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AN INFRARED SPECTROSCOPIC STUDY ON THE MECHANISM OF METHANOL FORMATION FROM CO AND H_2 OVER ZIRCONIA

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Formate and methoxide species formed by the CO-H_2 reaction over zirconia at 423-673 K were observed by IR method. Methoxide species were converted into formate ion while the conversion of formate ion into methoxide was accelarated when methoxide and formate species coadsorbed on the zirconia surface at 523 K. A mechanism of methanol formation was proposed.

Formation of methanol, dimethyl ether and iso-butene from the CO-H_2 reaction over zirconia in moderate conditions has been reported.1) To understand the mechanism of these reactions, surface adsorbed species during the reaction were studied by infrared spectroscopic method.

The infrared studies of adsorbed species formed by the CO-H_2 reaction have been reported over various metal-supported catalysts in connection with methanol and Fischer-Tropsch syntheses.2) It has been studied using infrared spectroscopy that over metal oxide catalysts such as MgO and ZnO, the decomposition of methanol proceeded via formate ion intermediates. Recently adsorbed formaldehyde species from CO-H_2 reaction over MgO was found by IR and TPD,4) formyl species was detected over Cu-ZnO catalyst by IR,5) and methoxide and formate species from the CO-H_2 reaction were detected over Cu-ZnO catalyst by using high pressure IR cell.6) We report here infrared studies of adsorbed species such as formate and methoxide from the CO-H_2 reaction over zirconia under low pressure conditions.

The catalysts were prepared by precipitation from solution of zirconium oxynitrate with NH_4OH and by calcination of the hydroxides at 773 K for 3 h as previously reported.1) The pressed disk samples were pretreated with oxygen at

723 K for 3 h. IR spectra were recorded on a JEOL 100 FT-IR spectrometer with 256 scans at 4 cm^{-1} resolution.

When hydrogen (67 kPa) was introduced over the catalyst at 473 K, OH bands at about 3780 and 3670 cm^{-1} were observed. However we could not find Zr-H species like Zn-H.7)

Figure 1 shows the spectra of surface species resulting from a mixture of $CO-H_2$ (1:3, 67 kPa) over zirconia at 423 K. The spectra were obtained by subtraction of background of zirconia catalysts observed at the same temperature. It was found for the first time that the surface formate ion3) (at 2960, 2870, 1569, 1390, and 1375 cm^{-1}) is formed over zirconia from the $CO-H_2$ reaction, under low pressure and low temperature conditions. The formate ion was also observed when CO was introduced at 673 K over the catalyst covered with OH. This fact suggests that the surface formate ion is formed by the reaction between OH(a) and CO. Figure 2 shows the spectra of adsorbed species resulting from the $CO-H_2$ reaction at 523 and 673 K.

Above 523 K, formation of methoxide species over the catalyst was observed at about 2930, 2830, 1140, and 1040 cm^{-1} in the infrared spectra.8) These assignments were confirmed by the experiments of the adsorption of formic acid and methanol on zirconia as shown in Figs. 1-(B) and 3-(A). At 523 K, main

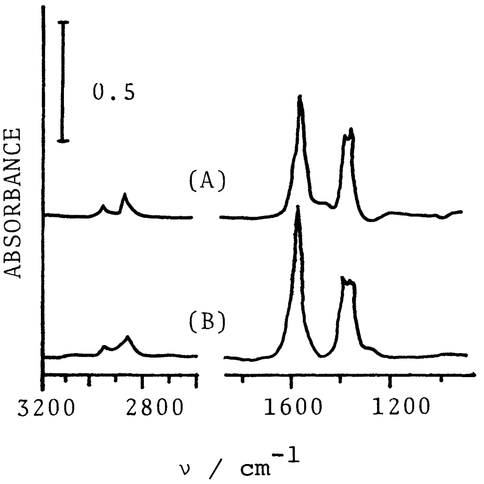


Fig. 1. FT-IR spectra of adsorbed species formed from $CO-H_2$ reaction over zirconia at 423 K. Spectra were taken under the reaction condition.
(A): Formed from $CO-H_2$ reaction.
(B): From HCOOH.

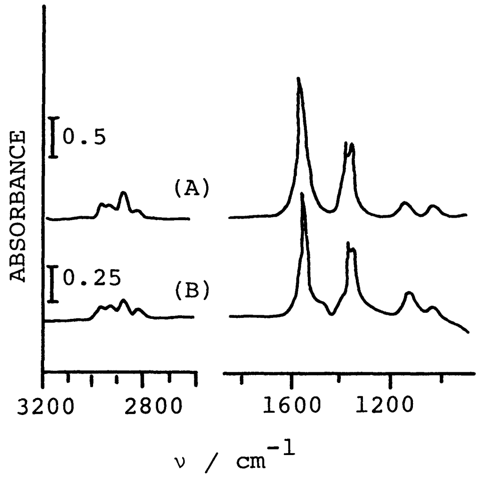


Fig. 2. FT-IR spectra of adsorbed species formed from $CO-H_2$ reaction over zirconia at 523 K and 673 K.
(A): Formed from $CO-H_2$ reaction at 523 K.
(B): Formed from $CO-H_2$ reaction at 673 K.

product was methanol in 99.4 mol% selectivity among C compounds except CO_2. At 673 K the adsorbed species on the catalyst were also formate ion and methoxide under the reaction conditions as shown in Fig. 2-(B). In this condition main product was iso-butene (60 mol%) among hydrocarbons produced.

Relative intensity of the methoxide to the formate species increased with increasing temperature above 523 K. However even at 673 K both species were observed under the reaction conditions. When gas phase was evacuated at 673 K, the formate ion on the surface rapidly disappeared and methoxide decreased slowly. These mean that methoxide is more stable adsorbed species than the formate ion.

The changes of FT-IR spectra of methoxide species formed from methanol adsorption over zirconia were shown in Fig. 3. It was found that methoxide species was converted into formate ion above 373 K. This reaction was accelerated in the presence of hydrogen:

$$CH_3OH(g) \longrightarrow CH_3O(a) \xrightarrow[H_2(g)]{373\ K} HCOO(a)$$

Formate ion formed from formic acid adsorption or from the $CO\text{-}H_2$ reaction at 423 K were heated at 523 and 573 K in the hydrogen atmosphere. Formate ion began to decompose to form Co, CO_2, H_2, and H_2O, and methoxide species however were hard to detect in this condition.

$$\left.\begin{array}{l} HCOOH(g) \\ H_2(g) \ + \ CO(g) \end{array}\right\} \xrightarrow{423\ K} HCOO(a) \xrightarrow[H_2(g)]{573\ K} \left\{\begin{array}{l} CO(g) \ + \ H_2O(g) \\ CO_2(g) \ + \ H_2(g) \end{array}\right.$$

At 523 K, HCOO(a) and $CH_3O(a)$ formed from the $CO\text{-}H_2$ reaction were heated in hydrogen atmosphere at the same temperature and behavior of adsorbed species were followed by FT-IR as shown in Fig. 4. It is clearly demonstrated that at 523 K formate ion decreases (lower side peaks) while methoxide species increase (upper side peaks). This means that the conversion from formate ion into methoxide is accelarated when methoxide and formate species coexist on the catalyst surface at 523 K as follows:

$$H_2(g) + CO(g) \xrightarrow{523\ K} \left\{\begin{array}{l} HCOO(a) \\ CH_3O(a) \end{array}\right\} \xrightarrow[H_2(g)]{523\ K} \left\{\begin{array}{ll} HCOO(a) & \text{decrease} \\ CH_3O(a) & \text{increase} \end{array}\right.$$

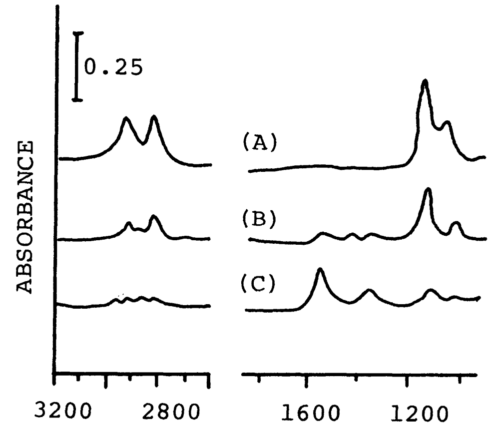


Fig. 3. The changes of FT-IR spectra of methoxide species formed from methanol over zirconia.
(A): CH_3OH was adsorbed at 298 K and evacuated at 373 K for 30 min.
(B): Heated at 373 K for 2 h in H_2 atmosphere.
(C): Heated at 523 K for 30 min in H_2 atmosphere.

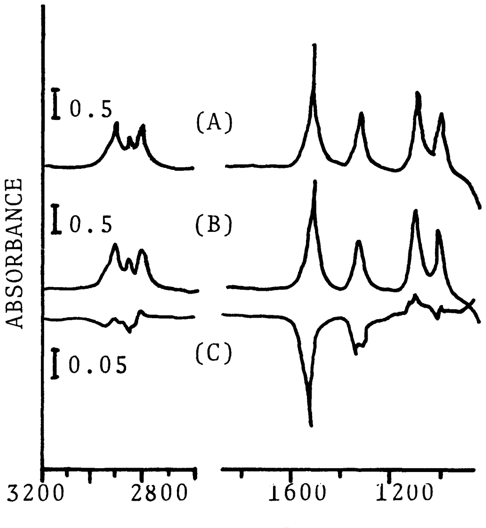
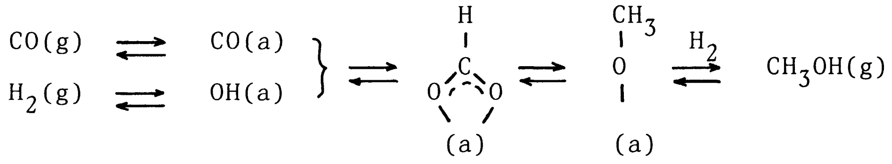


Fig. 4. FT-IR spectra of adsorbed species from $CO-H_2$ reaction at 523 K.
(A): Adsorbed species at 523 K for 48 h.
(B): (A) was evacuated at 523 K for 30 min.
(C): The ratio spectrum of (B)/(A).

At this condition gaseous products in a liquid nitrogen trap from the decomposition of adsorbed species were mainly methanol and water.

On the basis of above experimental results, a mechanism of methanol synthesis from the $CO-H_2$ reaction over a zirconia catalyst at 523 K is proposed as follows:



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