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Pronounced Improvement of Methanation Activity by Modification of the Pore Structure of the Catalyst Support

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Summary Spherical catalyst supports having a unimodal meso and macro pore structure were remarkably improved as supports for CO_2- and CO-methanation catalysts by, respectively, high temperature calcination and coating of the macro-pore wall with very fine silica particles.

Efforts to synthesise methane efficiently from carbon oxides and hydrogen have been concentrated recently to provide for limited petroleum naptha supplies. Although there have been many investigations[1–3] to improve the catalysts's performance, little attention has been paid to the effect of the pore structure of the support upon catalytic performance. We have previously reported[4] the very high catalytic performance of composite catalysts such as Ni–La_2O_3–Ru for the methanation of CO_2 and CO. High catalytic activity was especially noticeable when the three-component catalyst was supported on spherical supports having bimodal meso (5 nm)–macro (600 nm) pore structures, with a unimodal meso- or macro-pore supported catalyst showing little activity. The improved catalytic activity on the bimodal meso–macro pore structures was attributed to both uniform dispersion of the catalyst constituents on the macro-pore surface and a high effective diffusivity for reactants.[4]

We present here two methods to improve both the unimodal meso- and macro-pore catalyst supports, by altering their structures to approach the bimodal pore structure. The properties of three typical types of supports are summarized in the Table. All of them were preformed into a 3·0 mm diameter sphere. The bimodal meso–macro silica-support (**1**) was from the same batch as used

Table. Properties of the supports used and their effect upon the catalytic activities of methanation catalysts

Support	Pore structure	Composition	Porosity/%	Mean pore diameter[b]/ nm	Surface area/ $m^2 g^{-1}$	D_e[d]/ $cm^2 s^{-1}$	Ni content/ g dm^{-3}	Ni diameter[e]/ nm	Methanation activity CO_2 yield[f]/mol $dm^{-3} h^{-1}$	Methanation activity CO yield[f]/mol $dm^{-3} h^{-1}$
(**1**)	Bimodal meso–macro	Silica	66	600, 5	270	0·071	33	5·3	13·8	5·50
(**2**)	Unimodal meso	Alumina[a]	55	— 6	210	0·005	37		0·03	0·025
	Modified by 1100 °C calcination		69	38, 18	45	0·025	35		9·33	5·96
(**3**)	Unimodal macro	Silica + alumina	32	760 —	1·0	0·080	41	150	1·55	0·18
	Modified by fine silica-particle coating		30	750, 6[c]	4·4	0·069	39	14	6·31	0·83

[a] Manufactured by Mizusawa Kagaku Co. Ltd., Neobead-C5. [b] Measured by Aminco 60 000 p.s.i. mercury porosimeter. [c] Assumed value. [d] Measured by the diaphragm method (see ref. 4). [e] Determined by the CO adsorption method, (see ref. 4). [f] Yield of methane (see ref. 4) at 250 °C.

previously.[4] The unimodal meso- and macro-pore supports, (**2**) and (**3**), respectively were chosen as their pore diameters were similar to those of (**1**).

The unimodal meso-pore support (**3**), calcined at 900—1150 °C for 30 min in order to convert it partially into a macro-pore support. As the calcination temperature increased, the B.E.T.-surface area decreased, the bulk volume decreased slightly, and the porosity and effective diffusivity, D_e, increased. As shown in the Table, when support (**2**) was calcined at 1100 °C, the B.E.T.-surface area and D_e varied 1/5 and 5 times, respectively, and the meso-pore diameter (6 nm) increased to 18 and 38 nm the pore volumes of which were approximately equal. Morphological observation by means of a scanning electron microscope showed that the larger pore which was generated by calcination corresponds to a channel between particles of the support in which the original smaller pore remains. Comparison of the effect of the pore structure on the performance of the methanation catalyst was then conducted as follows. An Ni–La_2O_3 catalyst (Ni/La atomic ratio = 5) was used in an amount corresponding to *ca.* 1 vol% of the pore volume of supports (**1**)—(**3**), as described previously.[4] A gas mixture containing 6% CO_2 or CO, 18% H_2, and 76% N_2, was passed over the catalyst at 250 °C at a rate of 90 000 $dm^3\,h^{-1}\,dm^{-3}$. The maximum yield of methane was obtained when support (**2**), calcined at 1100 °C, was used when the CO_2- and CO-methanation activities, relative to the non-calcined support, improved 310 and 240 times, respectively (see Table). In order to increase the surface area of the unimodal macro-pore support (**3**), very fine silica particles (6—7 nm) (colloidal silica, Rudox SM, Du Pont) were used to impregnate an amount of silica occupying several vol % of the pore volume. When the support was dried, the porosity and D_e were found to have decreased, while the B.E.T.-surface area had increased 4·4 times. Electron microscopic observation showed that the colloidal silica was well distributed on the surface of the macro-pore support as a thin layer, in which perhaps some meso-pores, made by the inter-particle space, could be contained. The meso-pore diameter was thought to be of the same order as that of the coated silica particles. When modified support (**3**) was used the CO_2- and CO-methanation activities increased as the B.E.T.-surface area increased.

These results clearly demonstrate the significance of the pore structure of the support and provide practical and effective methods to improve the catalytic performance for a variety of porous supports.

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