CHEMISTRY LETTERS, pp. 251-252, 1978. Published by the Chemical Society of Japan

METHANATION OF CARBON DIOXIDE AND CARBON MONOXIDE ON SUPPORTED Ni-La_2O_3-Ru CATALYST[1)]

Tomoyuki INUI and Masaki FUNABIKI
Department of Hydrocarbon Chemistry, Faculty of Engineering,
Kyoto University, Sakyo-ku, Kyoto 606

A novel type composite catalyst in which small amounts of La_2O_3 and Ru are incorporated with Ni substrate supported on a granulated silica having bimodal pore structure, was found to be a very efficient hydrogenation catalyst for selective methane formation from carbon oxides. Contrary to the case of Ni, the rate of CO_2 methanation on the presented catalyst was greater than that of CO methanation.

Efficient methane synthesis by hydrogenation of carbon oxides has become recognized as having special importance for a clean energy fuel from abundant coal resources instead of petroleum naphtha which will be limited supply in near future. Although a large number of catalytic studies[2)] has been done about the subject during the past 75 years, there is much room for further improvement in the catalytic system. In particular, CO_2 methanation has not been investigated extensively.

The present paper concerns with a novel type catalyst unique to the pore structure and the combination of catalyst components exhibiting highly effective hydrogenation catalysis for methane formation from carbon oxides, especially from carbon dioxide.

Spherically granulated silica support[3)] of 3.0 mm in diameter, which had been calcined at 800°C and having both macro pore(600 nm in diam.) and micro pore(5 nm in diam.) was used. Its BET-surface area was 360 m^2/g. The catalyst was prepared by following procedures. Concentrated aqueous solution of nitrate of catalyst elements was sprayed[4)] on the support. After the treatment with gaseous ammonia, it was decomposed by heating in atmosphere. The catalyst was reduced in hydrogen stream, followed by heat treatment at 400°C. Ni was supported by several wt% as substrate. Contents of La and Ru atoms were set at 0.2 and 0.1 of Ni, respectively.

Catalyst-performance test was carried out by a continuous flow method at atmospheric pressure. The test reactor was a Pyrex glass U-tube of 3.8 mm diameter filled with catalyst in one side. The catalyst charge of 16 granules filled the 4.8 cm length of reactor tube. Feed flow rate was set at 10000 hourly space velocity. Effluent gas was directly analyzed by a TCD-FID type gas chromatograph with columns of Porapack Q, X-28 or MS-5A.

Performance of each catalyst is shown in Table 1 compared with the data of references. On the Ni catalyst, methanation rate of CO was greater than that of CO_2, as well as the results of Luengo et al.[9)], however, the reverse order was obtained by the catalyst containing La_2O_3 and by the Ru catalyst.

In CO methanation, although selectivity of methane was rather lower due to formation of by-products, $C_2 \sim C_6$ hydrocarbons and carbon dioxide, it attained nearly 100% by the catalyst containing La_2O_3 and by the Ru catalyst. On the other hand, in CO_2 methanation, methane was formed almost selectively, regardless of a variety of catalyst and reaction conditions. Only trace of ethane and CO were observed.

The ratio of catalytic activities in CO_2 methanation at 227°C are Ni : Ru(0.7%) : Ni-Ru :

Table 1 Catalyst performances for methanation of CO and CO_2

Ref.	Catalyst	Pco (atm)	Pco_2 (atm)	P_{H_2}/Pco or P_{H_2}/Pco_2	227°C			250°C			EM
					NM $(\frac{10^3}{sec})$	STYM $(\frac{mol}{l \cdot hr})$	SelM (%)	NM $(\frac{10^3}{sec})$	STYM $(\frac{mol}{l \cdot hr})$	SelM (%)	$(\frac{kcal}{mol})$
1)	5%Ni/SiO_2	0.06		3.0	10.7	0.83	87.2	28	2.23	95.5	22.3
			0.06	3.0	7.5	0.56	99.9	17.8	1.32	99.9	19.6
1)	0.7%Ru/SiO_2		0.06	3.0	9.0	0.77	100	19.9	1.70	100	19.6
1)	5.5%Ni-0.8%Ru/SiO_2		0.06	3.0		1.40	99.8		3.17	100	19.6
1)	(4.6%Ni-2.6%La_2O_3/SiO_2)	0.06		3.0	38	5.13	60.0	64	11.5	100	31.4
			0.06	3.0	32	4.57	99.3	57	8.13	99.7	19.6
1)	(4.3%Ni-2.5%La_2O_3-0.7%Ru/SiO_2)	0.06		3.0	23	2.24	44.2	110	11.0	64.5[a]	36.1
			0.06	3.0	96	9.55	98.6	127	12.6	99.6	19.6
1)	3.3%Ru/SiO_2	0.06		3.0	23	0.79	67.3	84	3.02	95.4	29.6
			0.06	3.0	199	6.46	100	390	12.6	100	19.6
5)	5%Ni/Al_2O_3	x[b]		3.2	3.9			11.2		82.4[c]	25.0
6)	5%Ni/ZrO_2	0.19		3.0	6.2			23.5		37	28.0
5)	5%Ru/Al_2O_3	x[b]		3.0	21		36[d]	60			24.2
6)	1.5%Ru/Al_2O_3	0.19		3.0	1.7			6		54	24
7)	0.5%Ru/Al_2O_3	0.25		3.0		0.10[e]	60[e]				
			4.28[f]	4.0		1.84[f]	84.6[f]				
8)	0.5%Ru/Al_2O_3		0.344	4.0		0.016					

NM : Turnover number for methane formation expressed as molecules of CH_4 formed per second per metal site[5].

STYM : Space time yield expressed as moles of CH_4 formed per hour per catalyst volume.

SelM : Selectivity of CH_4 formed expressed as percentage of converted carbon oxide.

EM : Apparent activation energy in the rate of methane formation.

a) 100% at above 265°C. b) Unknown. c) 242°C. d) 210°C. e) 222°C. f) Total pressure : 21.4 atm., 224°C.

Ni-La_2O_3 : Ni-La_2O_3-Ru = 1.00 : 1.37 : 2.50 : 8.2 : 17.1. The activity of three-component catalyst is far beyond the sum of those of single component catalysts. Its activity is comparable to that of a higher concentration(3.3%) Ru catalyst which is known as the most active catalyst for the Sabatier reaction[5][8]. Even single component catalysts of this work as Ni and Ru, their activities and selectivities are higher than those of references. It is probably due to the preferable effect of pore structure of the support on the catalyst performance.

The authors are grateful to Professor Kenichi Fukui of this university for his helpful discussions and support.

References

1) Hydrogenation on Supported Polygenous Composite Catalyst I.
2) G. A. Mills and F. W. Steffgen, Catal. Rev., 8, 159(1973).
3) T. Inui, M. Murasawa, and H. Shingu, Shokubai, 17, 109P(1975).
4) T. Inui, J. Kohashi, and H. Shingu, Nippon Kagaku Kaishi, 1975, 1186.
5) M. A. Vannice, J. Catal., 37, 449(1975).
6) R. A. Dalla Betta, A. G. Peken, and M. Shelef, J. Catal., 35, 54(1974).
7) F. S. Karn, J. F. Shultz, and R. B. Anderson, I. & E. C. Prod. Res. Dev., 4, 265(1965).
8) P. J. Lunde and F. L. Kester, J. Catal., 30, 423(1973).
9) C. A. Luengo, A. L. Cabrera, H. B. Mackey, and M. B. Maple, J. Catal., 47, 1(1977).

(Received December 5, 1977)