CHEMISTRY LETTERS, pp. 1829-1832, 1994.

Reaction Routes between CO and Hydrogen over an Sm_2O_3 Catalyst Observed by *in situ* Infrared Spectroscopy

Yoshihisa SAKATA,* Yukihiro KANECHIKA, Hayao IMAMURA, and Susumu TSUCHIYA
Department of Advanced Materials Science and Engineering, Faculty of Engineering, Yamaguchi University,
2557 Tokiwadai Ube 755

Reaction routes between CO and hydrogen over an Sm_2O_3 catalyst were clearly observed by *in situ* infrared spectroscopy. CO directly reacted with surface hydride species to form surface hydrogenation products but the surface carboxylate or oxalate produced from adsorption of CO were inert to the reaction with hydrogen.

CO hydrogenation has been investigated over various catalyst systems. Especially, oxides, such as ZrO_2 and lanthanide oxides, were known to the catalysts that exhibit characteristic activity and selectivity to CO hydrogenation.[1-3] A number of studies by using infrared spectroscopy have been performed to make clear the reaction between CO and hydrogen over the oxide catalyst surfaces.[4-8] In those studies, identification of the surface intermediates that were produced from the reaction and examination of the reaction of the produced species were mainly performed. However, there were a few studies that suggest the mechanisms of production of the surface intermediate from the reactants directly and clearly. We take notice of the catalytic activity of the lanthanide oxides and have been investigating the reactivity of surface species produced over an Sm_2O_3 surface from CO hydrogenation.[9,10] In this paper, we report a reaction mechanism in the initial stage of CO hydrogenation over an Sm_2O_3 surface.

The preparation and pretreatments of the Sm_2O_3 used were shown in previous report.[9-11] The infrared spectra were recorded on an FT-IR (Jasco. model FT/IR 7300) equipped with MCT detector which was cooling with liquid nitrogen. Spectra were measured with 256 scans at 4 cm^{-1} resolution and obtained by rationing the background spectra of Sm_2O_3 to those of adsorbed gases.

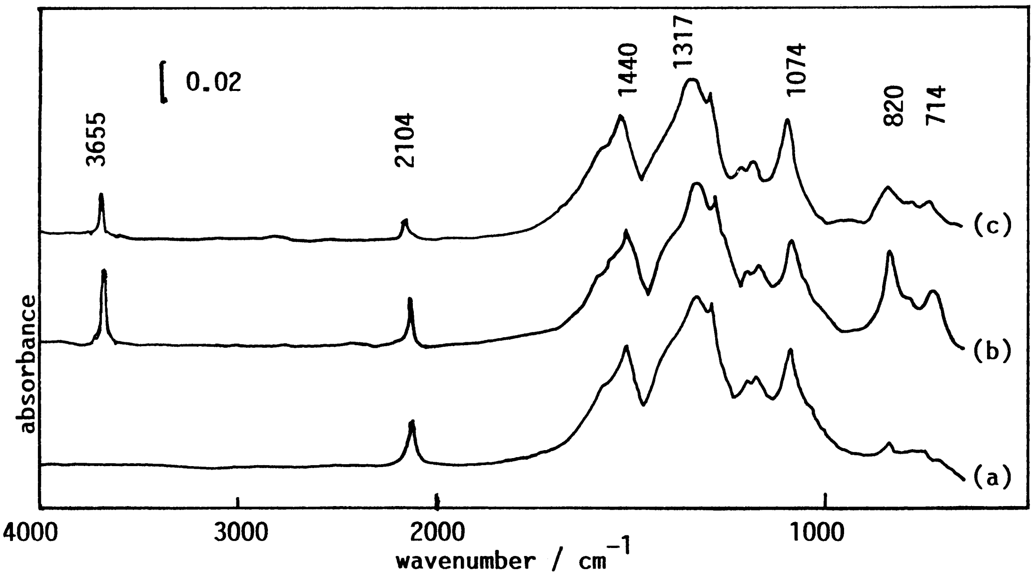

Fig. 1. Infrared spectra of adsorbed species over Sm_2O_3 formed from (a) adsorption of CO at 300 K after evacuating the gas phase, and the species under H_2 atmosphere at (b) 300 K and (c) 400 K.

Infrared spectra of the surface species produced from adsorption of CO and the species under H_2 atmosphere are shown in Fig. 1. When the surface was exposed to CO, some infrared bands attributed to the surface species were appeared. The produced species were stable after evacuating the CO in gas phase and any significant changes of the infrared spectra did not observe before or after evacuating the gas phase at 300 K. The spectrum are shown in Fig. 1(a). From a previous report of CO adsorption on MgO,[12)] the bands appeared below 2200 cm^{-1} in Fig. 1(a) can be assigned to carboxylate and oxalate type species, which were generated from the reaction of CO. Then, the reactivity of the produced species under H_2 atmosphere was examined. When the surface was exposed to H_2 at 300 K, producing new bands at 3655, 820 and 714 cm^{-1} that have been assigned to surface OH and hydride species produced from adsorption of H_2 over Sm_2O_3,[11)] were observed as shown in Fig. 1(b). However, production of any surface species originated to the reaction between the surface species from CO and hydrogen is not observed at 300 K from the spectrum. Infrared spectrum of the surface species under H_2 atmosphere at 400 K is shown in Fig. 1(c). No significant changes of the spectrum can be observed in Fig. 1(c) compared to the spectrum in Fig. 1(b) except for decreasing the intensities of the bands due to hydrogen adsorbed species. These results suggest that hydrogen adsorption and activation occurred over the surface but the surface species originated from CO were too stable to react with the activated hydrogen. From these results, it is clear that surface species produced from adsorption of CO show poor reactivity toward hydrogen over the Sm_2O_3 surface.

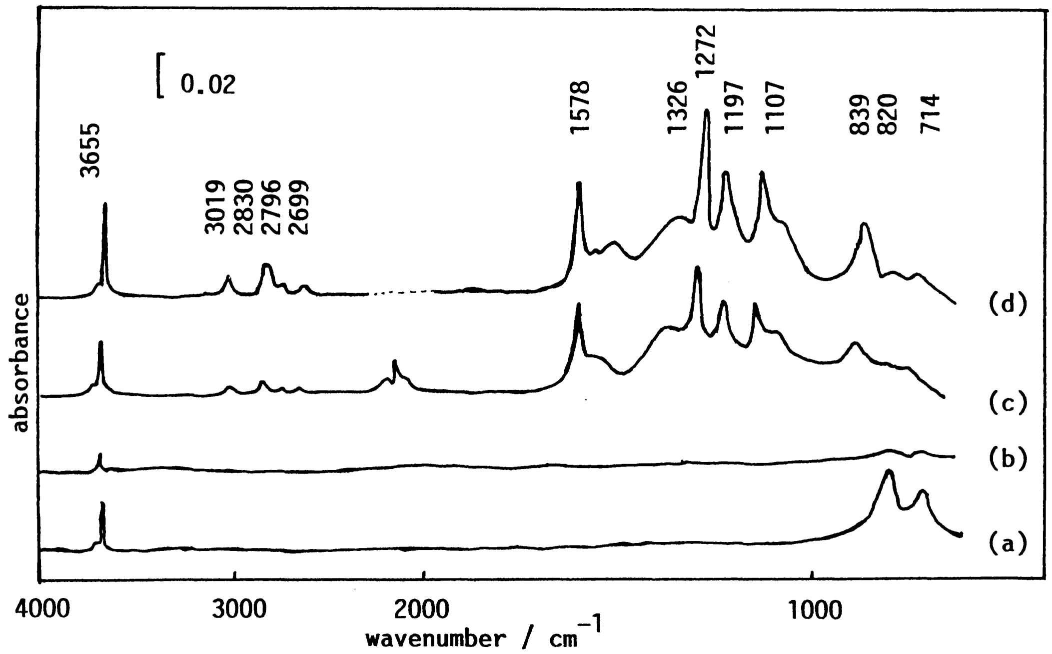

Fig. 2. Infrared spectra of adsorbed species over Sm_2O_3 at 300 K formed from adsorption H_2 and then evacuating the gas phase for (a) 5 min. and (b) 1 h, (c) adsorption of CO over 5 min. evacuated hydrogen preadsorbed Sm_2O_3, and (d) adsorption of mixed gas of H_2 and CO (H_2/CO=3, 13 kPa).

Infrared spectra of surface species formed from adsorption of hydrogen (13 kPa) over Sm_2O_3 at 300 K, where H_2 in gas phase was evacuated for 5 min. and 1 h, are shown in Figs. 2(a) and (b), respectively. The bands attributed to ν(OH) and hydrides[11)] are clearly observed after evacuating H_2 in the gas phase for 5 min. as shown in Fig. 2(a). These bands were gradually decreased with the increase of time and the bands almost disappear by evacuating the gas phase for 1 h as shown in Fig. 2(b).

Infrared spectrum of the surface species formed from the adsorption of CO (400 Pa) at 300 K over the 5 minutes evacuated hydrogen preadsorbed surface is shown in Fig. 2(c). When the surface was exposed to CO, the infrared bands attributed to produced surface species are observed as shown in Fig. 2(c). The shape of the spectrum in Fig. 2(c) is quite different from that shown in Fig. 1. In Fig. 2(c), four bands at 3019, 2830, 2796 and 2699 cm^{-1} due to ν(C-H) are observed. This result suggests the formation of new surface species that have C-H bond from reacting CO with preadsorbed hydrogen over Sm_2O_3 surface. From the infrared spectrum in Fig. 2(c), the produced new surface species can be assigned to several kinds of formyl type adsorbed species from a previous review.[12)] For hydrogen adsorbed species, it is observed that the bands at 820 and 714 cm^{-1} attributed to hydride species completely disappear in the spectrum by adsorbing CO, while the band at 3655 cm^{-1} due to surface OH species is remained at nearly the same intensity as that before adsorbing CO. From these results, it is clear that CO is immediately reacted with preadsorbed hydride species to form formyl type adsorbed species over the surface.

Infrared spectrum of the surface species produced from adsorption and reaction of CO and hydrogen mixture is shown in Fig. 2(d). When the pretreated Sm_2O_3 surface was exposed to H_2 and CO mixed gas (H_2/CO=3, 13 kPa) at 300 K, the surface species that give the infrared bands as shown in Fig. 2(d) were produced. It is interesting to note that the shape of the spectrum shown in Fig. 2(d) is in good agreement with that shown in Fig. 2(c). This result suggests that the mechanism of producing the surface species from CO hydrogenation at 300 K is the same as that from adsorption of CO over hydrogen preadsorbed surface and indicates that, when CO hydrogenation occurred at 300 K over the surface, the reaction proceeds by way of following steps; the first hydrogen was adsorbed over the surface to form OH and hydride type adsorbed species and then CO is selectively reacted with the produced hydride species to form formyl type adsorbed species.

There have been various discussions about the reaction mechanisms of CO hydrogenation over heterogeneous catalysts.[14] However, it is very difficult to obtain the evidences of the initial stage reaction of CO hydrogenation directly and clearly. The present results suggest the reaction mechanism and rule between CO and hydrogen clearly at 300 K over an Sm_2O_3 surface.

References

1) R. Kieffer, J. Varela, and A. Deluzarehe, *J. Chem. Soc., Chem. Commun.*, **1983,** 763.
2) T. Arai, K. Maruya, K. Domen, and T. Onishi, *J. Chem. Soc., Chem. Commun.*, **1987,** 1757.
3) K. Maruya, T. Maehashi, T. Haraoka, S. Narui, Y. Asakawa, K. Domen, and T. Onishi, *Bull. Chem. Soc. Jpn.*, **61,** 667 (1988).
4) J. Saussey, J-C Lavalley, J. Lamotte, and T. Rais, *J. Chem. Soc., Chem. Commun.*, **1982,** 278.
5) M-Y. He, and J. G. Ekerdt, *J. Catal.*, **87,** 381 (1984).
6) T. Onishi, H. Abe, K. Maruya, and K. Domen, *J. Chem. Soc., Chem. Commun.*, **1986,** 103.
7) J. Kondo, H. Abe, Y. Sakata, K. Maruya, K. Domen, and T. Onishi, *J. Chem. Soc., Faraday Trans. 1*, **84,** 511 (1988).
8) C. Li, K. Domen, K. Maruya, and T. Onishi, *J. Catal.*, **141,** 540 (1993).
9) Y. Sakata, M. Yoshino, H. Imamura, and S. Tsuchiya, *J. Chem. Soc., Faraday Trans.*, **86,** 3489 (1990).
10) Y. Sakata, M. Yoshino, T. Fukuda, H. Yamaguchi, H. Imamura, and S. Tsuchiya, L. Guczi, et. al., "New Frontiers in Catalysis,"(1993), P. 1519.
11) Y. Sakata, H. Imamura, and S. Tsuchiya, *Chem. Lett.*, **1991,** 349.
12) A. Zecchina, S. Coluccia, G. Spoto, D. Scarano, and L. Marchese, *J. Chem. Soc., Faraday Trans.*, **86,** 703 (1990).
13) J. A. Gladysz, *Adv. Organomet. Chem.*, **20,** 1 (1982) and the references therein.
14) J. P. Hindermann, G. J. Hutchings, and A. Kiennemann, *Catal. Rev.-Sci. Eng.*, **35,** 1 (1993).

(Received June 27, 1994)