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Infrared Studies of the Adsorption of Synthesis Gas on Zirconium Dioxide

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The adsorption of CO, CO_2, H_2, HCOOH, and CH_3OH was studied over ZrO_2 using FTIR. Bicarbonate, formate, and methoxide species were observed. Bicarbonate was the major species formed from CO_2 and was converted into formate in the presence of sufficient hydrogen. Formate was observed following CO adsorption even in the absence of hydrogen. The formate was reduced to methoxide in the presence of hydrogen. The different behavior for CO/H_2 and CO_2/H_2 demonstrated that different mechanisms should be proposed for CO versus CO_2 hydrogenation over ZrO_2. Formate to methoxide conversion was reversible. Experiments conducted with D_2O revealed that surface OH (OD) groups participate in formate formation and in formate to methoxide conversion.

I. INTRODUCTION

Carbonates, bicarbonates, and formates are possible surface species which may form upon adsorption of CO and H_2 on metal oxides (*1–6*). A temperature programmed desorption/temperature programmed decomposition (TPD/TPDE) study of the adsorbed species resulting from synthesis gas postulated the formation of carbonate, formate, and methoxide species over ZrO_2 (*7*). The approach of the TPD/TPDE study involved separating the different surface species by temperature programming and inferring their origin by the distribution of the decomposition products. The temperature distribution patterns and decomposition patterns were indirectly verified by using HCOOH and CH_3OH. This paper reports direct evidence for the formate and methoxide surface species.

Infrared studies have been conducted over ZrO_2. Most have concentrated on the chemical nature of the surface hydroxyl groups (*2, 8–10*). Carbonates and bicarbonate have been reported following CO_2 adsorption (*2*). No infrared studies of the $CO/H_2/ZrO_2$ system have been reported.

Fourier transform infrared spectroscopy (FTIR) was used in the present study to investigate the $CO/H_2/ZrO_2$ and $CO_2/H_2/ZrO_2$ systems. The objectives included obtaining direct evidence for the presence of surface species suggested by an earlier study (*7*) and acquiring a better understanding of the synthesis gas reaction over ZrO_2. The results are used to propose surface reactions during CO and CO_2 hydrogenation.

II. METHODS

The zirconia (Alfa-Ventron) was 99% pure and in the form of 1- to 3-μm spheres with a BET area of 5.8 m^2/g. X-Ray powder diffraction patterns for the zirconia, as supplied or after being subjected to any treatment described in the paper, were characterized by the monoclinic form.

Wafers for the infrared experiments were prepared between pieces of paraffin paper mounted, using stopcock grease, to the faces of a 25.4-mm-diam die. Zirconia powder, 30 mg, was spread uniformly on the paper and pressed at 27.6 MPa. The area of the wafer was about 1 cm^2. An ir spectrum of this wafer without additional treatment showed large paraffin signals. The signals were removed after the wafer was evacuated and heated at 500°C in 101.3 kPa O_2 overnight.

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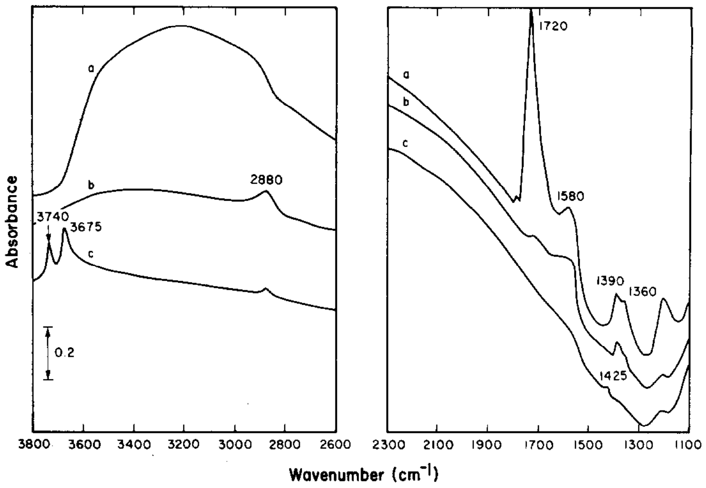


FIG. 1. Adsorption of HCOOH on ZrO_2: (a) treated with 2.67 kPa HCOOH at 25°C; (b) evacuation at 250°C for 0.5 hr; and (c) evacuation at 550°C for 0.5 hr.

The infrared quartz cell was a common design which permitted evacuation, purging, and heating the sample (wafer). The sample was heated by raising it into a furnace area. Calcium fluoride optics were used. Infrared spectra were recorded in absorbance using a Nicolet 7199 FTIR at a resolution of 2 cm^{-1}. The ZrO_2 was at 25°C for all spectra reported. Three hundred interferograms were taken per spectra. All spectra reported herein have been corrected by subtraction of the gas phase and CaF_2 background absorbance, which was collected immediately after each sample spectrum.

The normal adsorption procedure involved O_2 oxidation overnight at 500°C, evacuation of the ZrO_2 to 0.13 Pa at 500°C, and cooling to 25°C in vacuum. The adsorbate gas was then admitted to the cell and continued to flow through the cell at a pressure of 101.3 kPa as the ZrO_2 temperature was increased to 540°C and lowered back to 25°. The sample was evacuated at different temperatures, specified in the text, prior to recording spectra. In the case of D_2O, HCOOH, and CH_3OH adsorption, 1.33–5.32 kPa of the vapor was introduced to the cell at 25°C. All evacuations were performed at a pressure of 0.13 Pa.

Carbon monoxide (Matheson UHP, 99.8%) was heated to 180°C over molecular sieves to decompose metal carbonyls. Carbon dioxide (Wilson UHP, 99.9%) was used without further treatment. The hydrogen (Matheson UHP, 99.999%) was passed through a deoxo cylinder and a bed of 4-Å molecular sieves to remove oxygen and water.

III. RESULTS AND DISCUSSION

Adsorption of HCOOH and CH_3OH

Formic acid was adsorbed at 2.67 kPa and 25°C. Figure 1a corresponds to the spectrum recorded in the presence of gas phase HCOOH (the cell was not evacuated). The broad absorbance between 3600 and 2900 cm^{-1} and the intense band at 1720 cm^{-1} were removed by evacuating the ZrO_2 sample at 250°C for 0.5 hr (Fig. 1b). These bands were associated with the OH and carbonyl stretching frequencies of formic acid molecules physisorbed through hydrogen bonding (*11, 12*). Spectrum 1b also reveals four bands at 2880, 1387, 1580, and 1360 cm^{-1}, which are associated with the anticipated formate structure. They are assigned to the C–H stretching, C–H in plane deformation, COO^- asymmetric, and

COO^- symmetric stretching vibrations, respectively (*11–14*). Evacuation of the sample used in 1b at 550°C for 0.5 hr produced spectrum 1c. The formate bands are nearly attenuated indicating most of the formate was desorbed or underwent decomposition during the evacuation procedure. The weak band at 1425 cm^{-1} was unassigned. The bands at 3740 and 3675 cm^{-1} are associated with terminal and bridged hydroxyl groups, respectively (*9, 10*), which are not removed by 500°C oxidation or evacuation.

Methanol was adsorbed at 25°C at a total pressure of 3.99 kPa. Spectrum 2a was recorded prior to evacuation; a broad absorbance band was observed in the OH region, 3600 to 3000 cm^{-1}, two intense bands were observed at 2950 and 2840 cm^{-1} and a weak band appeared at 1460 cm^{-1}. Spectra 2b, c, and d refer to sequential evacuation at 25, 100, and 200°C, respectively. The broad absorbance band was attenuated at the highest temperature indicating that some residual molecular MeOH may have been present in the system for spectra 2b and 2c. The band at 1460 cm^{-1} was barely visible following 25°C evacuation. The band at 2840 cm^{-1} decreased with increasing temperature; and the band at 2950 cm^{-1} decreased and finally split into two bands, 2960 and 2930 cm^{-1}, at 100°C.

Surface methoxylation occurred at 25°C and the methoxide concentration decreased with increasing thermal treatment. The methoxide bands at 2950 and 2840 cm^{-1} are associated with C–H stretching and the band at 1460 cm^{-1} is associated with C–H bending in accordance with published spectra over other oxides (*13, 15, 16*). The apparent splitting of the band at 2950 cm^{-1} is in accord with these assignments because it probably results from the sum of the bands at 2960 and 2930 cm^{-1}. [Morrow (*17*) studied methanol adsorption over silica and found intense C–H stretching bands at 3000, 2958, and 2858 cm^{-1}.]

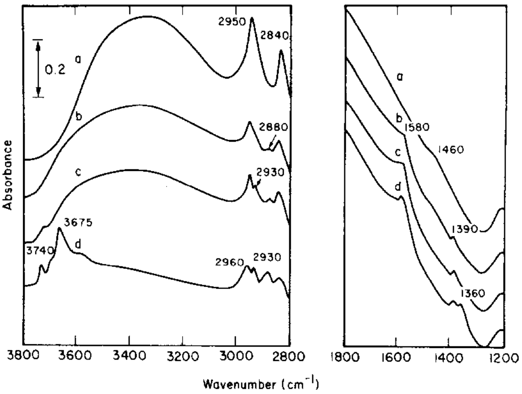


FIG. 2. Adsorption of CH_3OH on ZrO_2: (a) treated with 3.99 kPa CH_3OH at 25°C; (b) evacuation at 25°C for 0.5 hr; (c) evacuation at 100°C for 0.5 hr; and (d) evacuation at 200°C for 0.5 hr.

The spectra in Fig. 2 also reveal that additional bands appear and increase in intensity with increasing thermal treatment. Studies of methoxide over Al_2O_3 (*18*) and MgO (*19*) have demonstrated that the methoxide can be oxidized to the formate in the presence of alcohol. The alcohol serves as the oxidant and hydrogen is liberated (*18*). The broad absorbance band indicated that a reservoir of alcohol existed on the surface for spectra 2a–c. Formate has bands at 2880, 1580, 1387, and 1360 cm^{-1}. With increasing thermal treatment bands appear at 2880, 1580, 1390 cm^{-1} (spectra 2b–d) and finally at 1360 cm^{-1} (spectrum 2d) indicating that methoxide was oxidized to formate over ZrO_2. Hydroxyl bands, 3740 and 3675 cm^{-1}, are also observed after 200°C evacuation. Other studies revealed that the formate and methoxide structures in Fig. 2 could be removed by evacuation at 500°C.

H–D Exchange of Surface Hydroxyl Groups

Exchange studies were conducted to obtain independent evidence that OD groups were present on the surface in the previous study (*7*) and to determine their stability in the presence of added hydrogen. Zirconia was oxidized at 500°C and evacuated at 500°C. Spectrum 3a was expected (*2*), and displays the O–H stretches characteristic terminal (3740 cm^{-1}) and bridging (3675 cm^{-1}) hydroxyl groups on ZrO_2 (*9, 10*). The

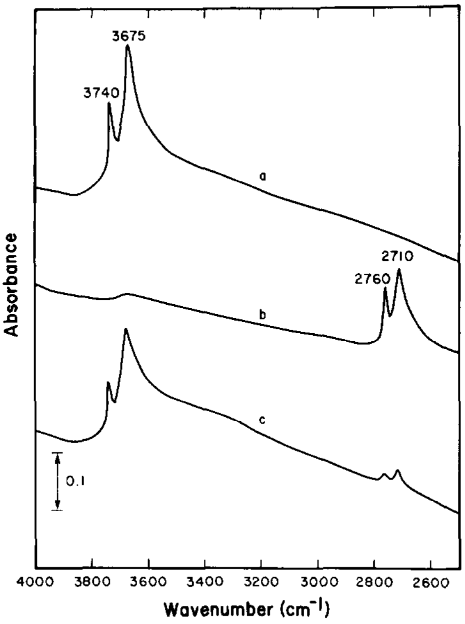


FIG. 3. H–D exchange of surface hydroxyl groups: (a) ZrO_2 treated in O_2 at 500°C for 16 hr and evacuated at 500°C for 0.5 hr; (b) treated with 1.33 kPa D_2O at 25°C and evacuated for 0.5 hr; and (c) treated with H_2 at 200°C for 0.5 hr.

OH bands were converted into OD bands by contacting the ZrO_2 with 1.33 kPa D_2O vapor at 25°C. Spectrum 3b was recorded following evacuation of the D_2O treated sample. The bands at 2760 and 2710 cm^{-1} correspond to terminal and bridged OD, respectively. The low-frequency tailing for the 3765 and 2710 cm^{-1} bands was associated with weakly adsorbed molecular water (*2*).

The deuteroxyl groups were converted back to hydroxyl groups by contacting the sample for 3b with 40 kPa H_2 at 200°C for 0.5 hr (spectrum 3c). The exchange was nearly complete. This spectrum demonstrates that hydrogen dissociates over ZrO_2 and that the OH (OD) groups are labile, at least at 200°C, in the presence of gas phase hydrogen.

Adsorption of CO, CO/H_2, CO_2, and CO_2/H_2

Figure 4a presents the spectrum for flowing CO_2 adsorption. A single band at 1610 cm^{-1} can be seen. This band is characteristic of bicarbonate species over other oxides (*1, 20, 21*) and was assigned to a bicarbonate over ZrO_2 by Tret'yakov *et al.* (*2*). Similar spectra with a single band were found for carbon monoxide and 1/1 CO/H_2 admitted to the cell at 1.33–5.32 kPa while maintaining the ZrO_2 at 400–500°C for 0.5 hr. After 0.5 hr evacuation at 25°C the spectra (not shown) displayed only one band at 1610 cm^{-1} in the 1200- to 3200-cm^{-1} range. Carbon dioxide adsorption at 2.33 kPa and 500°C for 0.5 hr or in flowing 101.3 kPa CO_2 produced the same spectra following evacuation at 25°C.

Adsorption of CO, CO/H_2, or CO_2/H_2 in *flowing gas* produced different results. The spectra are presented in Fig. 4, spectra 4b–d. Absorbance bands were detected at 2950, 2880, 1580, 1390, and 1360 cm^{-1} for all spectra. A weak band was also detected at 1610 cm^{-1} for CO (spectrum 4b) and CO_2/H_2 (spectrum 4d). The bands 2880, 1580, 1390, and 1360 cm^{-1} correspond to the bands observed following formic acid adsorption and are associated with surface formate. The band at 2950 cm^{-1} signifies that methoxide was also present. Methox-

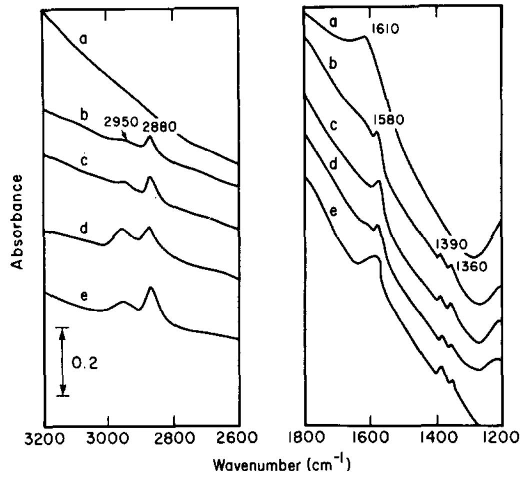


FIG. 4. Adsorption at 101.3 kPa while flowing the following gases followed by evacuation at 25°C for 0.25–0.5 hr: (a) CO_2; (b) CO; (c) CO/H_2 1/1; (d) CO_2/H_2 1/1; and (e) sample (b) after exposure to flowing CO for 18 hr at 25°C.

ide bands were observed at 2950, 2840, and 1460 cm^{-1} in Fig. 2a; the 2950 cm^{-1} band was the most intense. A weak absorbance may be present in spectra 4c and 4d at 2840 cm^{-1}, but is obscured by the band at 2880 cm^{-1}. In addition to formate and methoxide species, bicarbonate was formed from CO alone and CO_2/H_2. Additional methoxide and possibly bicarbonate formed in the presence of CO at 25°C. Figure 4e presents the spectrum recorded after exposing the sample used in 4b to flowing CO for 18 hr at 25°C. These results indicate that CO and CO_2 interact differently with ZrO_2; CO forms the formate directly, whereas CO_2 conversion to formate required the presence of added hydrogen.

The TPD/TPDE study indicated that CO and CO_2, adsorbed in the absence of gas phase hydrogen, gave rise to a surface species which desorbed at 120 to 180°C (*7*). This species was assigned to a bidentate carbonate species by comparing the desorption temperature to the stability of carbonates over ZrO_2 (*2*) and ThO_2 (*5*). Contrary to other ir studies over ZrO_2 (*2*) and over ThO_2 (*5*) we do not find infrared evidence that carbonates form over ZrO_2 at the conditions of the study. The ranges of frequencies for bidentate carbonate are 1630–1590 cm^{-1} and 1270–1260 cm^{-1} (*1*). The reported carbonate bands over ZrO_2 are 1750, 1560, and 1300 cm^{-1}, with the 1560 cm^{-1} band being the most intense (*2*). A small amount of a bidentate carbonate, producing a weak band at 1560 cm^{-1}, would have been obscured by the formate band at 1580 cm^{-1}.

Carbonate may not have been detected for two reasons. First, the combined effect of low concentrations on a low area oxide. Previous thoria studies were conducted over samples with a BET area of 35–40 m^2/g (*3, 5*) and the ZrO_2 studies were conducted over a sample with a BET area of 80 m^2/g (*2*). Our studies were conducted over a 5.8 m^2/g area sample. Adsorption was always conducted at elevated temperatures which caused multiple species to form, with the possibility that carbonates were present in small concentrations. The second reason is associated with interconversion of the various adsorbed species. Results which will be shown in Fig. 5 demonstrate that bicarbonate reacts to formate and methoxide. Tanaka and White (*21, 22*) demonstrated that CO and CO_2 formed a bidentate carbonate over TiO_2 via a bicarbonate species. The absence of detectable amounts of any carbonate suggests that they are less stable than the formate or bicarbonate at the conditions of this study.

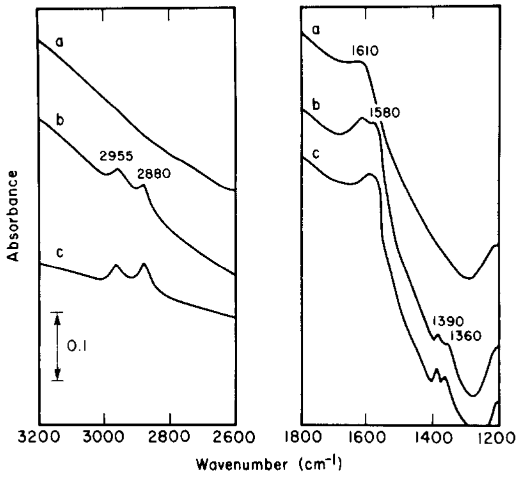


FIG. 5. Reduction of bicarbonate: (a) CO_2 adsorption at 101.3 kPa; (b) treated with 101.3 kPa H_2 at 150°C for 0.25 hr; and (c) treated with 101.3 kPa H_2 at 200°C for 0.5 hr.

Our previous assignment (*7*) of the carbonate remains unchanged. That study detected gas phase products evolved during temperature programming in He. This was a dynamic process in which surface species were interconverting, whereas the infrared measurements were taken after cooling the ZrO_2 to 25°C.

Bicarbonate, Formate, and Methoxide Interconversion

The TPD/TPDE studies revealed that CO_2/H_2 could be converted to CH_4; a mechanism was proposed in which CO_2 formed a bicarbonate which was reduced to the formate (*7*). Figure 5 presents evidence for a bicarbonate intermediate when CO_2 is

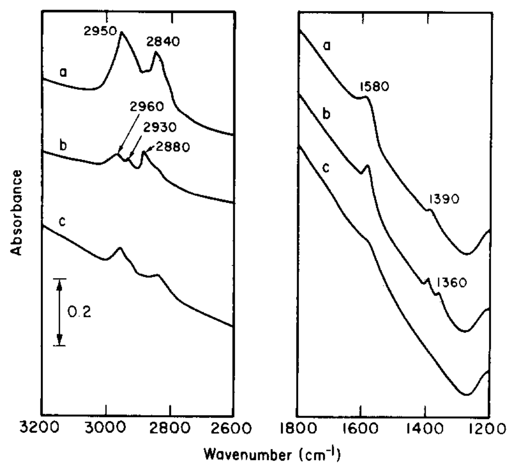


FIG. 6. Interconversion of methoxide and formate: (a) following exposure to 3.99 kPa CH_3OH and evacuation at 25°C; (b) treated with 1.33 kPa O_2 at 300°C for 0.25 hr; and (c) evacuation at 300°C followed by exposure to 26.6 kPa H_2 at 300°C for 0.25 hr.

the carbon source. Carbon dioxide adsorption was performed to obtain the bicarbonate species (Fig. 5a). This sample was then heated at 150°C in flowing H_2 for 0.25 hr and evacuated at 25°C. Figure 5b reveals that new bands appeared at 2955 cm^{-1}, a methoxide band, and at 2880, 1580, 1390, and 1360 cm^{-1}, the formate bands. Additional heating in hydrogen at 200°C for 0.5 hr (Fig. 5c) was found to cause complete conversion of the bicarbonate.

The conversion of surface methoxide into formate was revealed in Fig. 2. This has been shown to be an oxidation process over other oxides in which alcohol or air have served as the oxidant (*18*, *19*). Oxygen and hydrogen were used to determine if the conversion was reversible. Methanol was adsorbed at 25°C. As seen from Fig. 6a, methoxide bands, 2950 and 2840 cm^{-1}, and formate bands, 1580 and 1390 cm^{-1}, were present. This sample was treated with 1.33 kPa O_2 at 300°C for 0.25 hr prior to recording spectrum 6b. The intensities of bands at 2950 cm^{-1} (in this case 2960 and 2930 cm^{-1}) and 2840 cm^{-1} corresponding to C–H stretching of the methoxide groups decreased significantly. The band at 2880 cm^{-1}, formate C–H stretching, became the most intense. The sample was then evacuated at 300°C and hydrogen was introduced at a pressure of 26.6 kPa for 0.25 hr at 300°C. The resulting spectrum (Fig. 6c) shows two C–H stretching bands for the methoxide at 2960 and 2840 cm^{-1} and only weak signals for the formate at 1580 cm^{-1}. Hydrogen treatment may have caused some of the surface species to desorb; however, the methoxide bands show a noticeable increase in Fig. 6c over those in Fig. 6b demonstrating that the methoxide to formate conversion was reversible.

Reaction between CO and Hydroxyl Groups

In a previous study (*7*) a mechanism was postulated for the CO/H_2 reaction over ZrO_2 in which surface OH groups acted as the hydrogen source for formate formation. Surface OH groups were converted to OD groups by two treatments of D_2O vapor as described earlier. This sample was then subjected to flowing CO adsorption and evacuated at 25°C. Figure 7a shows that the COO^- stretching bands at 1580 and 1360 cm^{-1} of formate are present. Bands are not seen for C–H stretching or bending for the formate, 2880 and 1390 cm^{-1}, respectively.

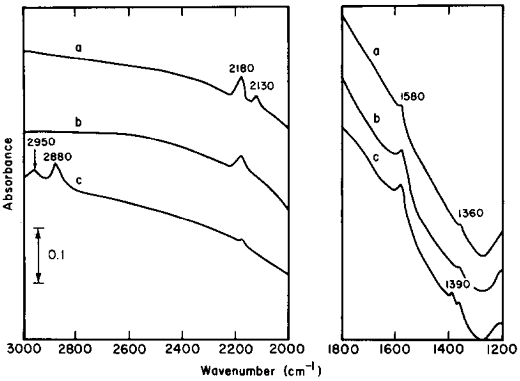
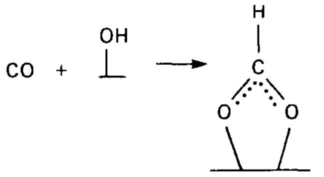


FIG. 7. Reaction between CO and surface OD groups: (a) 101.3 kPa CO adsorption on a D_2O treated sample; (b) evacuation at 100°C for 0.25 hr; and (c) treated with 101.3 kPa H_2 at 200°C for 0.5 hr.

The C–D bending band was below the usable range of the CaF_2 optics. The C–D stretching band was revealed by evacuating the sample at 100°C for 0.25 hr (Fig. 7b). This procedure removed molecular CO. The band at 2180 cm^{-1} was assigned to C–D stretching of the formate in accordance with other work (*6, 12, 13, 15*). This demonstrated that CO interacted with surface OD groups to form the formate. Additional evidence that CO interacted with OD groups was provided by the fact that OD groups were observed prior to CO adsorption and were absent in spectra 7a and 7b.

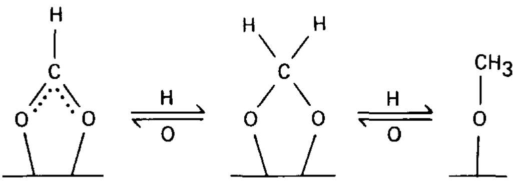
Hydrogen was introduced into the sample cell at 101.3 kPa and 200°C for 0.5 hr. The results in Fig. 3 indicated that this converts OD back to OH. Figure 7c presents the spectrum recorded after hydrogen treatment. Bands at 2880 and 1390 cm^{-1} corresponding to $HCOO^-$ are clearly visible and the band at 2180 cm^{-1} is nearly attenuated. Methoxide was also formed, as evidenced by the band at 2950 cm^{-1}, in accordance with the results presented in Fig. 6. This experiment established that H–D exchange occurred between $DCOO^-$ and added hydrogen. The nature of this hydrogen was not revealed, atomic H versus O–H, in this study. The results in Figs. 4b and 4e revealed that CO adsorption, in the absence of added hydrogen, produced formate and methoxide species via interaction with hydroxyl groups. This provides evidence that the H–D exchange and methoxide formation shown in Fig. 7c occurred via OH groups.

The infrared results support the postulated mechanism for CO/H_2 interaction over ZrO_2 (*7*) in which CO interacts with surface OH to form a formate,



(1)

and the formate is reduced to methoxide:



(2)

Formate was shown to react to methoxide in the presence of H_2 (Figs. 6 and 7) and to react to methoxide when CO was adsorbed at 101.3 kPa (Fig. 4). Reaction (2) is proposed to proceed via the oxymethylene intermediate, H_2CO_2, because Denise *et al.* (*23*) suggested this intermediate for formate reduction over a Cu/Zn-oxide catalyst.

IV. CONCLUSIONS

Formate formation from CO and formate conversion to methoxide were proposed on the basis of TPD/TPDE studies of CO, CO_2, and H_2 over ZrO_2 (*7*) and were substantiated in this study using transmission FTIR. Additional evidence was provided in this study to support hydroxyl hydrogen as the hydrogen source in surface reduction of the formate to the methoxide as well as the initial formate forming reaction. Furthermore, surface OD groups were shown to be labile at 200°C.

Bicarbonate, formate, and methoxide species formed. Their formation was dependent upon the adsorbing gas mixture and pressure. Bicarbonate was shown to convert to formate and formate was shown to convert to methoxide. Differences between CO_2 and CO adsorption lead to two different hydrogenation routes.

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