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SYNERGISTIC EFFECT OF Ni-La_2O_3-Ru CATALYST ON THE DIRECT METHANATION OF CARBON[1)]

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The three-component catalyst, in which small amounts of La_2O_3 and Ru are combined with Ni-substrate supported on an active carbon by several percent, exerted a marked synergistic effect on the catalytic methanation of the active carbon. The effect was considered from the viewpoint of a hydrogen-spillover mechanism.

The subject of direct catalytic synthesis of gaseous hydrocarbons from solid carbon and hydrogen has become recognized as having special importance for the production of a clean energy source. Many ambiguous factors still remains in the precursory study of Tomita and Tamai[2)] using the single-component catalysts.

In our previous paper,[3,4)] we reported that the entitled catalyst on a silica support has the highly effective hydrogenation catalysis for methane formation from CO_2 and CO. The present communication concerns with the synergistic effect also found by the use of the entitled composite catalyst for the hydrogenation of an active carbon.

The active carbon A-3 (Shimadzu Seisakusho Co.) was used for the reaction material and, concurrently, as the catalyst support. It had a BET-surface area of 1230 $m^2\ g^{-1}$, a porosity of 0.46, a bulk density of 0.32 g cm^{-3}, and a size range of 30 to 60 mesh. The active carbon was immersed in an impregnating aqueous solution of nickel nitrate, lanthanum nitrate, or ruthenium chloride (G. R. Nakarai Chemicals Co.). It was dried thoroughly with well stirring on a boiling water bath. Then it was exposed in a saturated vapor of 10% aqueous ammoniac solution at 20°C for 2 min,[4)] followed by heating in a nitrogen stream containing more than 10% hydrogen. The mixed salt solution was used for the preparation of bicomponent catalyst. However, for the three-component catalyst, ruthenium metal was first dispersed on the support, then the other two components were additionally supported at the same time. La_2O_3 and Ru were incorporated with Ni in atomic ratios of 0.2 and 0.15 (for one Ni), respectively.

A 20 mg portion of the sample was placed in a sample pan, held in a gas-flow tube of the micro-TG, Rigaku Denki 8002-H2. 10% H_2 diluted with N_2 or pure hydrogen was flowed with a flow rate of 100 $cm^3\ min^{-1}$. The temperature was elevated at a constant rate of 10°C min^{-1} from room temperature to 800°C. The effluent gas was analysed by gas chromatographs with columns of Porapack Q, X-28, and MS-5A.

The temperature dependence of the methanation rate (r) on each catalyst of the Ni-La_2O_3-Ru system is presented in Fig. 1. After the decomposition and subsequent reduction of the catalyst-metal salt, methane formed exclusively at above ca. 300°C for each sample without shrinkage of its bulk volume even to 42% in carbon conversion.

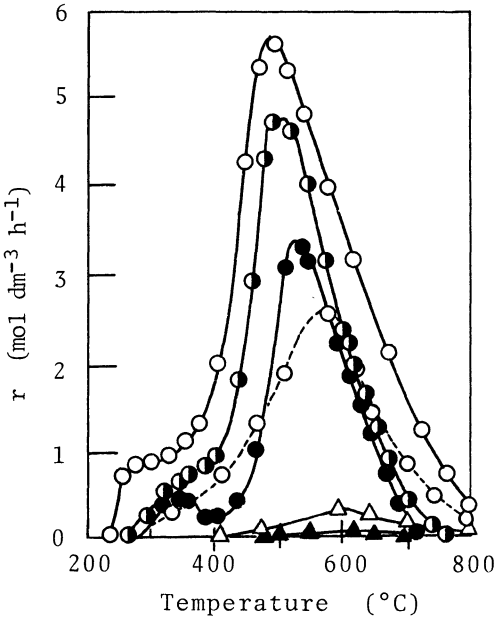

Fig. 1 Comparison of the methanation activity among various catalysts of Ni-La_2O_3-Ru system
○:4.6%Ni-2.5%La_2O_3-1.2%Ru,
◑:4.6%Ni-2.5%La_2O_3, ●:5.0%Ni,
△:1.2%Ru, ▲:2.8%La_2O_3.
Dotted line: Impregnated with the mixed salt solution of the three components.

Table 1 Performance of the various catalysts of the Ni-La_2O_3-Ru system

Catalyst	P_{H_2} (atm)	r_m (mol dm^{-3}h^{-1})	θ_m (°C)	M (mmol g^{-1})	Conv. (%)
2.8%La_2O_3	0.10	0.09	610	0.07	0.08
1.2%Ru	0.10	0.41	600	0.35	0.42
5.0%Ni	0.10	3.36	530	2.05	2.46
4.6%Ni-2.8%La_2O_3	0.10	4.85	505	3.39	4.07
4.6%Ni-2.5%La_2O_3-1.2%Ru	0.10	5.73	470	5.33	6.40
4.6%Ni-2.5%La_2O_3-1.2%Ru	1.00	51.8	576	35.2	42.3

Accordingly, the r is expressed on the basis of the initial sample-volume. The temperature (θ_m) of the maximum methanation rate (r_m), the total amount of methane formed per initial weight of the active carbon (M), and the conversion of the active carbon consumed below 800°C are listed in Table 1. As shown in Fig. 1 and Table 1, the activity of the Ni catalyst was markedly enhanced by the combination with La_2O_3. Moreover, the additional enhancement of the activity for this two-component catalyst was observed by the incorporation of a small amount of Ru. Both the r_m and the M sensitively depended on hydrogen pressure as compared in Table 1. As can be seen in Fig. 1, the effect of Ru was not exerted when the Ru was mixed with the other two components.

The synergistic effect for the methanation of the carbon by the Ni-La_2O_3-Ru catalyst may be interpreated as the following two-step catalytic mechanism on the gas-solid reaction. Combination of La_2O_3 with the Ni catalyst increases the hydrogen-adsorption capacity of the Ni.[4] The dispersed particle of Ru, which exists closely but separately from the Ni-La_2O_3 part, plays the role of the porthole of the hydrogen-spillover[5,6] consisting of the Ni-La_2O_3 part as the hydrogen acceptor. Further, this catalyst part in close contact with the carbon acts as the porthole of the hydrogen-spillover for the carbon,[2] which itself has rather minor hydrogen-adsorption capacity at the reaction temperature, achieving a smooth taking in of hydrogen from the ambient gas phase into the reaction phase of the solid carbon.

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