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Selective Formation of Ethene from CO Hydrogenation Reaction over In_2O_3-CeO_2, -La_2O_3, and -Y_2O_3 Mixed Oxide Catalysts

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CO hydrogenation over mixed oxides of 3A and 4A Groups (Y_2O_3, La_2O_3, CeO_2, and ZrO_2) with 3B Group (Al_2O_3, Ga_2O_3, and In_2O_3) was carried out. The addition of Ga_2O_3 or In_2O_3 to Y_2O_3, La_2O_3, and CeO_2 enhances the formation of light alkenes. An In_2O_3-CeO_2 catalyst shows the highest selectivity (43%) for ethene with the lowest selectivity (0.5%) for ethane in total hydrocarbons produced. The addition of In_2O_3 to CeO_2 results in an increase in activity for the CO hydrogenation reaction. From the results of an ethene hydrogenation reaction over mixed oxide catalysts, the high selectivity for alkene formation over In_2O_3-containing catalysts is due to a suppression of alkene hydrogenation by the addition of In_2O_3. Indium in CeO_2 is highly dispersed while keeping an oxidation state of +1 or +3 under the reaction conditions.

The selective, direct formation of light alkenes from CO hydrogenation has been studied over specifically supported metal catalysts under limited conditions. Propene is selectively formed over an Al_2O_3-supported $Fe_3(CO)_{12}$ catalyst at the initial stage of the reaction,[1,2] and also over a Co-zeolite catalyst reduced by Cd vapor.[3] Ott et al.[4] reported that the formation of ethene and propene proceeds with selectivity of 25% over freshly reduced Fe-Ru alloys. Vannice et al.[5–7] found that ethene is formed with a selectivity of 25—30% over K-promoted Fe-Mn cluster catalysts; however, the activity decreases rapidly upon carbon deposition due to a CO disproponation reaction. These metal catalysts are generally not so stable as to keep the high activity for a long-time reaction and are not selective for ethene formation.

On the other hand, CO hydrogenation over oxide catalysts, such as ThO_2, known as an iso-synthesis catalyst, proceeds to form branched hydrocarbons selectively under severe conditions such as at 723—743 K and 30—60 MPa.[8] Maehashi et al.,[9] reported that isobutene is selectively formed over ZrO_2 under moderate conditions, such as at 623—673 K and 67—2000 kPa. The formation of branched hydrocarbons with specific selectivity[10] is a characteristic of oxide catalysts on the CO hydrogenation reaction.

In this paper, we report on the CO hydrogenation reaction over mixed oxide catalysts: 3A and 4A group metal oxides with 3B Group metal oxides and the role of In_2O_3, which is the most effective for the selective formation of ethene among the added 3B Group oxides.

Experimental

Catalyst Preparation. Oxide catalysts (CeO_2, La_2O_3, Y_2O_3, and ZrO_2) were prepared as follows: Metal hydroxide was precipitated by the hydrolysis of each metal(III) nitrate with a 5% aqueous ammonia solution, washed with distilled water, dried overnight at 393 K, and then calcined to form oxide at 773 K for 3 h. Mixed oxide catalysts were prepared by co-precipitation from a mixed aqueous solution of each metal nitrate via the same procedure as that of the oxide. The atomic ratios of M_I (Al, Ga, and In) to M_{II} (Y, La, Ce, and Zr) were 1 : 10. All catalysts used were evacuated at 973 K for 3 h before the reaction, except for La_2O_3 and its mixed oxides which were evacuated at 973 K for 1 h.

Chracterization. The surface areas of the used catalysts were measured by the BET method. The crystal structures were determined by X-ray diffraction (Rigaku geigerflex rad-B system). Surface analyses of the catalysts were conducted by using an X-ray photoelectron spectrometer equipped with a glovebox (Shimadzu ESCA-750). The binding energies were corrected by Au $4f_{7/2}$ (83.8 eV).

Procedure. CO hydrogenation reactions were carried out over catalysts in a closed circulation system. A typical reaction was performed at 673 K and the initial pressure was 67 kPa (H_2 : CO=3 : 1).

Ethene hydrogenation reactions were carried out over catalysts at 195 and 273 K, and 60 kPa (H_2 : C_2H_4=20 : 1). The activities were obtained from the initial rate of ethane formation.

Analyses. Products, except for methane, were collected by a liquid-nitrogen trap. Quantitative analyses were conducted by a GC equipped with a Porapak-Q column for hydrocarbons, CO_2, and H_2O, VZ-7 and VZ-10 columns for C_2 and C_3 hydrocarbons and isomers of C_4 hydrocarbons, and a Molecular Sieve-5A column for CH_4 and CO.

Results and Discussion

CO Hydrogenation over Oxide and Mixed Oxide Catalysts. Table 1 shows the activity and selectivity for hydrocarbon formation over catalysts which were stable for 17.5 h, except for In_2O_3 and Ga_2O_3. The products were hydrocarbons, CO_2, H_2O, and a small amounts of oxygenates, such as methanol and dimethyl ether.

Y_2O_3, La_2O_3, CeO_2, and ZrO_2 showed a relatively high selectivity for C_4, C_5, and C_6 hydrocarbons which consist mainly of branched alkenes, while Ga_2O_3 produced only CH_4. In_2O_3 was rapidly reduced to metallic indium under the reaction conditions and produced large amounts of CO_2 and H_2O with no hydrocarbons from CO hydrogenation. The addition of In_2O_3 or Ga_2O_3 to CeO_2, La_2O_3, and Y_2O_3 resulted in an

Table 1. The CO Hydrogenation over Oxide and Mmixed Oxide Catalysts at 673 K and 67 kPa ($H_2/CO=3$)

Catalysts[a]	Activity[b]		Selectivity (carbon-base %)					
(surface area)[c]	Hydrocarbons	CO_2	C_1	C_2	C_3	C_4	C_5	$C_{6}+$
Y_2O_3 (51)	18 (0.35)[d]	30	10	4(67)[e]	7(86)[e]	30	23	26
Al_2O_3-Y_2O_3 (60)	10 (0.17)	12	6	6(75)	9	42	26	11
Ga_2O_3-Y_2O_3 (50)	16 (0.32)	13	5	21(90)	16	41	16	2
In_2O_3-Y_2O_3 (47)	18 (0.38)	15	5	19(94)	22(90)	34	13	7
La_2O_3 (17)	9 (0.53)	18	15	7(40)	8(60)	19	21	30
Al_2O_3-La_2O_3 (53)	10 (0.19)	16	9	7(47)	9	27	31	17
Ga_2O_3-La_2O_3 (59)	9 (0.15)	6	7	24(90)	16	28	22	3
In_2O_3-La_2O_3 (17)	12 (0.71)	14	7	34(92)	16(93)	20	16	7
CeO_2 (21)	43 (2.0)	34	25	29(96)	9(84)	21	8	8
Al_2O_3-CeO_2 (64)	180 (2.8)	130	18	30(97)	13(91)	24	13	2
Ga_2O_3-CeO_2 (59)	160 (2.7)	130	25	43(97)	14(96)	15	3	+
In_2O_3-CeO_2 (28)	160 (5.7)	130	24	43(99)	10(94)	13	7	3
ZrO_2 (50)	10 (0.20)	14	5	6(64)	7(90)	77	5	+
Al_2O_3-ZrO_2 (81)	6 (0.07)	8	19	14(85)	14	49	4	+
Ga_2O_3-ZrO_2 (59)	13 (0.22)	13	36	16(90)	14	21	5	8
In_2O_3-ZrO_2 (39)	23 (0.59)	47	99	1(96)	+	+	+	+
In_2O_3-Al_2O_3 (164)	9 (0.05)	76	100	+	+	+	+	+
Ga_2O_3 (18)	3 (0.17)	3	100	+	+	+	+	+
In_2O_3[f] (60)	+ (0)	200	—	—	—	—	—	—

a) The amounts of catalysts used were 1.5 g except CeO_2 and CeO_2 mixed oxide catalysts (0.5 g) and the atomic ratios of Al_2O_3, Ga_2O_3, and In_2O_3 to Y_2O_3, La_2O_3, CeO_2, and ZrO_2 were 1/10. b) The values are the average rates from initial 2.5 to 17.5 h in carbon-base $\mu mol \cdot g\text{-cat.}^{-1} \cdot h^{-1}$. c) $m^2 \cdot g^{-1}$. d) Parentheses show the specific activity based on surface area in carbon-base $\mu mol \cdot m^{-2} \cdot h^{-1}$. e) Parentheses show the selectivity for alkenes. f) In_2O_3 was reduced to metallic indium under the reaction conditions.

increase in the selectivity for C_2 and C_3 hydrocarbons, while CH_4, C_4, C_5, and C_6+ hydrocarbons decreased. The alkene selectivities in C_2 and C_3 hydrocarbons also increased. Especially, the In_2O_3-CeO_2 catalyst exhibited the highest selectivity (43%) for C_2 hydrocarbons which consist of 99% ethene. The addition of Al_2O_3, Ga_2O_3, or In_2O_3 to ZrO_2 resulted in an increase in the selectivity for methane. In_2O_3-Al_2O_3 produced methane only. These results indicate that In_2O_3- or Ga_2O_3-combined 3A group oxides are effective for the selective formation of ethene and that In_2O_3 is the most effective among the additives.

The catalytic activity, based on the surface area of the oxide and mixed oxide catalysts (Table 1), show that CeO_2 and its mixed oxides exhibit a high specific activity. Especially, In_2O_3-CeO_2 indicates the highest value among them and the addition of In_2O_3 to CeO_2 leads to an enhancement of the activity for hydrocarbon formation. The activity of In_2O_3-Y_2O_3 and In_2O_3-La_2O_3 are nearly equal to that of Y_2O_3 and La_2O_3, respectively.

The Effect of In_2O_3 Addition to CeO_2, La_2O_3, and Y_2O_3 on the Hydrocarbon Formation. The product distribution change upon the addition of In_2O_3 suggests that the role of In_2O_3 is to retard the rate of carbon-carbon bond formation and to accelate the rate of the hydrogenation of surface species. However, the facts that the addition of In_2O_3 does not increase the selectivity for methane and that it retards alkane formation seem to be inconistent with the above-mentioned suggestion. Although there is a little difference among the three oxides, it may be a common feature that the addition of In_2O_3 to 3A Group oxides results in the retardation of the carbon-carbon bond formation and alkane formation, including methane, without lowering the activity for hydrocarbon formation.

CO Hydrogenation Reaction over In_2O_3-CeO_2 and Effect of In_2O_3 Addition. Figures 1 and 2 show the time course of the activity and selectivity for hydrocarbon formation over In_2O_3-CeO_2, respectively. The constant catalytic activity and the selectivity for hydrocarbon formation were observed during 2—48 h reactions. Large amounts of CO_2 and H_2O (totally 600 $\mu mol\,g^{-1}$) were formed at the initial stage (0—1 h), but decreased remarkably after 1 h, the reaction proceeded with a good material balance during 2—48 h reactions.

Figure 3 shows the dependence of the reaction temperatures on the selectivity over In_2O_3-CeO_2 and CeO_2 catalysts. In_2O_3-CeO_2 shows the high selectivity (40—45%) for C_2 hydrocarbons, which consist of 98—99% ethene in the temperature range 573—723 K.

In the case of a single CeO_2 catalyst, the selectivity for C_2 hydrocarbons is only 4% at 573 K, and the ethene content in C_2 hydrocarbons is 71%; however, these values increase to 36 and 96%, respectively, at 723 K.

The activity of the In_2O_3-CeO_2 catalyst based on the surface area is remarkably high in comparision with that of CeO_2 at temperatures below 673 K, as shown in Fig. 4. Thus, the addition of In_2O_3 to CeO_2 leads to an

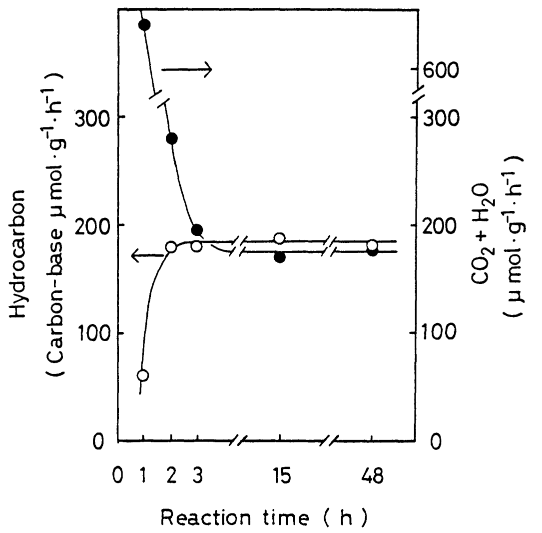

Fig. 1. Time course of the activity over In_2O_3–CeO_2 at 673 K, 67 kPa, and H_2:CO=3. This long run reaction of 48 h was carried out in the closed circulation system by exchanging the reaction gas to maintain the pressure about 60—67 kPa.
(○): Hydrocarbon, (●): CO_2+H_2O.

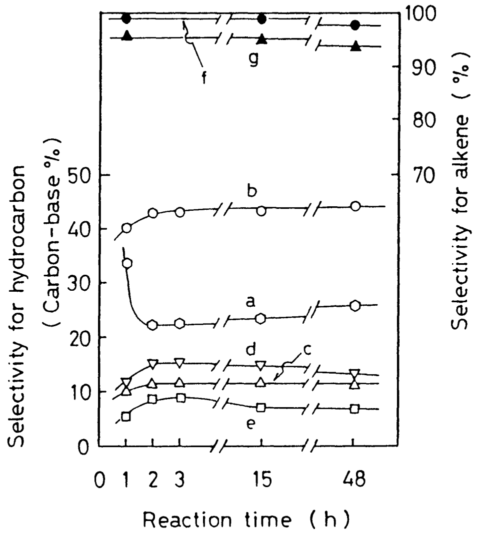

Fig. 2. Time course of the selectivity over In_2O_3–CeO_2 at 673 K, 67 kPa, and H_2:CO=3.
a(○): C_1 hydrocarbon, b(○): C_2, c(△): C_3, d(▽): C_4, e(□): C_{5+}.
f(●): C_2H_4 in C_2 hydrocarbons, g(▲): C_3H_6 in C_3 hydrocarbons.

increase in the activity for hydrocarbon formation, the selectivity for C_2 hydrocarbons, and the selectivity for alkene. These effects become clearer at lower reaction temperatures.

C_2H_4 Hydrogenation Reaction over Single and In_2O_3-Containing Mixed Oxides. The rates of C_2H_4 hydrogenation at 195 and 273 K over CeO_2, La_2O_3, and Y_2O_3 and their mixed oxides with In_2O_3 are shown in Table 2. The rates of C_2H_4 hydrogenation over CeO_2 and In_2O_3-CeO_2 are much slower than those over the other oxide catalysts. The addition of In_2O_3 results in

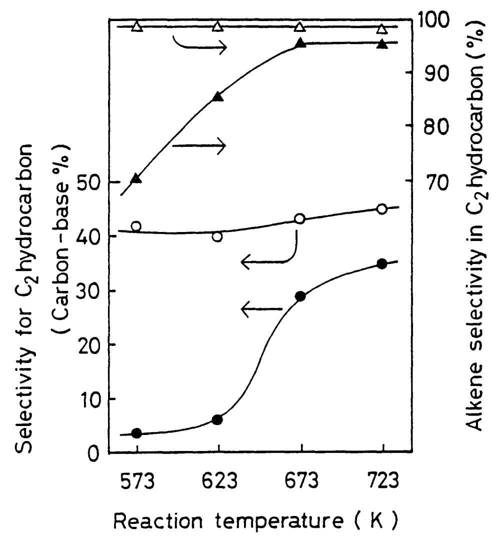

Fig. 3. The effect of reaction temperature on the selectivity.
a(○): In_2O_3–CeO_2; selectivity for C_2 hydrocarbons. b(●): CeO_2; selectivity for C_2 hydrocarbons. c(△): In_2O_3–CeO_2; selectivity for ethene in C_2 hydrocarbons. d(▲): CeO_2; selectivity for ethene in C_2 hydrocarbons.

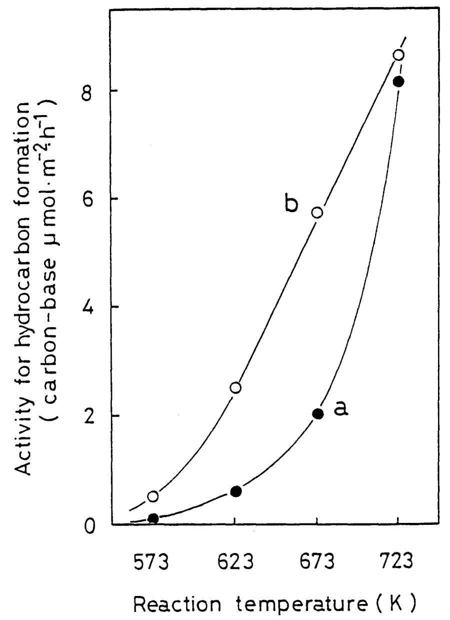

Fig. 4. The effect of reaction temperature on the activity for hydrocarbon formation.
a(●): CeO_2 and b(○): In_2O_3–CeO_2.

a decrease in the rate of C_2H_4 hydrogenation. The catalysts which have the lower rate for the C_2H_4 hydrogenation show a higher selectivity for alkene, as shown in Fig. 5. This indicates that the high selectivity for alkene formation over CeO_2 and In_2O_3-containing mixed oxides is due to the low rate of alkene hydrogenation as a side reaction of CO hydrogenation.

Among single oxides, CeO_2 shows the lowest and

La_2O_3 shows the highest activity for ethene hydrogenation, respectively, as reported by Minachev et al.[11] To the contrary, the activity for a CO hydrogenation reaction is highest over CeO_2 and lowest over La_2O_3. These facts show that there is a great difference between the hydrogenation reactions of C_2H_4 and CO. These results suggest the following possibilities: (1) a key step of hydrocarbon formation from CO and H_2 is neither the step of hydrogenation nor the activation of H_2, (2) the activation site or process of CO is different from that of C_2H_4, and (3) the hydrogen species which reacts with CO or intermediates to form hydrocarbons is different from that which reacts with ethene.

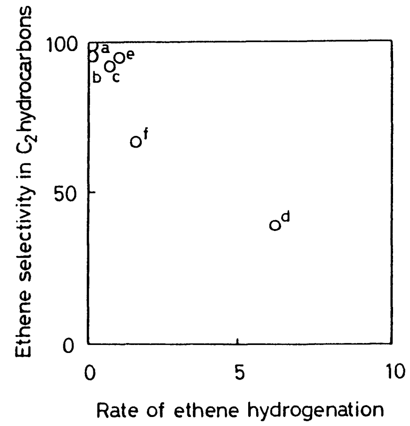

Fig. 5. Correlation between the ethene selectivity (%) in C_2 hydrocarbon on CO hydrogenation reaction at 673 K and the rate (10^3 μmol g-cat.$^{-1}$ h^{-1}) of ethene hydrogenation at 195 K.
a; In_2O_3–CeO_2, b; CeO_2, c; In_2O_3–La_2O_3, d; La_2O_3, e; In_2O_3–Y_2O_3, and f; Y_2O_3.

Table 2. Rate of Hydrogenation of C_2H_4

Catal.[a]	Rate μmol g-cat^{-1} h^{-1} 273 K	 195 K
CeO_2	20	0 (0)[b]
In_2O_3-CeO_2	3	0 (0)
La_2O_3	fast	6100 (360)
In_2O_3-La_2O_3	fast	680 (40)
Y_2O_3	fast	1500 (30)
In_2O_3-Y_2O_3	fast	940 (20)

a) Catalysts of 0.1 g (La_2O_3, Y_2O_3, and their In_2O_3-containing mixed oxides) or 0.5 g (CeO_2 and In_2O_3-CeO_2) were used on C_2H_4 hydrogenation reaction as maintaining the conversion below ca. 30%.
b) Parentheses show the activity based on specific surface area, μmol m^{-1} h^{-1}.

The addition of In_2O_3 to CeO_2 enhances CO hydrogenation while supressing C_2H_4 hydrogenation. Therefore, the role of added In_2O_3 is different in the hydrogenation of CO and alkene.

Characterization of In_2O_3-Containing Mixed Oxides. XRD and XPS results of the oxides and In_2O_3-containing mixed oxides are shown in Table 3. For In_2O_3-CeO_2, only the diffraction patterns of CeO_2 (fluorite type) were observed, although the catalyst contained 10% In_2O_3. On the other hand, a slight amount of $LaInO_3$ and $YInO_3$ in addition to La_2O_3 and Y_2O_3 were observed for In_2O_3-La_2O_3 and In_2O_3-Y_2O_3, respectively. However, no peaks due to In_2O_3 appeared for all In_2O_3-containing mixed oxides. The binding energies of In $3d_{5/2}$ for the mixed oxides after the reaction were observed between 444.4 and 444.7 eV. The values are higher than that at 443.3 eV for metallic indium. Indium in the mixed oxides still kept the higher oxidation state under the reaction conditions.

The surface composition on the In_2O_3-CeO_2 catalyst was estimated from the peak area of Ce3d and In3d and corrected by the ionization cross section[13] and escape depth[14] using formula,[15]

$$\frac{C_{In}}{C_{Ce}} = \frac{A_{In}}{A_{Ce}} \times \frac{I_{Ce}}{I_{In}} \times \frac{D_{Ce}}{D_{In}}$$

where C, A, I, and D denote the surface concentration, peak area, total ionization cross section, and escape depth, respectively.

It was found that the surface ratio of In/Ce is close to the bulk ratio, as shown in Table 3.

From these results, it can be seen that indium in CeO_2 is highly dispersed as small crystalline forms of

Table 3. Characterization of the Oxides and In_2O_3-Containing Mixed Oxides

Catal.	XRD	XPS Binding energy of In $3d_{5/2}$ (eV)	 Surface ratio (%) of In to M (Ce, La, or Y)
CeO_2	CeO_2	—	—
In_2O_3-CeO_2	CeO_2	444.4	11
La_2O_3	La_2O_3	—	—
In_2O_3-La_2O_3	La_2O_3+($LaInO_3$)	444.5	9
Y_2O_3	Y_2O_3	—	—
In_2O_3-Y_2O_3	Y_2O_3+($YInO_3$)	444.7	5
In_2O_3	In_2O_3	444.4	—
In[a]	—	443.3	—

a) Commercial metallic indium (99.99%) was spattered by Ar ion bomberdment before the measurement, and the binding energy obtained for In$3d_{5/2}$ agreed with the literature.[12]

In_2O_3 or as a substitutional solution state, and that indium in La_2O_3 and Y_2O_3 exists partialy as mixed oxide compounds of $LaInO_3$ and $YInO_3$, while keeping the oxidation state under the reaction conditions. To the contrary, single In_2O_3 is rapidly reduced to metallic indium and forms no hydrocarbons from a mixture of CO and H_2 under the above-stated reaction conditions. The valency of indium could not be determined by XPS, since the binding energies of In^+ and In^{3+} are close to each other. On the other hand, In_2O_3-CeO_2 produces large amounts of CO_2 and H_2O (total ca. 600 μmol g^{-1}) during the initial stage (0—1 h). It is known that In_2O_3 is easily reduced[16] and that CeO_2 is partially reduced to CeO_{2-x} (x=0—0.5)[17] to form Ce^{3+},[18] under the reductive conditions, such as the CO hydrogenation reaction. Single CeO_2 forms relative small amounts of CO_2 and H_2O (totally ca. 50 μmol g^{-1}) during the initial stage of the reaction at 673 K. These facts indicate that the In_2O_3 addition to CeO_2 enhances the reduction of the catalyst to form In^+ and/or Ce^{3+}. CeO_2 exhibits a high activity and selectivity for ethene formation, similar to In_2O_3-CeO_2, at a high reaction temperature of 723 K (Figs. 3 and 4). This means that the active centers for hydrocarbon formation exist on cerium ions in In_2O_3-CeO_2. Details concerning the active center for CO hydrogenation reaction over In_2O_3-CeO_2 will be published elsewhere.

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