

## Selective and Direct Formation of Ethene from CO and H<sub>2</sub> over In<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub>, -La<sub>2</sub>O<sub>3</sub>, and -CeO<sub>2</sub> Catalysts

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Ethene is selectively formed from CO and H<sub>2</sub> over In<sub>2</sub>O<sub>3</sub>-containing oxide catalysts such as In<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub>, -La<sub>2</sub>O<sub>3</sub>, and -CeO<sub>2</sub> at 673 K and 67 kPa with the highest selectivity of 43% for hydrocarbons.

Many studies on the selective synthesis of low molecular weight hydrocarbons from CO and H<sub>2</sub> have been described. The selective syntheses of ethane,<sup>1</sup> propene,<sup>2,3</sup> n-butenes,<sup>4</sup> and isobutene<sup>5</sup> have been reported. However, the direct and selective synthesis of ethene has not been successful. We report here the marked effect that addition of In<sub>2</sub>O<sub>3</sub> to several oxides, such as Y<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, and CeO<sub>2</sub>, has in enhancing the selective formation of ethene.

In<sub>2</sub>O<sub>3</sub>-containing oxide catalysts (In<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub>, -La<sub>2</sub>O<sub>3</sub>, and -CeO<sub>2</sub>) were prepared by co-precipitation from the aqueous solution of each metal nitrate with NH<sub>4</sub>OH and calcination of the hydroxides at 773 K for 3 h. The atomic ratios of In to M (M = Y, La, and Ce) were 1:10. The oxide catalysts (Y<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, and CeO<sub>2</sub>) were prepared from the aqueous solution of each metal nitrate by the same procedure. The catalysts were evacuated before the reactions at 973 K. The reactions were carried out in a closed gas-circulating reaction system at 673 K and 67 kPa (H<sub>2</sub>:CO = 3) initial pressure.

Table 1 shows the activities and selectivities for hydrocarbons formed from CO and H<sub>2</sub> over the oxides and In<sub>2</sub>O<sub>3</sub>-containing oxide catalysts. The single oxide catalysts (Y<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, and CeO<sub>2</sub>) produce mainly branched-chain C<sub>4</sub> and C<sub>5</sub> hydrocarbons.<sup>6</sup> However, the addition of In<sub>2</sub>O<sub>3</sub> to these oxides results in an increase in the selectivity for ethene and a decrease in C<sub>4</sub>, C<sub>5</sub>, and C<sub>6+</sub> hydrocarbons. In<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> exhibits the highest selectivity for ethene formation (43%) and the highest activity for hydrocarbon formation at 673 K. The In<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> catalyst was stable for more than 48 h with a good carbon mass balance. When a mixture of H<sub>2</sub> and CO, ratio H<sub>2</sub>:CO = 50, is introduced over In<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>, the selectivity of ethene formation is still high, while the formation of methane increases. In contrast, the CO-H<sub>2</sub> reaction over In<sub>2</sub>O<sub>3</sub> alone, which was reduced to metallic indium under the reaction conditions, proceeds to form a large amount of CO<sub>2</sub> instead of hydrocarbons.

From results of X-ray photoelectron spectroscopy (XPS)

**Table 1.** Activity and selectivity for the CO-H<sub>2</sub> reaction over oxide and In<sub>2</sub>O<sub>3</sub>-containing oxide catalysts.

Catalysts	B.E.T. <sup>a</sup> surface area	Activity <sup>b</sup>		Selectivity in hydrocarbons (carbon-base %)								Alkene <sup>c</sup> selectivity
		Hydrocarbon	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6+</sub>	
Y <sub>2</sub> O <sub>3</sub>	51	18 (0.35)	30	10	3	1	6	1	30	23	26	75
In <sub>2</sub> O <sub>3</sub> -Y <sub>2</sub> O <sub>3</sub>	47	18 (0.38)	15	5	19	0.2	22	0.2	34	13	7	99
La <sub>2</sub> O <sub>3</sub>	17	9 (0.53)	18	15	3	4	5	3	19	21	29	43
In <sub>2</sub> O <sub>3</sub> -La <sub>2</sub> O <sub>3</sub>	17	12 (0.71)	14	7	31	3	15	1	20	16	7	92
CeO <sub>2</sub>	21	43 (2.0)	34	25	28	1	8	1	21	8	8	96
In <sub>2</sub> O <sub>3</sub> -CeO <sub>2</sub>	28	160 (5.7)	130	24	43	0.5	9	0.5	13	7	2	99
In <sub>2</sub> O <sub>3</sub> -CeO <sub>2</sub> <sup>d</sup>	28	21 (0.75)	4	48	42	0.5	7	0.3	2	0.2	+	99
In <sub>2</sub> O <sub>3</sub> <sup>e</sup>	—	trace	200	—	—	—	—	—	—	—	—	—

<sup>a</sup> Brunauer-Emmett-Teller, m<sup>2</sup>/g. <sup>b</sup> The values are the average from the initial 2.5 to 17.5 h in carbon-base (μmol g-cat<sup>-1</sup> h<sup>-1</sup> and parentheses show activity based on specific surface area in carbon-base (μmol) m<sup>-2</sup> h<sup>-1</sup>. <sup>c</sup> C<sub>2</sub>H<sub>4</sub>/(C<sub>2</sub>H<sub>4</sub> + C<sub>2</sub>H<sub>6</sub>) × 100. <sup>d</sup> 50 kPa and H<sub>2</sub>/CO = 50. <sup>e</sup> In<sub>2</sub>O<sub>3</sub> was reduced to metallic indium under the reaction conditions.

measurements of In<sub>2</sub>O<sub>3</sub>-Y<sub>2</sub>O<sub>3</sub>, -La<sub>2</sub>O<sub>3</sub>, and -CeO<sub>2</sub> after the reaction, the binding energies of In 3d<sub>5/2</sub> corrected by reference to Au 4f<sub>7/2</sub> (83.8 eV) were observed in the range 444.4–444.5 eV which are noticeably higher than the value of 443.3 eV for metallic indium.<sup>†</sup> These results indicate that In<sub>2</sub>O<sub>3</sub> supported on the oxides is not reduced to the metallic state under the reaction conditions. It was also found that the surface atomic ratios of In to M (M = Y, La, and Ce) by XPS were close to values for the bulk composition. The X-ray diffraction (XRD) patterns of In<sub>2</sub>O<sub>3</sub>-containing catalysts showed only the support oxides: Y<sub>2</sub>O<sub>3</sub> (cubic), La<sub>2</sub>O<sub>3</sub> (hexagonal), and CeO<sub>2</sub> (cubic). These results suggest that indium oxide is highly dispersed and this state probably has a

direct bearing on the highly selective formation of ethene. Similar results were obtained over Ga<sub>2</sub>O<sub>3</sub>-containing oxide catalysts.

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<sup>†</sup> Commercial metallic indium (99.99%, Mitsuwa Co.) was spattered by Ar ion before the measurement, and the binding energy obtained for In 3d<sub>5/2</sub> was in good agreement with previous results.<sup>7</sup>