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An *in Situ* FT-IR Study of CO Hydrogenation over Cerium Oxide

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The CO hydrogenation over cerium oxide was studied by using a closed circulating reaction system and *in situ* Fourier transform infrared spectroscopy (FT-IR) at 300–673 K. The major products of the $CO-H_2$ reaction over cerium oxide were found to be olefins ($C_2-C_4^=$), CH_4, CO_2, and H_2O. IR bands due to surface oxygen-containing species such as formate, dioxymethylene, methoxy, and formyl were always detected during the $CO-H_2$ reaction at 300–573 K over cerium oxide. No direct relationship between the surface oxygen-containing species and the production of hydrocarbons were found. The mechanism of CO hydrogenation on cerium oxide involving the surface redox was discussed. © 1993 Academic Press, Inc.

I. INTRODUCTION

CO hydrogenation has long been the most important topic in catalysis (*1*) and it has been extensively studied on group VIII metals. However, similar investigations on pure metal oxides are much less than those on metal, although metal oxides have been frequently used as support or promoter of many metal catalysts. The fundamental knowledge about the $CO-H_2$ reaction over metal oxides is far from extensive. In fact, a detailed study of this reaction on rare earth oxides is nearly absent. From the view of industrial interest, the formation of unsaturated hydrocarbons and oxygenates with high selectivity is more valuable than the production of saturated hydrocarbons. During the last decade, the emphasis on the $CO-H_2$ reaction has been shifting to the synthesis of highly selective unsaturated hydrocarbons and oxygen-containing compounds (*2*). It has been found that the reactions over metal catalysts can be switched to different distributions of products by using special oxides as support or promoter. However, the role that the oxides as support or promoter played in the reaction and the role of surface species formed on oxide supports are still unclear or controversial in some cases. Studies of the $CO-H_2$ reaction on metal oxide catalysts will provide direct information about the surface activity and properties of oxides, and will shed light on reaction mechanisms over oxide-supported metal catalysts. This is also desirable for developing new catalysts with high selectivity and activity.

We have reported that the $CO-H_2$ reaction on cerium oxide exhibited two characteristics of producing hydrocarbons (*3*) and having high selectivity for olefin (*4*). This is a unique phenomenon to metal oxide catalysts, since the CO hydrogenation on metal oxide catalysts generally produces oxygen-containing compounds. Our previous studies (*5*) have shown that formate species were readily formed even at room temperature when CO was interacted directly with the surface of partially reduced cerium oxide. Besides the formate species, some weak bands appearing in the 1200–800 cm^{-1} region due to dioxymethylene and methoxy species were detected (*6*). These oxygen-containing species could be the possible intermediates of methanol and other oxygen-

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ate products. Nevertheless, only trace amounts of oxygenates could be detected in the products from the CO hydrogenation over cerium oxide. In the present study, *in situ* FT-IR spectroscopy was used to identify the surface species derived from the CO hydrogenation on cerium oxide and to find some relationships between surface species and products, with the aim of elucidating the reaction mechanism of the CO hydrogen over cerium oxide.

II. EXPERIMENTAL

Sample preparation, spectroscopic technique, and other experimental conditions were described in our previous papers (*5*, *6*). Prepared cerium oxide was pressed into a disc with a diameter of 20 mm for infrared study. A partially reduced cerium oxide was obtained by treating a well dehydroxylated cerium oxide, symbolized as CeO_2(100 K), in H_2 at 673 K for a given time and then evacuating at this temperature for 1 h to remove adsorbed water. The partially reduced cerium oxide sample was generally referred to as CeO_2(673-H) and in detail the reduction time (t, hour) is also indicated in the way as CeO_2(673-H-t), e.g., CeO_2(673-H-4). A dehydroxylated CeO_2(673-H-4) was obtained by treating the CeO_2(673-H-4) at 1000 K in vacuum for 30 min. All above pretreatments and reactions were carried out in an *in situ* IR cell in which the sample disc can be heated up to 1000 K. After the treatments either the CeO_2(1000 K) or CeO_2(673-H) sample was stepwise cooled to a desired temperature *in vacuo* for the adsorption experiment, while background spectra were recorded from 673 K to room temperature with each interval of 100 K during the cooling process. IR spectra were recorded on a JEOL JIR-100 FT-IR Spectrometer with 256 scans at 4 cm^{-1} resolution using a liquid-nitrogen-cooled MCT detector.

Adsorption of CO and CO_2 were investigated at room temperature (300 K). Samples were in contact with adsorbate gas until the IR spectrum of the adsorbed species no longer changed with time. It was found that the adsorption equilibrium of CO on a partially reduced cerium oxide usually takes more than 60 min. Hydrogenation of CO was performed in a closed circulation system. The reactions were tested in two ways, i.e., steady-state reaction and surface reaction. The former was under $CO+3H_2$ (1 : 3) atmosphere, while the latter is a reaction of H_2 with surface species which had been generated prior to the admission of H_2. All the reactions were carried out from 300 to 673 K in stepwise fashion, as shown in Fig. 1. The products of the three reaction regions I, II, and III at 473, 573, and 673 K, respectively, were sampled after reaction for about 2 h. The sampled products were analyzed with a gas chromatography equipped with a Porapak Q column for hydrocarbons, CO_2, and H_2O, and a molecular sieve 5A column for CH_4 and CO. Hydrocarbons were detected by a FID detector, and H_2O, CO_2, and all inorganic products were detected by a TC detector. After each sampling, H_2 was again admitted in the system as depicted in Fig. 1, for surface reaction, and $CO+H_2$ mixture was admitted in for steady-state reaction. *In situ* IR spectra were recorded during every reaction regime.

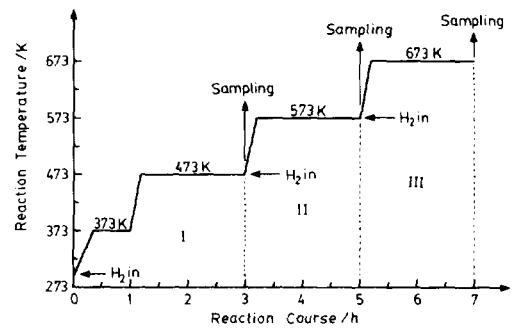

FIG. 1. Procedure for hydrogenation of surface species formed either at 300 K or high temperatures. After each sampling, fresh H_2 is introduced again for the next regime.

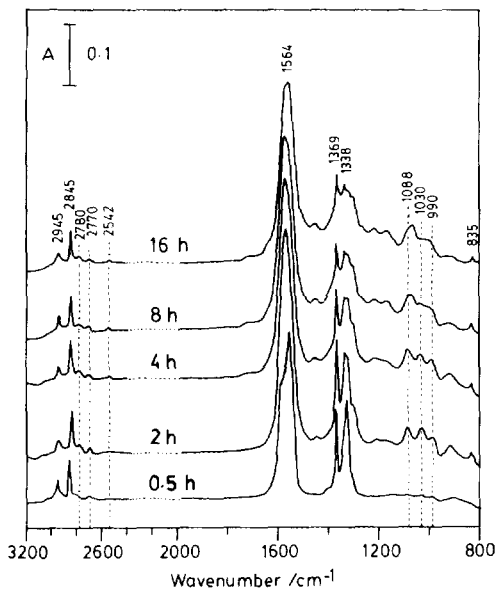

FIG. 2. IR spectra of surface species derived from CO adsorption on a series of CeO_2(673-H-*t*), *t*, reduction time of cerium oxide, as indicated for every spectrum. The spectra were recorded after admission of CO (30 Torr) for 70 min at 300 K.

III. RESULTS

1. Effect of Reduction Extent of Cerium Oxide on CO Adsorption

Figure 2 displays a set of spectra recorded after CO adsorption on CeO_2(673-H-*t*) at 300 K for 70 min. The reaction time, *t* as noted in Fig. 2, was varied from 0.5 to 16 h. A similarity in the five spectra (Figs. 2a–2e)can be observed that formate species (*5*) characterized by IR bands at 2945, 2845, 1564, 1369, and 1338 cm^{-1} were formed on all the different CeO_2(673-H-*t*). Weak bands at 2770 and 2542 cm^{-1} tentatively attributed to formyl species also appear, except the 2541-cm^{-1} band was not detected on CeO_2(673-H-0.5) and CeO_2(673-H-2). Weak bands in the frequency range of 1300–800 cm^{-1} slightly increased in absorbance and became broad for the samples with increase in reduction time. These weak bands are most probably ascribed to dioxymethylene (*7*) and methoxy (*7, 8*) species, as demonstrated by absorption of formaldehyde and methanol on cerium oxide (*6*). The variations of two absorbance features near 1564 and 2845 cm^{-1} of the formate species were plotted in Fig. 3 as a function of reduction time. The maximum absorbance is found for CeO_2(673-H-2), and the intensities decline somewhat with reduction time. This might be interpreted as that the surface OH groups were partly removed during the prolonged reduction.

2. Hydrogenation of Surface Species Formed from Adsorption of CO on CeO_2(673-H)

Reaction behaviors of surface species formed from CO adsorption on partially reduced cerium oxide were examined in a closed circulating system under H_2 atmosphere according to the procedures given in Fig. 1. The CeO_2(673-H-*t*) samples had been in contact with CO for more than 1 h until IR spectrum of the adsorbed species no longer varied. Then the system was evacuated for 30 min prior to the admission of H_2 at 300 K. Figure 4 shows the IR spectra recorded during the H_2 treatment of adsorbed species on CeO_2(673-H-*t*) samples. At 300 K, the spectrum was unchanged when the sample was exposed to H_2 (Fig. 4a) and still not affected after heating the sample to 373 K (Fig. 4b). Upon heating the sample to 473 K (Fig. 4c), bands due to

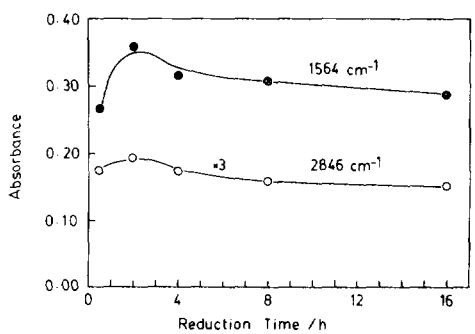

FIG. 3. Correlation between band absorbances of formate species (data from Fig. 2) and reduction time.

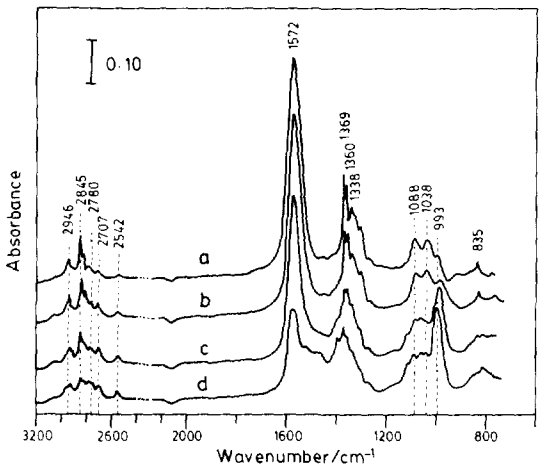

FIG. 4. (a) IR spectrum recorded after an equilibrium of CO with CeO_2(673-H-4) at 300 K for 3 h and then an evacuation for 1 h. (b)–(d): Spectra recorded during H_2 treatment of the adsorbed species at elevated temperatures. (b) 373 K for 20 min, (c) 473 K for 2 min, and (d) 473 K for 2 h.

formate species in the C–H stretching region and at 1572, 1469, 1360, and 1338 cm^{-1} were simultaneously weakened, while a band at 993 cm^{-1} range grew significantly. A standing of 2 h at 473 K led to more evident change in spectrum (Fig. 4d). Bands of formate species were markedly reduced in intensity and the band at 993 cm^{-1} developed further. Meanwhile the two weak bands at 2707 and 2542 cm^{-1} became stronger as the sample was heated from 300 to 473 K in the presence of H_2. This suggests that the formate species might be hydrogenated to the dioxymethylene and methoxy species at 473 K. Likewise, formyl species may be evolved from a reduction of the formate species. A separate experiment on desorption of formate species in vacuo at elevated temperature proved that the formate species were stable at 473 K and obviously decomposed at temperatures exceeding 530 K. Hence the sharp decrease of surface formate species at 473 K under H_2 were caused by the hydrogenation of the species. A dramatic change of spectrum can be seen in Fig. 5e, which was recorded after Fig. 4d when the temperature was raised from 473 to 573 K. The bands in the 3000–2500 cm^{-1} range disappeared and the bands due to formate species in the 1600–1200 cm^{-1} range were replaced by bands at 1518, 1452, and 1377 cm^{-1}. The 1092- and 1034-cm^{-1} bands might be an indication of residual methoxy species, and these two bands vanished soon at 573 K, as shown in Fig. 5f. According to the assignment in our previous paper (9), the band at 1518 cm^{-1} is ascribed to carboxylate species and the two bands at 1452 and 1377 cm^{-1}, together with 858 cm^{-1}, are attributed to monodentate carbonate species. Both the carboxylate and carbonate species were likely produced from the decomposition of residual formate species (6). The band at 1518 cm^{-1} of carboxylate species perished when the sample was heated to 673 K but the other two bands at 1452 and 1377 cm^{-1} seem almost the same from 573 to 673 K, and even for 2 h at 673 K (Figs. 5e–5g).

3. *Surface Species Observed during the CO–H_2 Reaction on CeO_2(673-H)*

For a better understanding of reaction behavior of surface species in the CO hydrogenation, *in situ* spectra were also recorded in the course of the CO–H_2 reaction on CeO_2(673-H-4) complying with the procedures in Fig. 1. Figure 6a gives the IR spec-

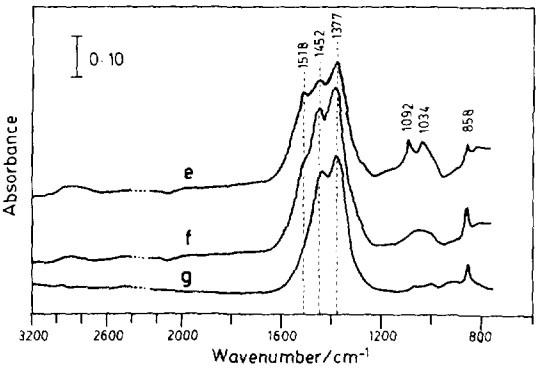

FIG. 5. (Continued from Fig. 4) (e) 573 K for 2 min, (f) 573 K for 75 min, and (g) 673 K for 2 h.

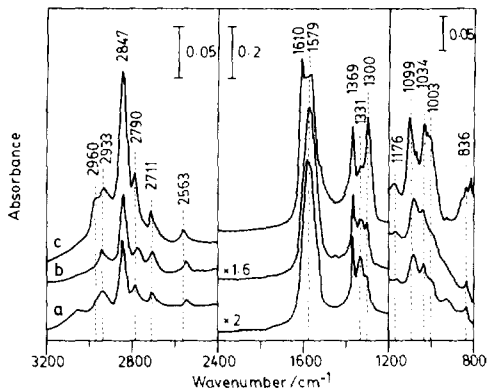

FIG. 6. IR spectra recorded during reaction of CO and H_2 (CO, 30 Torr; H_2, 90 Torr) on CeO_2(673-H-4) at elevated temperatures. (a) 300 K for 12 h, (b) 373 K for 20 min, and (c) 473 K for 2 h.

trum taken after admission of CO and H_2 mixture to CeO_2(673-H-4) for 12 h at 300 K. It was found that the spectrum is nearly identical to that in Fig. 4a. This indicates that the presence of H_2 does not alter the spectrum of adsorbed CO at room temperature. No obvious change was observed after heating the sample up to 373 K. However, the spectrum (Fig. 6c) recorded at 473 K under CO + H_2 atmosphere for 2 h exhibits intense bands in the frequency region due to formate, dioxymethylene, and methoxy species. Two striking features in the spectrum should be pointed out. First, at least three strong bands at 1099, 1034, and 1033 cm^{-1}, together with several weak bands below 1200 cm^{-1} due to dioxymethylene and methoxy species, developed with prolonged time at 473 K. Second, IR bands in the region of 2400–1200 cm^{-1} also increased in intensity and two additional strong bands at 1610 and 1300 cm^{-1} attributed to monodentate formate species appeared at 473 K. The two bands near 2711 and 2563 cm^{-1} slightly increased from 300 to 473 K (Figs. 6a to 6c). The band at 2790 cm^{-1} might be attributed to the C–H vibration of methoxy species, and growth of this band was accompanied by the bands in the 1200–800 cm^{-1} range. Figure 7a shows the spectrum taken as soon as the temperature was raised to 573 K. Bands of formate species were reduced markedly, while the bands due to carbonate species appeared. The two weak bands at 2711 and 2563 cm^{-1} due to formyl species disappeared. But the bands in the 3000–2700 cm^{-1} region due to formate and methoxy were still clearly detected. With duration at 573 K bands near 2920 and 2785 cm^{-1} attenuated in parallel with the weakening of two bands at 1090 and 1034 cm^{-1}. These bands can be attributed to methoxy species (6). The bands at 2975 and 2841 cm^{-1} coexisted with bands at 1574, 1371, and 1300 cm^{-1} even standing for 2 h at 573 K. This suggested that the formate species can be accumulated on the surface even up to 573 K under CO + H_2 atmosphere, whereas the formate species decomposed completely *in vacuo* at this temperature. When the sample was heated to 673 K a similar spectrum to that in Fig. 5g was obtained, i.e., the spectrum was predominated by the bands of carbonate species, while those bands due to both formate and methoxy species disappeared.

4. *Products from Hydrogenation of Surface Species on CeO_2(673-H)*

In order to correlate the surface species with products from CO hydrogenation, the surface species formed from CO adsorption on the five partially reduced cerium oxides,

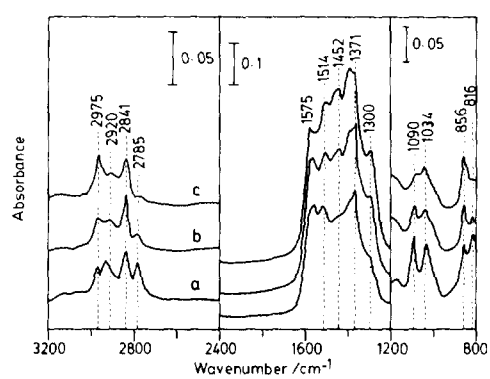

FIG. 7. (Continued from Fig. 6) (a) 573 K for 2 min, (b) 573 K for 15 min, and (c) 573 K for 2 h.

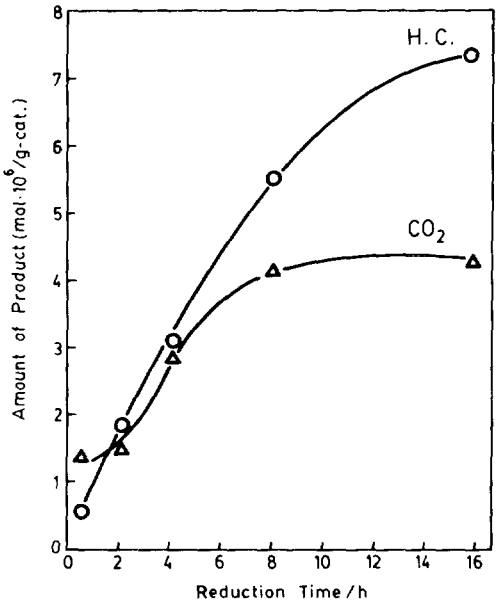

FIG. 8. Variation of total product amount from hydrogenation of surface species (Fig. 2) vs reduction time of cerium oxide. H.C., hydrocarbons (carbon-based).

as described in Fig. 2, were respectively treated with H_2. Surface reactions were investigated by following the procedure designed in Fig. 1. Figure 8 represents the total amount of products (sum of the three reaction regimes) from hydrogenation of the surface species formed from adsorption of CO on the five CeO_2(673-H-*t*) samples. It is somewhat surprising that the hydrocarbons increased appreciably with deeper reduction of the cerium oxide. Amount of CO_2 also increased with reduction time in 0.5–8 h and no longer enhanced from 8 to 16 h. The hydrocarbons were distributed mainly from C_1 to C_5. In Figs. 2 and 3, the observed bands and their intensities seem to be essentially the same for the five samples with different prereduction times. By comparing Figs. 2 and 3 with Fig. 8, the formate is responsible for the products. It is speculated that additional surface species other than formate may be the real intermediate for formation of the hydrocarbons.

IV. DISCUSSION

1. Formation of Surface Formate, Dioxymethylene, and Methoxy Species

Production of formate species via the direct reaction of CO with surface OH groups has been dealt with in Ref. (*5*). Surface hydroxyls on partially reduced cerium oxide are so active toward adsorbed CO that the formation of formate species or the making of the C–H bond on cerium oxide via an OH group is visible even at room temperature. Subsequently, formation of dioxymethylene and methoxy species can be considered as results of successive reaction of formate species with surface OH groups, namely,

$$CO + OH \rightarrow HCOO^- \quad (1)$$

$$HCOO^- + OH^- \rightarrow H_2COO^- + O^{2-} \quad (2)$$

$$H_2COO^- + OH^- \rightarrow H_3CO^- + O^{2-}, \quad (3)$$

and the methoxy may also be produced via the Cannizzaro mechanism of dioxymethylene species, as established in (*6*, *7*):

$$2H_2COO^- \rightarrow HCOO^- + H_3CO^- + O^{2-}. \quad (4)$$

Existence of proximate OH groups around a formate ion is necessary to the further hydrogenation of formate species. The reactions (2)–(4) must be accompanied with the oxidation of surface, i.e., oxidation of surface Ce^{3+} to Ce^{4+} ion. We presumed that just the chemical potential from Ce^{3+} to Ce^{4+} ion makes further hydrogenation of formate possible. This assumption can explain the fact that the weak bands in Fig. 2 due to dioxymethylene and methoxy species seems to be somewhat prominent with deeper reduction of cerium oxide. The formyl species has been assumed to be an intermediate of formate species (*5*). On the other hand, the formyl species can be generated via a reduction of formate species along with the oxidation of surface (*8*). When surface formate species were reduced at elevated temperatures (Fig. 4), dioxymethylene and methoxy species in-

creased. This indicates that the conversion from formate to dioxymethylene and methoxy is facilitated at higher temperatures. Figure 5e shows the results that the decomposition of formate species produced carbonate and methoxy species:

$$3HCOO^- \rightarrow H_3CO^- + O^{2-} + 2CO_2(\text{carbonate}) \quad (5)$$

$$HCOO^- \rightarrow H(1/2H_2) + CO_2(\text{carbonate}). \quad (6)$$

The above reactions can be further deduced from the results of Figs. 6 and 7 in which the formate, dioxymethylene, and methoxy species were greatly enhanced owing to the presence of CO and $3H_2$ atmosphere. The dioxymethylene and methoxy species were accumulated from hydrogenation of formate species which were constantly compensated from CO + H_2 atmosphere. The formate, dioxymethylene, and methoxy species are predominant on the surface during the CO–H_2 reaction at temperature up to 573 K, and begin to decompose above 573 K. Correspondingly, the carbonate species are always produced above this temperature.

2. *Relation of Adsorbed Species to CO Hydrogenation*

Although very strong bands of formate species were detected after CO adsorption on partially reduced cerium oxide, no direct correlation was found between the band intensities of formate species and hydrocarbons produced by H_2 treatment of these adsorbed species. The band intensities of formate species (Fig. 3) declined slightly with reduction time of cerium oxide, while the hydrogenation products increased almost linearly with reduction time. This indicates the possibility that there are other unobserved or weak absorbance surface species by IR spectrum in addition to the formate species contributing to the production of hydrocarbons.

On the other hand, there is another problem on the products formed from the CO–H_2 reaction and the hydrogenation of surface adsorbed species. The CO–H_2 reaction at 523 K initially forms methanol from almost 1 day and isobutanol and C_7 ketone as main products in the steady state after 4 days from the reaction start, but only a trace amount of hydrocarbons (*10*). The hydrogenation of adsorbed species from CO on partially reduced cerium oxide forms only hydrocarbons consisting mainly of linear carbon chain (*11*). The CO–H_2 reaction over cerium oxide at 673 K forms exclusively hydrocarbons, but the main isomer in C_4 hydrocarbons, which is one of the main products, consists mostly of isobutene (*3*). Therefore, there seems to be no relation between the CO–H_2 reaction over cerium oxide and the hydrogenation of adsorbed species from CO adsorption on partially reduced cerium oxide.

However, the CO–H_2 reaction is not so simple, i.e., C_5 hydrocarbons formed at 673 K over cerium oxide consist mainly of isoprene, whose selectivity in total hydrocarbons exceeds 20% (*12*), and the CO–H_2 reaction in the presence of H_2O forms ketones such as acetone, methyl ethyl ketone, and methyl isopropyl ketone as one of the main oxygenates (*13*). Again these products have branched carbon chain. Therefore, it may be possible that the formation of C_1 and/or C_2 species are importantly shared to all product formation and there are several kinds of mechanisms for higher product formation, and that the adsorbed species from CO adsorption over partially reduced cerium oxide correspond to the C_1 adsorbed species. At least the adsorbed species can be an intermediate for linear hydrocarbons formed over oxide catalysts (*14*). The participation of the adsorbed species in the formation of the other products and the detailed knowledge of the adsorbed species are under investigation.

REFERENCES

1. Ponec, V., *in* "Catalysis" (G. C. Bond and G. Webb, Eds.), Vol. 5, p. 48. Specialllist Periodic Reports, Chem. Soc., London, 1982.

2. Lee, G. v. d., and Ponec, V., *Catal. Rev.-Sci. Eng.* **29,** 183 (1987).
3. Maruya, K., Inaba, A., Maehashi, T., Domen, K., and Onishi, T., *J. Chem. Soc. Chem. Commun.*, 487 (1985).
4. Arai, T., Maruya, K., Domen, K., and Onishi, T., *J. Chem. Soc., Chem. Commun.*, 1757 (1987).
5. Li, C., Sakata, Y., Arai, T., Domen, K., Maruya, K., and Onishi, T., *J. Chem. Soc. Faraday Trans. 1* **85,** 1451 (1989).
6. Li, C., Domen, K., Maruya, K. Onishi, T., *J. Catal.* **125,** 445 (1990).
7. Busca, G., Lamotte, J., Lavalley, J. C., and Lorenzelli, V., *J. Am. Chem. Soc.* **109,** 5197 (1987).
8. Edwards, J. F., and Schrauder, G. L., *J. Phys. Chem.* **89,** 782 (1985).
9. Li, C., Sakata, Y., Aria, T., Domen, K., Maruya, K., and Onishi, T., *J. Chem. Soc. Faraday Trans. 1* **85,** 929 (1989).
10. Maruya, K., Aria, T., Aikawa, M., Domen, K., and Onishi, T., "Catalytic Science and Technology, Vol. 1" (Y. Satohiro, N. Takezawa, and T. Ono, Eds.), p. 457. Kodansha, Tokyo, 1991.
11. Arai, T., Maruya, K., Domen, K., and Onishi, T., *Chem. Lett.*, 47 (1989).
12. Maruya, K., Ito, K. Kushihashi, K., Kishida, Y., Domen, K., and Onishi, T., *Catal. Lett.*, in press.
13. Kushihashi, K., Maruya, K., Domen, K., and Onishi, T., *J. Chem. Soc. Chem. Commun.*, 259 (1992).
14. Arai, T., Maruya, K., Domen, K., and Onishi, T., *J. Catal.*, submitted for publication.