Selective and Direct Formation of Ethene from CO and H_2 over In_2O_3–Y_2O_3, –La_2O_3, and –CeO_2 Catalysts

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Ethene is selectively formed from CO and H_2 over In_2O_3-containing oxide catalysts such as In_2O_3–Y_2O_3, –La_2O_3, and –CeO_2 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_2 have been described. The selective syntheses of ethane,[1] propene,[2,3] n-butenes,[4] and isobutene[5] 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_2O_3 to several oxides, such as Y_2O_3, La_2O_3, and CeO_2, has in enhancing the selective formation of ethene.

In_2O_3-containing oxide catalysts (In_2O_3–Y_2O_3, –La_2O_3, and –CeO_2) were prepared by co-precipitation from the aqeuous solution of each metal nitrate with NH_4OH 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_2O_3, La_2O_3, and CeO_2) 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_2 : CO = 3) initial pressure.

Table 1 shows the activities and selectivities for hydrocarbons formed from CO and H_2 over the oxides and In_2O_3-containing oxide catalysts. The single oxide catalysts (Y_2O_3, La_2O_3, and CeO_2) produce mainly branched-chain C_4 and C_5 hydrocarbons.[6] However, the addition of In_2O_3 to these oxides results in an increase in the selectivity for ethene and a decrease in C_4, C_5, and C_{6+} hydrocarbons. In_2O_3–CeO_2 exhibits the highest selectivity for ethene formation (43%) and the highest activity for hydrocarbon formation at 673 K. The In_2O_3–CeO_2 catalyst was stable for more than 48 h with a good carbon mass balance. When a mixture of H_2 and CO, ratio H_2 : CO = 50, is introduced over In_2O_3–CeO_2, the selectivity of ethene formation is still high, while the formation of methane increases. In contrast, the CO–H_2 reaction over In_2O_3 alone, which was reduced to metallic indium under the reaction conditions, proceeds to form a large amount of CO_2 instead of hydrocarbons.

From results of *X*-ray photoelectron spectroscopy (XPS)

Table 1. Activity and selectivity for the CO–H_2 reaction over oxide and In_2O_3-containing oxide catalysts.

Catalysts	B.E.T.[a] surface area	Activity[b]		Selectivity in hydrocarbons (carbon-base %)								Alkene[c] selectivity
		Hydrocarbon	CO_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4	C_5	C_{6+}	
Y_2O_3	51	18 (0.35)	30	10	3	1	6	1	30	23	26	75
In_2O_3–Y_2O_3	47	18 (0.38)	15	5	19	0.2	22	0.2	34	13	7	99
La_2O_3	17	9 (0.53)	18	15	3	4	5	3	19	21	29	43
In_2O_3–La_2O_3	17	12 (0.71)	14	7	31	3	15	1	20	16	7	92
CeO_2	21	43 (2.0)	34	25	28	1	8	1	21	8	8	96
In_2O_3–CeO_2	28	160 (5.7)	130	24	43	0.5	9	0.5	13	7	2	99
In_2O_3–CeO_2[d]	28	21 (0.75)	4	48	42	0.5	7	0.3	2	0.2	+	99
In_2O_3[e]	—	trace	200	—	—	—	—	—	—	—	—	—

[a] Brunauer–Emmett–Teller, m^2/g. [b] The values are the average from the initial 2.5 to 17.5 h in carbon-base (μmol g-cat^{-1} h^{-1} and parentheses show activity based on specific surface area in carbon-base (μmol) m^{-2} h^{-1}. [c] $C_2H_4/(C_2H_4 + C_2H_6) \times 100$. [d] 50 kPa and H_2/CO = 50. [e] In_2O_3 was reduced to metallic indium under the reaction conditions.

measurements of In_2O_3–Y_2O_3, –La_2O_3, and –CeO_2 after the reaction, the binding energies of In $3d_{5/2}$ corrected by reference to Au $4f_{7/2}$ (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.† These results indicate that In_2O_3 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_2O_3-containing catalysts showed only the support oxides: Y_2O_3 (cubic), La_2O_3 (hexagonal), and CeO_2 (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_2O_3-containing oxide catalysts.

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† Commercial metallic indium (99.99%, Mitsuwa Co.) was spattered by Ar ion before the measurement, and the binding energy obtained for In $3d_{5/2}$ was in good agreement with previous results.[7]