Support Effect of Re Catalyst on Methanol Synthesis from CO_2 and H_2 under a Pressure of 5 atm

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Methanol synthesis by the reaction of CO_2 with H_2 over Re supported on ZrO_2, CeO_2, La_2O_3, and Al_2O_3 was studied under a pressure of 5 atm by the use of a flow reactor. Methanol was formed over Re/CeO_2, Re/ZrO_2, and Re/La_2O_3, but not over Re/Al_2O_3 and ZrO_2 alone. On the basis of XPS analysis, the active state of Re was suggested to be Re^0 for Re/ZrO_2 and Re/CeO_2. For Re/Al_2O_3, Re was incompletely reduced, resulting in no formation of methanol. Methanol synthesis was inferred to proceed via CO in the case of Re/ZrO_2, and via the reaction of CO_2 with surface OH in the case of Re/CeO_2 by FT-IR analysis.

The support effect of rhenium catalyst on methanol synthesis from CO_2 and H_2 under 10 atm was reported to be remarkable, the selectivity for methanol formation being of the order Re/ZrO_2(73%)>Re/Nb_2O_5(52%)> Re/SiO_2(23%)>Re/Zeolon(18%)=Re/MgO (17.5%).[1,2] In the present work, we attempted to examine the effects of CeO_2, La_2O_3, and Al_2O_3, together with ZrO_2, as supports of a rhenium catalyst in the reaction of CO_2 with H_2 under 5 atm; we also studied the active sites and the reaction mechanisms by XPS and FT-IR analysis.

Experimental

Preparation of Catalysts. Supported Re catalysts were prepared by impregnating La_2O_3, CeO_2, ZrO_2, and Al_2O_3 (20—40 mesh) with an NH_4ReO_4 aqueous solution. This was followed by drying in a vacumm at 100 °C and reducing with hydrogen at 200 °C for 2 h, and then at 400 °C for 4 h; they were then cooled down to the reaction temperature under hydrogen and kept at the reaction temperature for 2 h. The amount of Re was adjusted to be 1.5 wt% for all catalysts. La_2O_3 and CeO_2 were obtained by thermal decomposition of $La(NO_3)_3$ and $(NH_4)_2Ce(NO_3)_4$ at 500 °C in air for 24 h. ZrO_2 was prepared by hydrolysis of $ZrOCl_2$ with aqueous ammonia, followed by drying at 110 °C for 12 h and calcining at 500 °C for 12 h. Al_2O_3 was a commercially available γ-Al_2O_3, which was used after calcination at 500 °C for 12 h.

Reaction Procedures. The reaction of CO_2 with H_2 was carried out in a flow reactor within the temperature range: 160—340 °C. A mixture containing H_2 and CO_2 at a mole ratio of 3:1 was fed through a constant volume of catalyst (1.8 ml) at a total pressure of 5 atm. The products were analyzed by gas chromatography using a column Porapak Q.

XPS and IR Measurements. Auger and X-ray photoelectron spectroscopic analyses were carried out by the use of an ESCA LABMK II electronic Auger spectrometer with an Al $K\alpha$ (1486.6 eV) excitation source. The infrared spectra of CO_2 and H_2 adsorbed on a catalyst placed in an in situ vacuum cell with CaF_2 windows were recorded with a NICOLET 5DX FT-IR spectrometer.

Results and Discussion

Catalytic Activity. Methanol was formed over Re/CeO_2, Re/ZrO_2, and Re/La_2O_3, but not over Re/Al_2O_3 and ZrO_2, or CeO_2 alone, although C_1 compounds (CH_3OH, CO, or CH_4) were the main products over all catalysts (Table 1). The product distribution changed, depending on the reaction temperature and space velocity. With an increase in the reaction temperature, the conversion of CO_2 increased and methanol selectivity decreased. With an increase in the space velocity, the conversion of CO_2 decreased, while methanol selectivity increased over the range 3000—12000 h^{-1}. Under the best reaction conditions, the highest selectivity for methanol formation was observed to be 76.7% over Re/CeO_2 at a reaction temperature of 160 °C.

Active Centers. The XPS spectra of Re/ZrO_2, Re/CeO_2, and Re/Al_2O_3 are shown in Figs. 1, 2, and 3, respectively. In both cases of Re/ZrO_2 and Re/CeO_2, the Re_{4f} peaks of those samples which were reduced with hydrogen at 400 °C were similar to the peak of Re metal, Re^0. The spectra of untreated NH_4ReO_4/ZrO_2 and NH_4ReO_4/CeO_2 were also similar to that of NH_4ReO_4, whose oxidation state of Re is 7+. This indicates that Re^{7+} on the surfaces was almost reduced to Re^0 by reduction

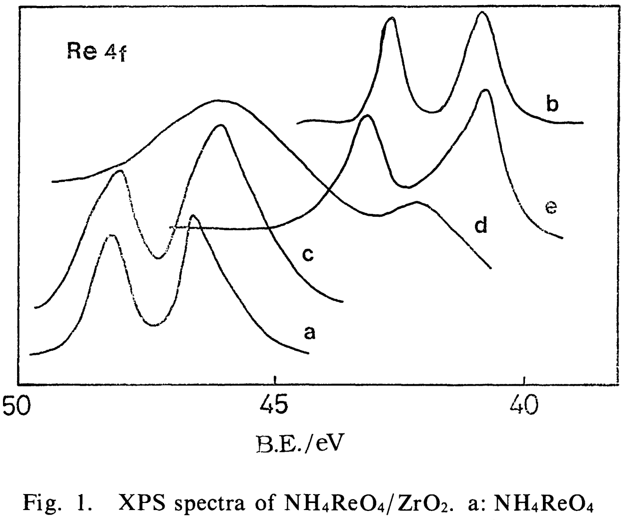


Fig. 1. XPS spectra of NH_4ReO_4/ZrO_2. a: NH_4ReO_4 powder, b: Re^0 powder, c: NH_4ReO_4/ZrO_2, d: NH_4ReO_4/ZrO_2 reduced with H_2 at 200°C, e: NH_4ReO_4/ZrO_2 reduced with H_2 400°C.

Table 1. Activity and Selectivity of Supported Re Catalyst[a)]

Catalyst	SV	Reac. temp	X_{CO_2}[b)]	Selectivity/%				Rate of reaction[d)]			Y[f)]
	h^{-1}	°C		CO+CH_4	CH_3OH	C_2–C_5[c)]	Me_2O	CO	C_2–C_5[c)]	CH_3OH	%
Re/CeO_2	6000	160	1.4	17.9	76.7	5.4	0	0.2	0.2	0.2	0.6
		200	4.0	41.9	56.3	1.8	0	0.6	0.6	0.4	1.5
		240	13.9	62.8	26.6	10.6	0	3.1	1.5	0.4	1.2
		260	20.8	77.6	7.9	16.2	0	4.4	2.4	0.2	0.6
		300	39.7	72.6	11.1	16.0	0.3	7.2	5.7	0.6	1.9
		340	49.8	73.0	0.3	26.4	0.3	7.4	8.8	0.0	0.1
	3000	200	5.3	44.8	16.0	39.2	0				
	12000	200	2.1	35.1	64.9	Trace	0	0.5	0.3	0.5	0.6
	24000	200	0.8	100.0	Trace	0	0	0.2	0.1	Trace	0
Re/ZrO_2	3750	260	15.5	60.0	26.3	12.0	1.7	3.6	2.2	0.8	1.9
Re/Al_2O_3	3330	260	19.3	83.0	0	16.9	0.2	6.0	2.1	0	0
Re/La_2O_3	5000	200	0.3	85.7	0	0	14.3	0.1	0.8[e)]	0	0
		260	3.4	46.1	52.1	0	1.8	0.9	0.2	10.5[e)]	0.4
ZrO_2		200	0.0	79.1	0	20.9	0				0
		240	0.2	87.1	0	12.9	0				0
CeO_2		200	1.0	100.0	0	0	0				0
		260	0.0	100.0	0	0	0				0

a) Reaction conditions: molar ratio of H_2/CO_2=3/1, total pressure 5 atm. Catalyst of 1.8 cm^3 was used after reduction with H_2 at 200 °C for 2 h and then at 400 °C for 4 h. b) X_{CO_2}=Conversion of CO_2 in 30 min when reaction became steady state. c) Hydrocarbons containing carbon number 2—5. d) mmol g^{-1} h^{-1}. f) Y=yield.

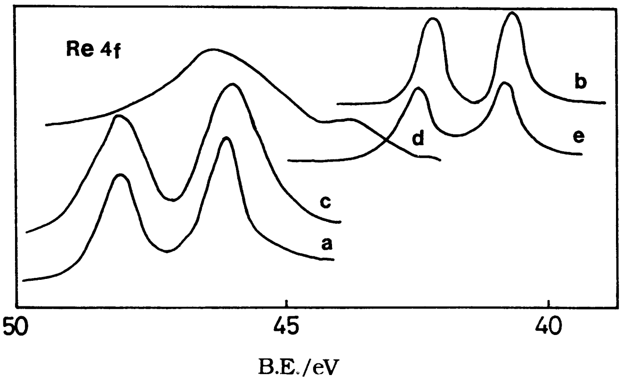


Fig. 2. XPS spectra of NH_4ReO_4/CeO_2. a: NH_4ReO_4 powder, b: Re^0 powder, c: NH_4ReO_4/CeO_2, d: NH_4ReO_4/CeO_2 reduced with H_2 at 200 °C, e: NH_4ReO_4/CeO_2 reduced with H_2 at 400 °C.

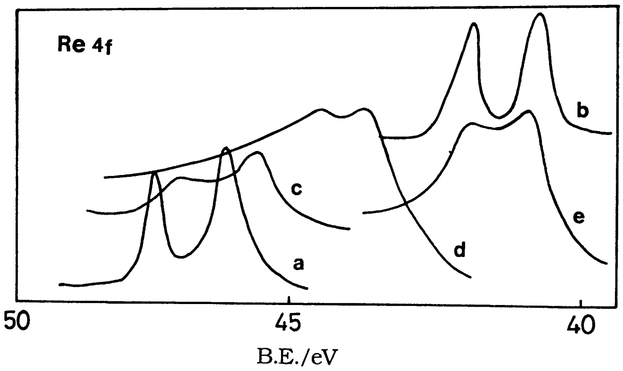


Fig. 3. XPS spectra of NH_4ReO_4/Al_2O_3. a: NH_4ReO_4 powder, b: Re^0 powder, c: NH_4ReO_4/Al_2O_3, d: NH_4ReO_4/Al_2O_3 reduced with H_2 at 400 °C, e: NH_4ReO_4/Al_2O_3 reduced with H_2 at 600 °C.

with hydrogen at 400 °C.

On the other hand, the spectra of Re/Al_2O_3 were different from that of Re metal, even when reduced with hydrogen at 600 °C; untreated NH_4ReO_4/Al_2O_3 also showed spectra different from NH_4ReO_4 alone. This is considered to be due to a strong interaction between the Re and Al_2O_3 support. This interaction makes the reduction of Re^{7+} to Re^0 difficult. This is in agreement with the conclusion by Yao and Shelef[3)] made on the bases of chemisorption, ESR, and temperature-programmed reduction. They reported that the dispersed phase of Re interacts strongly with the α-Al_2O_3 and, as a result, it can be reduced to a zero-valent state by H_2 only at a high temperature above 500 °C.

The methanol selectivity is considered to be affected by the adsorbed state of CO_2 on Re catalysts and, in particular, the the C–O bond strength. To determine the state of adsorbed CO_2, CO_2 was adsorbed and evacuated at room temperature and the XPS was measured. XPS in the region of O_{1s} are shown in Fig. 4. With the Re/γ-Al_2O_3 catalyst, C_{1s} peaks appeared at 290.3 and 284.6 eV. The former peak was assigned to the CO_3^{2-} species.

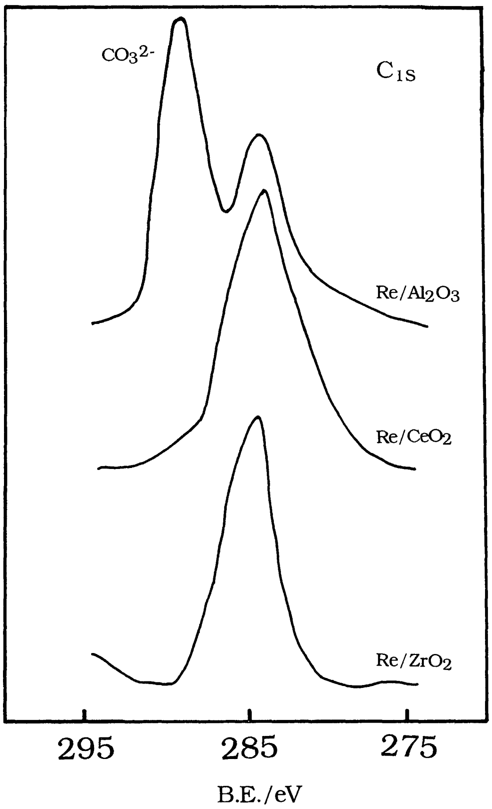


Fig. 4. XPS spectra of Re/CeO$_2$, Re/ZrO$_2$, and Re/Al$_2$O$_3$ after adsorption of CO$_2$ followed by evacuation at room temperature.

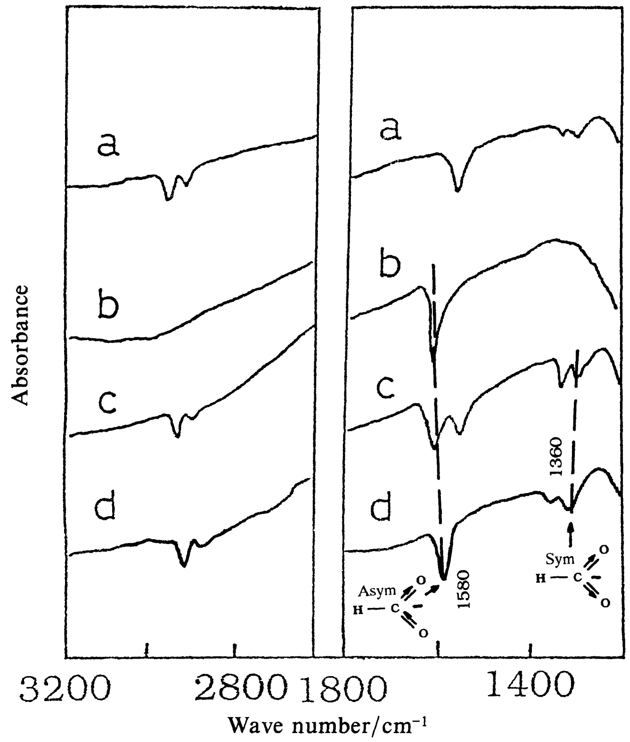


Fig. 5. IR spectra for CO$_2$/H$_2$ adsorbed on ZrO$_2$. a: CO$_2$/H$_2$, b: CO$_2$, c: CO$_2$/H$_2$ at 130°C, d: CO$_2$/H$_2$ at 230°C.

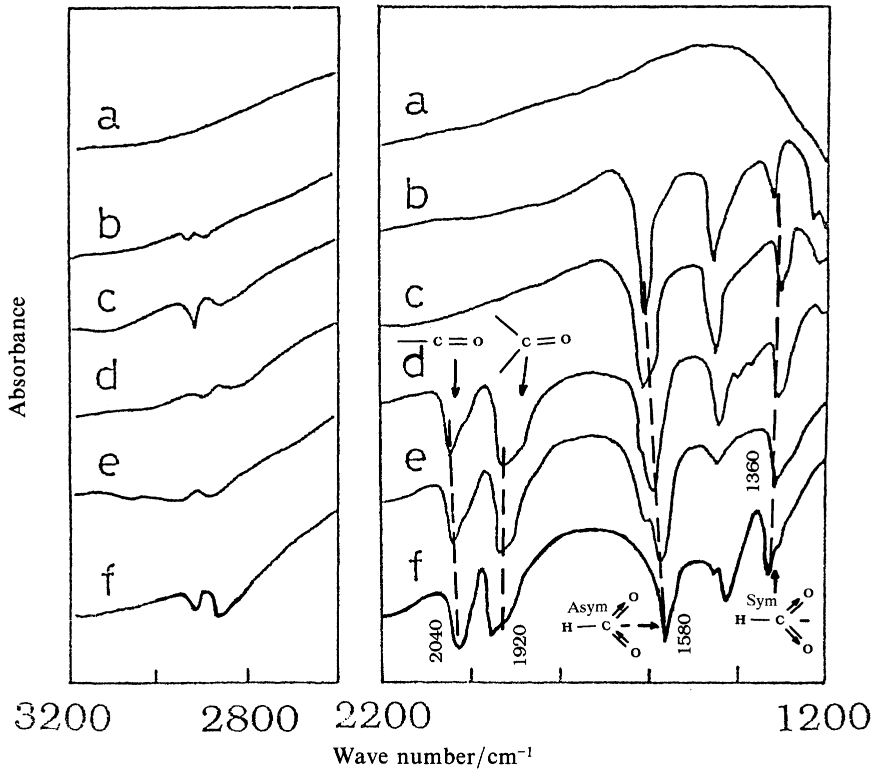


Fig. 6. IR spectra for CO$_2$/H$_2$ adsorbed on Re/ZrO$_2$. a: background, b: at 25°C, c: at 25°C in 8 h, d: at 100°C, e: at 200°C, f: at 300°C.

With Re/CeO_2 and Re/ZrO_2 catalysts, only one peak appeared at 284.6 eV, which was assigned to carbon atom. The C–O bond should be very strong in the state of CO_3^{2-}. No formation of methanol on Re/Al_2O_3 can be interpreted by the strong interaction between Re and γ-Al_2O_3, which causes a strong C–O bond.

Mechanism of Reaction. Figures 5, 6, and 7 show the FT-IR spectra of CO_2 and H_2 adsorbed on ZrO_2, Re/ZrO_2, and Re/CeO_2, respectively. The absorption bands at 1360, 1390, 1580, and 2880 cm^{-1}, which are assigned to $HCOO^-$(ad), appeared on the surfaces of both ZrO_2 and Re/ZrO_2 (Figs. 5 and 6). However, the bands at 2040 and 1920 cm^{-1}, which are assigned to CO(ad), appeared on Re/ZrO_2 (Fig. 6), but not on ZrO_2 (Fig. 5). The bonds at 2040 and 1920 cm^{-1} were assigned to linear and bridging carbonyls, respectively. Since the catalytic activity of Re/ZrO_2 for the reaction of CO_2 with H_2 was found to be much higher than that of ZrO_2, the $HCOO^-$(ad) species is not considered to be the active intermediate in the reaction. It seems likely that the CO(ad) species which was observed over Re/ZrO_2, but not over ZrO_2, is the active intermediate, although it is not certain which carbonyl is the intermediate. Since the CO species appeared at the adsorption temperature of 100 °C, at which no reaction took place, it is considered that the CO species did not result in the product, but from the adsorption of CO_2 and H_2. Thus, the reaction is considered to proceed by the conversion of CO_2 to CO(ad) followed by a reaction of CO(ad) with H(ad) formed on Re. This is in agreement with Iizuka's conclusion drawn from a comparative study between CO_2+H_2 and CO+H_2, for a Re/ZrO_2 catalyst.[2]

The spectra for Re/CeO_2 were different from those for Re/ZrO_2. The band at 1220, 1300, 1410, 1460, and 1570 cm^{-1} were observed at the room temperature. The 1570 cm^{-1} band, which has a shoulder band at 1610 cm^{-1}, decreased its intensity and shifted to 1580 cm^{-1} with an increase in the temperature up to 130 °C, two new weak bands being formed at 1397 and 1550 cm^{-1}. The bands

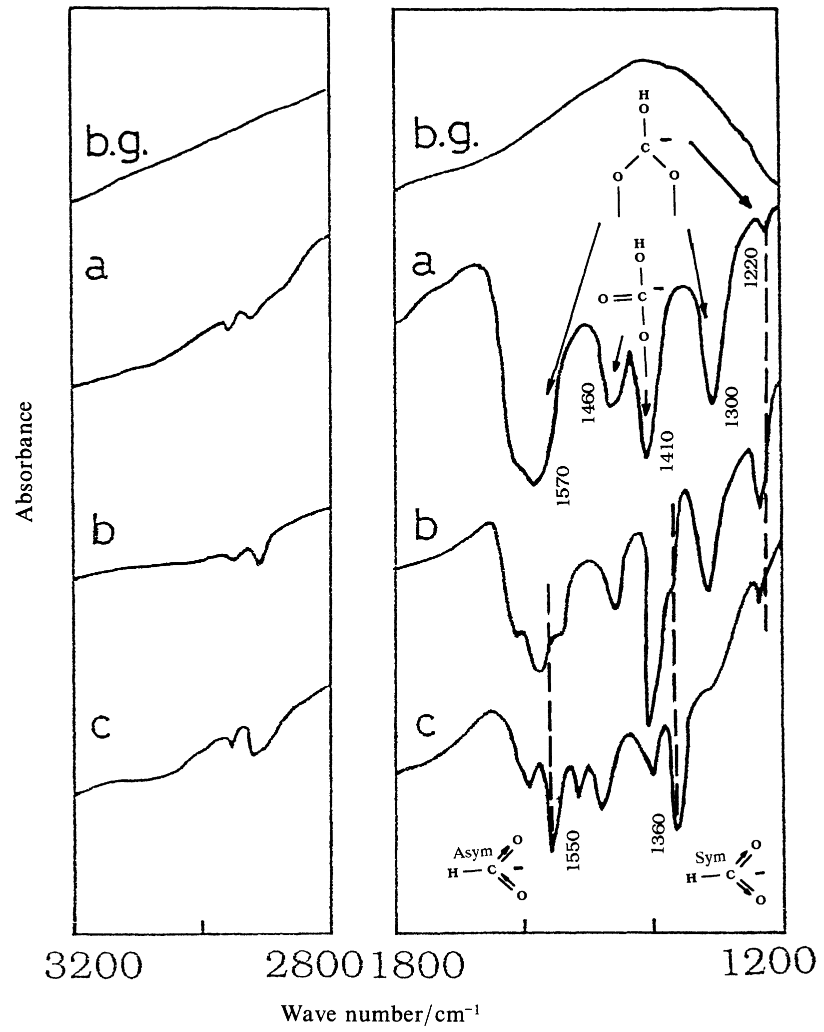
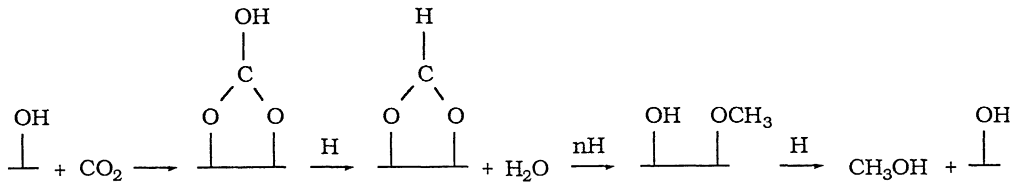


Fig. 7. IR spectra for CO_2/H_2 adsorbed on Re/CeO_2. b.g.: background, a: at room temp, b: at 130 °C, c: at 230 °C.



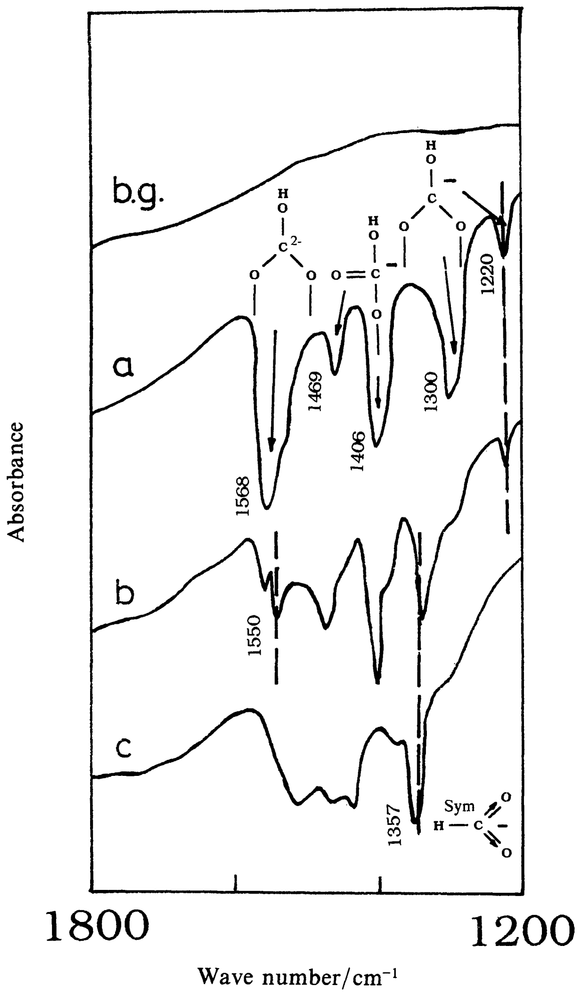


Fig. 8. IR spectra for CO_2 adsorbed on CeO_2. b.g.: background, a: at room temp, b: at 130 °C, c: at 230 °C.

at 1200 and 1610 cm^{-1} disappeared and the intensity of the bands at 1360, 1397, and 1550 cm^{-1} increased when temperature was raised to 230 °C. Since the $HCOO^-$(ad) species, which is evidenced by the bands at 1360 and 1550 cm^{-1}, exists on the surface of Re/CeO_2 at 230 °C under which a high yield of methanol was observed, it is suggested that the $HCOO^-$(ad) species is an active intermediate in the reaction over Re/CeO_2.

As shown in Fig. 8, the bands at 1220, 1300, 1406, 1469, and 1568 cm^{-1} were observed in the IR spectra of CO_2 adsorbed on CeO_2 at room temperature, but that the $HOCO_2^-$(ad) species, which is evidenced by 1220 cm^{-1}, disappeared when the temperature was increased to 230 °C; the 1357 cm^{-1} band was also observed at a higher temperature. This indicates that the $HOCO_2^-$(ad) and $HCOO^-$(ad) species could be formed on the surface of CeO_2 without Re. The XPS spectrum of the reduced Re/CeO_2 showed that an intense peak appeared at 530 eV, which was assigned to O_{1s} of the OH group. This indicates that a large amount of the OH group exists on the surface of Re/CeO_2. Therefore, CO_2 is considered to react with the surface OH (inserted to Ce–OH) to form $HOCO_2^-$(ad), as shown by the shoulder band at 1610 cm^{-1} in Fig. 6, in the first step. Then, $HOCO_2^-$(ad) reacts with H dissociated on Re (H–Re) to form $HCOO^-$(ad) over the surface Ce site on CeO_2 oxide, followed by the formation on CH_3O^- and CH_3OH by successive hydrogenation with hydrogen atoms which was dissociated on Re (H–Re). This can be illustrated by the scheme shown at the top of this page.

References

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