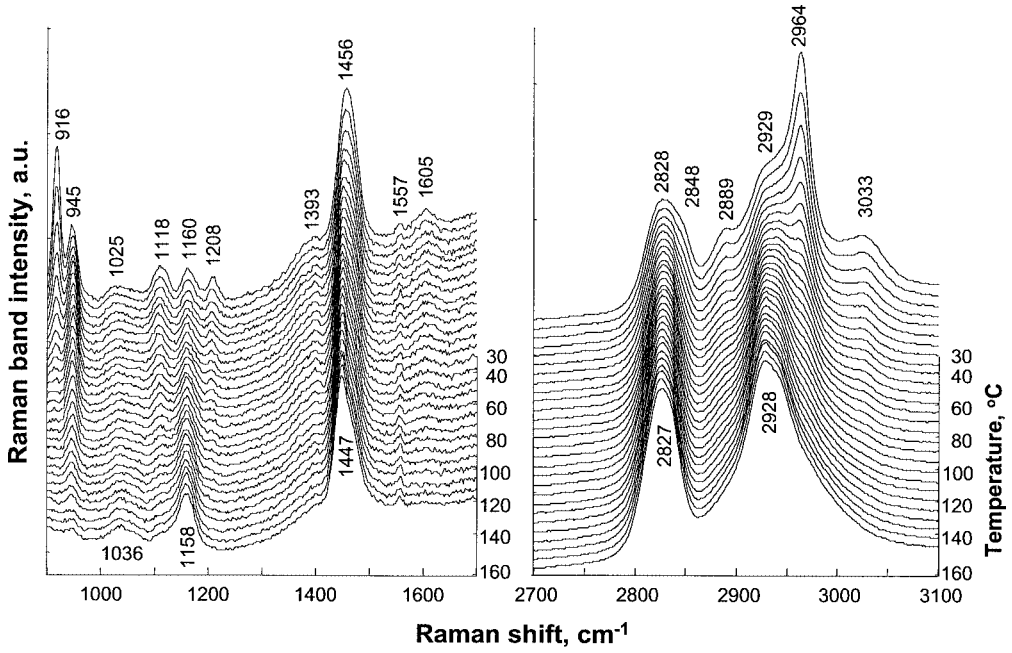


Figure 7. Raman spectra recorded during the temperature-programmed heating at 5 K/min in the presence of 0.5 kPa of DMC vapor. Spectra were recorded at 1 min intervals.

to produce CH_3O–Zr species and gas-phase H_2O, whereas CO_2 adsorbs on the surface of ZrO_2 to form carbonate species. Monomethyl carbonate species, $(CH_3O)COO(Zr)_2$, are formed by the reaction of methoxide and monodentate carbonate species and DMC is formed via the further reaction of monomethyl carbonate species with methanol. The decomposition of DMC is envisioned to occur via the reverse of this sequence.

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