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The Promotion Effect of Rare Earth Oxides on the Hydrogenation of Carbon Monoxide over Rh-Al_2O_3 Catalyst

Yusaku Takita,* Tamiyasu Yoko-o, Naoyoshi Egashira, and Fumiaki Hori
Department of Environmental Chemistry and Engineering, Faculty of Engineering, Oita University, Dannohara, Oita 870-11

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Synopsis. The addition of Dy_2O_3, Nd_2O_3, Yb_2O_3, La_2O_3, or Gd_2O_3 to the Rh–Al_2O_3 catalyst enhanced the activity of the hydrogenation of CO to methane. There was the linear relationship between the carbon skeleton propagation of the hydrocarbons formed and the basicity of the rare earth oxides.

Catalytic behaviors of rare earth oxides have been explored for many reactions and a wide variety of catalytic properties has been known.[1] Rare earth oxides are hardly reducible, La_2O_3 and Ce_2O_3, for example, remain three valent oxides after treatment in hydrogen at 673 K,[2] and Lu_2O_3 generates two valent ions even at 823—973 K by treatment in hydrogen.[3] These character is suited for the catalyst support which is applied under reducing atmosphere, there is, however, only a few paper investigated rare earth oxides as a catalyst support. It has been known that the incorporation of a small amount of La_2O_3 or Ce_2O_3 to supported Ni, Ni-Rh, and Ni-Ru catalysts brought about considerable increase of activity in the methanation of carbon oxides[4]. It was reported that the Rh carbonyl clusters dispersed on La_2O_3, Nd_2O_3, and CeO_2 were the effective catalysts for ethanol and C_2 oxygenated products formation as well as the catalysts dispersed on TiO_2, ZrO_2, and ThO_2.[5] However the effect of rare earth oxides other than these three oxides on the catalytic property of noble metals has remained obscure. The present paper dealt with the effect of rare earth oxides on the catalytic property of Rh–Al_2O_3 catalyst in the hydrogenation of carbon monoxide.

The results are given in Table 1 together with apparent activation energies. The products formed over these catalysts were similar to those over Rh–Al_2O_3 catalyst. The CO conversion at the temperatures below 573 K slightly decreased by the addition of Dy, Nd, Yb, or La, but it increased at above 613 K. The addition of Gd oxide and Ho oxide gave positive effect on the conversion only at 633 K. The addition of Pr oxide gave no significant effect on the CO conversion, while Tm or Eu oxide reduced the conversion over the temperature range examined.

The selectivity of CO_2 was raised by the addition of any rare earth oxide, especially high over the Nd and La containing catalysts.

Since water vapor should be formed during the reaction by the amount counterbalanced with the formation of hydrocarbons, there must be two possible reactions for CO_2 formation, *viz.*, water gas shift reaction and disproportionation of CO. The reaction were achieved in a good carbon balance ($100\pm3\%$) at

Table 1. Product distributions on the hydrogenation of carbon monoxide

Promoter[a]	Temp K	Conversion %	Selectivity/% CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_4H_8	CO_2	E_a
None	593	42.7	87.8	7.40	1.80	0.44	0.12	2.27	66.1
	613	60.7	89.9	5.90	0.57	0.06	—	3.60	
	633	80.7	89.6	2.76	0.11	—	—	7.55	
Dy_2O_3	593	43.8	84.9	5.90	1.63	0.30	0.12	6.90	92.0
	613	82.9	83.5	3.90	0.19	—	—	12.4	
	633	100.0	88.9	—	—	—	—	11.1	
Nd_2O_3	593	44.4	71.0	4.54	1.11	0.16	—	23.0	102.9
	613	86.0	72.0	1.90	0.20	—	—	25.9	
	633	100.0	87.3	—	—	—	—	12.7	
Yb_2O_3	593	47.9	83.7	5.28	1.32	0.23	0.07	9.45	92.5
	613	83.1	82.8	3.26	0.17	—	—	13.1	
	633	100.0	87.4	—	—	—	—	12.5	
La_2O_3	593	42.3	80.8	6.84	1.75	0.31	0.10	10.2	84.9
	613	74.8	78.7	4.55	0.39	0.03	—	16.3	
	633	100.0	84.5	—	—	—	—	15.5	
Gd_2O_3	613	59.8	85.0	4.13	—	0.03	0.03	10.7	90.0
	633	99.1	95.4	—	—	—	—	4.51	
Ho_2O_3	633	82.4	89.2	0.05	0.03	—	—	10.7	93.7
Pr_6O_{11}	633	83.0	87.3	—	0.02	—	—	12.6	109.2
Tm_2O_3	633	84.0	88.4	2.63	0.01	0.01	—	8.98	103.8
Eu_2O_3	633	59.4	83.8	2.78	0.08	—	0.01	13.3	96.7

Catalyst: Rh(1 wt%)–rare earth oxide(5%)–Al_2O_3, 1.50 g; reactant gas composition: CO 10 mol%, H_2 30 mol%, N_2 60 mol%; SV: 1970+30 cm^3 STP g-cat^{-1} h^{-1}. a) Starting material, E_a: apparent activation energy of methanation (kJ mol^{-1}).

least within initial 12 h even on the catalyst containing Nd oxide which showed the highest selectivity of CO_2. A small amount of carbon deposition was observed on the catalysts after the reaction for 3 d or more, so that the latter reaction is believed to be dominant under these reaction conditions.

The apparent activation energy was calculated to 66 kJ mol^{-1} for Rh–Al_2O_3 and those for the catalysts containing rare earth oxides were distributed in 85—110 kJ mol^{-1}. Although these values are considerably small comparing with those in references,[6] a distinction of activation energy between Rh supported on an acidic support such as Al_2O_3 and the basic catalysts containing rare earth oxides strongly suggests the direct interaction of Rh with rare earth oxide on Al_2O_3. The following facts would support this speculation. Specific surface area of the catalysts including Dy and Yb oxides, 197 and 247 m^2 g^{-1} respectively, were not smaller than 280 m^2 g^{-1} of the Rh–Al_2O_3 catalyst. Assuming that La_2O_3 makes a monolayer on Al_2O_3 as oriented its (0001) plane to the Al_2O_3 surface, the coverage of La_2O_3 is calculated to 27—40% of the surface.

The formation of CO_2 reduces the yield of hydrocarbons, the oder of the effect of the oxides as evaluated from the yield of hydrocarbons is

Dy, Nd, Yb>La>Gd>Ho, Pr, none>Tm>Eu.

This order is essencially the same as reported for hydrogenation of ethene.[7]

The selectivity of methane was relatively less sensitive to the reaction temperature over the catalysts, and it remained about 70—85% even at 573 K. As for the hydrocarbons with carbon-carbon bond, the lowering of temperature from 633 to 573 K resulted in a passable increase of selectivity. $\sum n_i S_i$ was plotted in Fig. 1 against logarithmic solubility product constant (log K) of hydroxides of tervalent rare earth metals[8] which is regarded as a scale of the basicity of the oxides. Where n_i represents the number of carbon-carbon bond of hydrocarbon i among hydrocarbons produced, so that $\sum n_i S_i$ is an index of chain growth over catalyst.[9] The figure shows an approximately linear relationship. Due to explaine the wide diversity of the products in the hydrogenation of CO, many reaction mechanisms have been proposed. These are divided broadly into three categories.[10] In the first category it is assumed that the CO dissiciates completely on adsorption and carbon chain is formed by the linking up of CH_2 or CHR. In the second category it is presumed that the CO chemisorbs associatively and chain growth occurs by H_2O elimination between neighbouring species such as $\mathrm{R{-}\underset{\underset{M}{\|}}{C}{-}OH}$ and $\mathrm{R{-}\underset{\underset{M}{\|}}{CH}{-}OH}$ where M represents a catalyst surface site and R represents H or alkyl. The associative CO chemisorption and CO insertion into M–H or M–CH_2R bond are assumed in the third category. Seeing the steps of the carbon chain propagation, carben type intermediates[11] take part in the first two categories, while the surface alkyl participates in the third one. It can not be decided which mechanism is dominant on the catalyst used in this work. However, it would be expected the stronger the basicity of the rare earth oxides added, the weaker the bond between surface carben or alkyl and Rh metal. Therefore the addition of strongly basic rare earth oxides to the catalyst would bring about the encouragement of either aggregation of the carben type intermediates or CO insertion into Rh–alkyl bond.

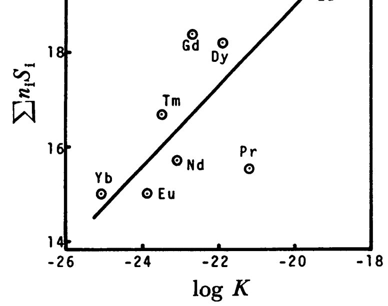

Fig. 1. The relation between carbon-carbon bond formation and the basicity of rare earth oxides.
n_i: The number of carbon-carbon bond in hydrocarbon i, S_i: selectivity of hydrocarbon i among the hydrocarbons produced in the reaction at 573 K, K: solubility product constants in aqueous solution at 291—298 K.

Experimental

Rh–Al_2O_3 catalyst was prepared by impregnation method. Al_2O_3 (Sunbead AN from Catalysts and Chemicals Ind. Co., 24—32 mesh) was poured into the solution of $RhCl_3 \cdot 3H_2O$ and the solution was then evaporated to dryness at about 363 K. The catalyst was calcined at 573 K for 4 h in air and it was then reduced in hydrogen stream at 723 K for 4 h.

Rh–rare earth oxide–Al_2O_3 catalysts were prepared as following procedure. Rare earth nitrate was supported on Al_2O_3 using its acidic solution. After the calcination at 823 K for 5 h, the catalyst was subjected to impregnation of Rh in the same manner as above.

Reactions were carried out using ordinary flow type reactor under atmospheric pressure. Reaction products were analyzed by gas chromatograph. Surface areas of the catalysts were determined by nitrogen adsorption at 77 K using BET method.

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