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HIGH PRESSURE IN SITU FT-IR STUDY OF CO HYDROGENATION OVER Rh/SiO_2 CATALYST

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The behavior of adsorbed CO and reaction intermediates on Rh/SiO_2 has been observed at high pressure CO hydrogenation condition by in situ FT-IR spectroscopy. A good relationship exists between turnover frequency of CO conversion and the ratio of bridged-CO/linear-CO adsorbed on Rh/SiO_2 at the reaction condition in terms of Rh dispersion of catalysts. Turnover frequency increases with the increase of this ratio as a general trend. Two kinds of acetate species as reaction products on SiO_2 have been observed.

Rh/SiO_2 catalyst is known as a good catalyst for a selective production of C_2-oxygenated compounds such as C_2H_5OH, CH_3CHO, and CH_3COOH from syngas at high pressure conditions.1) It has been proved Rh dispersion gives great influences on the selectivity and activity of CO hydrogenation over Rh/SiO_2. An optimum dispersion range of Rh on SiO_2 has been observed for C_2-oxygenated compounds formation.2) The object of this work is to clarify the behavior of adsorbed species such as CO and reaction intermediates at the reaction condition by in situ FT-IR spectroscopy and to get a clue to interpretations of a great influence of Rh dispersion.

In situ FT-IR studies of hydrocarbon formation from syngas under the pressurized reaction conditions have been reported by King(Fe/SiO_2 at 10 atm and 300 °C)3) and Bell(Ru/SiO_2 at 10 atm and 250 °C).4) However, it has not been studies that the performance of Rh/SiO_2 in CO hydrogenation under such high pressure as 50-70 atm at which C_2-oxygenated compounds formation is favorable. Most of IR studies of supported Rh catalysts have been undertaken at atmospheric pressure or reduced pressure5) in which hydrocarbon formation is predominant.6) Therefore, high pressure in situ FT-IR study is necessary to elucidate C_2-oxygenated compounds formation over Rh/SiO_2.

We have developed a special designed IR cell which is durable to use at high pressure(1-100 atm) and high temperature(20-450 °C).7) We wish to report here the first observation of adsorbed CO species and intermediates over Rh/SiO_2 at high pressure CO hydrogenation condition, 50 atm and 280 °C, by in situ FT-IR spectroscopy.

Six catalysts for IR spectroscopy were prepared by impregnation of SiO_2(16-32 mesh, Davison#57) with a methanol or an aqueous solution of $RhCl_3 3H_2O$.2)

Rh dispersion and mean particle size of Rh on SiO_2 are shown in Table 1.[2)]

High pressure in situ FT-IR study was conducted under the conditions of 400 ml/min gas flow, $H_2/CO=1$, 20-300 °C, and 1-70 atm by a double beam FT-IR spectrometer (JEOL JIR-100). Both sample wafer of Rh/SiO_2(100 mg, 20 mmφ) and reference wafer of SiO_2(100 mg, 20 mmφ) were mounted in a high pressure IR cell and reduced in H_2 flow at 400 °C for 1 h. First FT-IR spectrum of the catalyst in H_2 flow at 1 atm and reaction temperature(Spectrum 1) was recorded. Next in situ FT-IR spectrum during reaction(Spectrum 2) was recorded. In situ FT-IR spectra of adsorbed species were obtained by computor processing subtraction of Spectrum 1 from Spectrum 2.

Figure 1 shows the in situ FT-IR spectra of adsorbed species on CAT 4(4.7% Rh/SiO_2) at various conditions from 1 atm, 20 °C to 50 atm, 280 °C. The band of linear-CO species(A) is shifted from 2065 cm^{-1} to 2046 cm^{-1} with increasing reaction temperature. On the other hand, that of bridged-CO species at 1886 cm^{-1} is not shifted but the intensity of this peak is reduced and becomes broader. This suggests a certain amount of bridged-CO species varies to another CO adsorbed species(C)(in Fig. 2.). Adosrbed species such as (D),(F), (G), and (H) derived from products increase during reaction.

Figure 2 shows the diminishing behavior of adsorbed species by H_2 flushing at 1 atm, 280 °C. Linear-CO species(A) and bridged-CO species(B) decreased monotonously with flushing time. New adsorbed species(C) at 1975 cm^{-1} appears clearly during flushing. Isomer shift of this peak was not observed under D_2/CO gas instead of H_2/CO gas. From this result, this peak is supposed to be a CO species such as face-bridged-CO[8)] which is recognizable in IR spectra of $Rh_6(CO)_{16}$ at 1800 cm^{-1}.[9)] Adsorbed species (D),(F), and (H) proved to be very stable and hard to

Table 1. Rh dispersion and mean particle size of Rh on prepared catalyst

Catallyst		Rh dispersion (H/Rh)	mean particle size of Rh/ Å
CAT 1	1.0%Rh/SiO_2	0.83	14
CAT 2	2.0%Rh/SiO_2	0.50	23
CAT 3	4.7%Rh/SiO_2	0.44	26
CAT 4	4.7%Rh/SiO_2	0.36	31
CAT 5	9.0%Rh/SiO_2	0.32	35
CAT 6	14.2%Rh/SiO_2	0.23	48

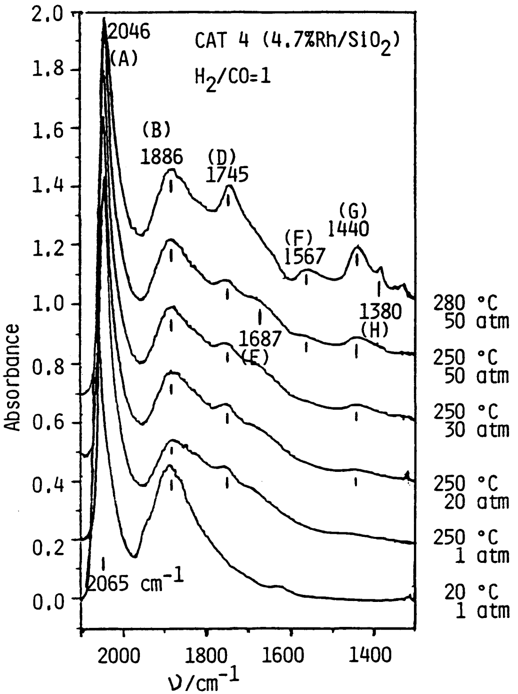

Fig. 1. In situ FT-IR spectra at various conditions.

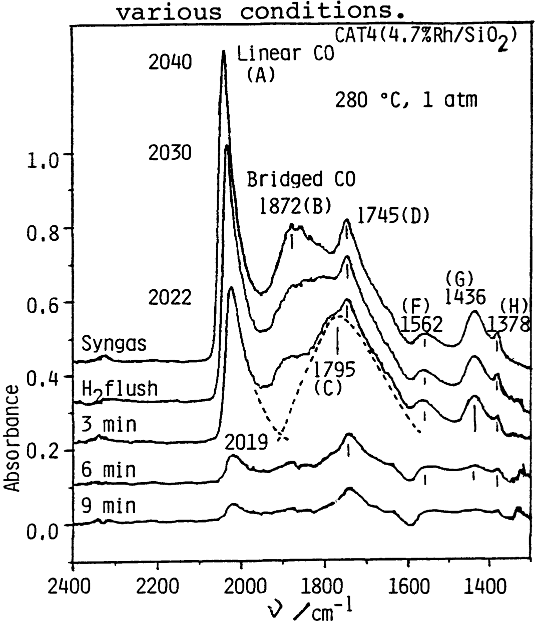

Fig. 2. H_2 flushing behavior of adsorbed species.

remove with H_2 flow in comparison with adsorbed CO. This suggests these species attach not on Rh but on SiO_2 support.

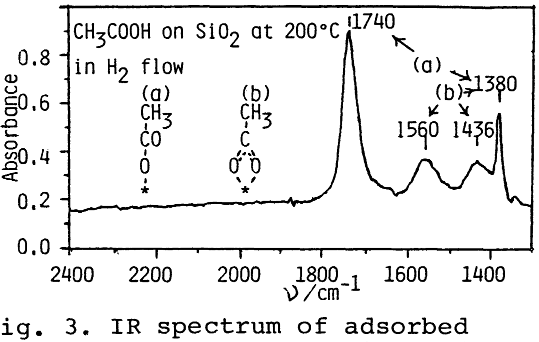

Fig. 3. IR spectrum of adsorbed CH_3COOH on SiO_2 in H_2 flow.

Figure 3 shows FT-IR spectra of adsorbed species of CH_3COOH on SiO_2 in H_2 flow at 200 °C. Four bands were observed and these bands at 1740, 1560, 1436, and 1380 cm^{-1} belong to acetate esters such as unidentate acetate(a) (νC=O 1740, δCH_3 1380 cm^{-1}) and bidentate acetate(b) (νC=O 1560, νC-O 1436 cm^{-1}).[10] These four bands are in good accord with (D), (F), (H), and (G). Therefore, it is possible to assign (D), (F), (G), and (H) bands as acetate species on SiO_2. Small and broad (E) at 1687 cm^{-1} will be assigned as a acetyl group attached to Rh.[11]

Figure 4 shows the high pressure in situ FT-IR spectra of adsorbed species on several Rh/SiO_2 catalysts at the conditions of 400 ml/min gas flow, $H_2/CO=1$, 280 °C, and 50 atm for 2 h. There are significant differences about adsorbed species among the catalysts. Linear-CO and face-bridged-CO are observed but not bridged-CO on CAT 1(1.0%Rh/SiO_2) which is a high dispersed Rh/SiO_2 catalyst. Bridged-CO

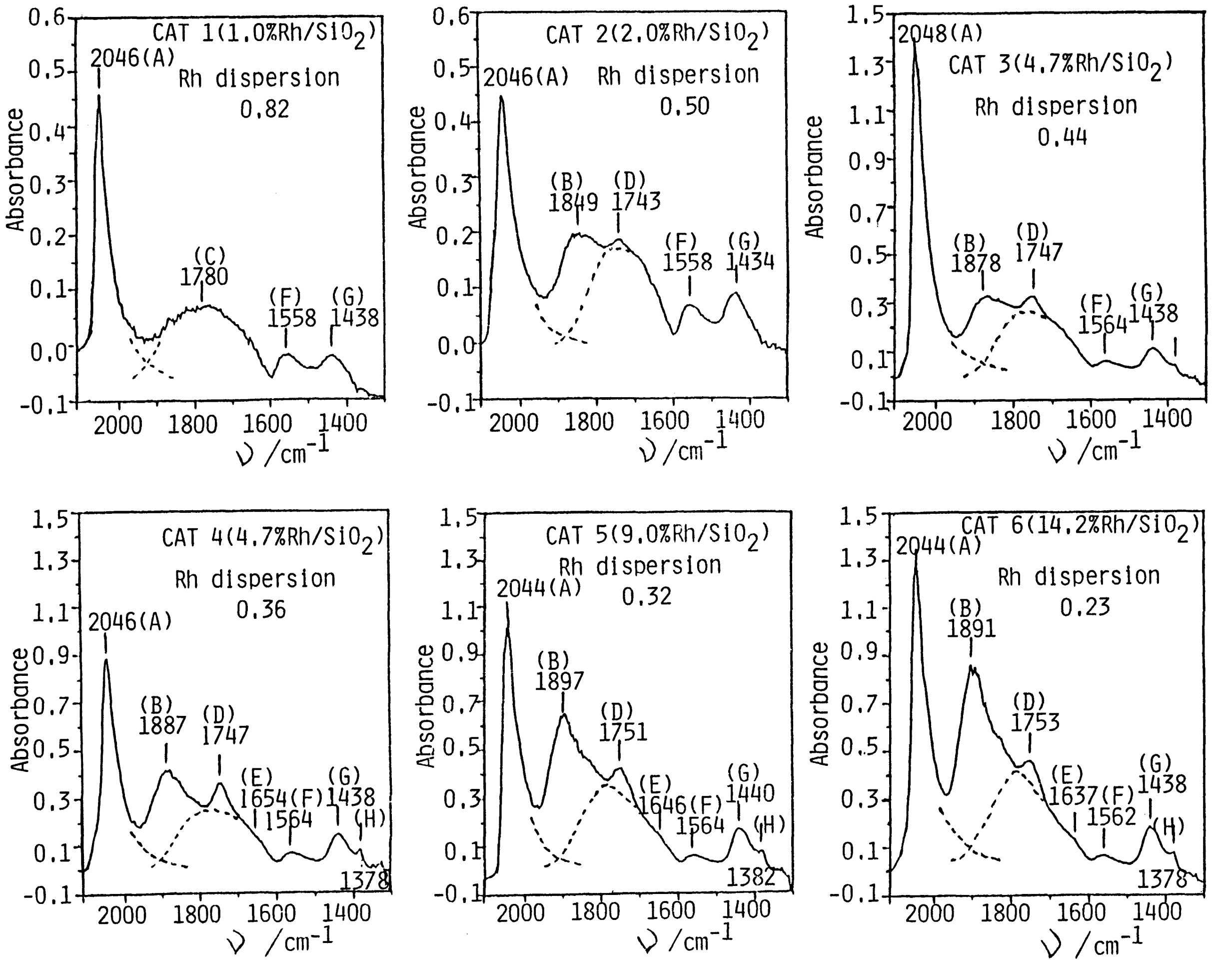

Fig. 4. High pressure in situ FT-IR spectra of adsorbed species on Rh/SiO_2 at 50 atm, 280 °C.

is present beside linear- and face-bridged-CO on CAT 2(2.0%Rh/SiO_2). The intensity of bridged-CO band on a low dispersed 4.7%Rh/SiO_2(CAT 4) is stronger than that on a high dispersed 4.7%Rh/SiO_2(CAT 3). It has been proved from Fig. 4. that the ratio of bridged-CO/linear-CO increases with the decrease of Rh dispersion of catalyst. The peak height was adopted as a measure of CO band intensity. The variation of this ratio represents the change of a physical property of Rh particle on SiO_2.

This ratio and turnover frequency of CO conversion(N_{CO}) of each catalyst are plotted as a function of Rh dispersion in Fig. 5. There is a good relationship between N_{CO} and the ratio of bridged-CO/linear-CO in terms of Rh dispersion. From these results, it might be possible to conclude that N_{CO} of a large Rh particle is higher than that of a small Rh particle because of favor of bridged-CO adsorption on a large Rh particle on SiO_2. In other words, the reactivity of bridged-CO is higher than that of linear-CO on Rh/SiO_2.

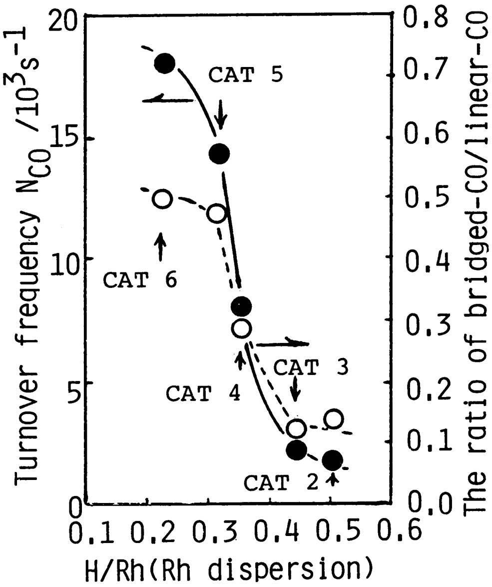

Fig. 5. Relationship between N_{CO} and the ratio of bridged-CO/linear-CO.

● : Turnover frequency (N_{CO})

○ : The ratio of bridged-CO/linear-CO at 50 atm, 280 °C

Further investigation is necessary to clarify the relationship between the CO adsorbed species and its reactivity.

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