Catalytic methanol decomposition to carbon monoxide and hydrogen over Ni/SiO$_2$ of high nickel content

Yasuyuki Matsumura [a,*], Naoki Tode [b], Tetsuo Yazawa [a], Masatake Haruta [a]

[a] Osaka National Research Institute, AIST, Midorigaoka, Ikeda, Osaka 563, Japan
[b] Osaka Institute of Technology, Asahi-ku, Osaka 535, Japan

Abstract

The methanol decomposition to carbon monoxide and hydrogen is catalyzed at 250°C over nickel–silica composites prepared by the sol–gel method while the activity is increased with increase in the content of nickel up to 40 wt%. The activity of nickel supported on silica prepared by the conventional impregnation technique is also increased with the nickel content but almost reaches a plateau at the nickel content of 10 wt%. The maximum activity found with the former is significantly higher than that with the latter.

Keywords: Carbon monoxide; Decomposition; Hydrogen; Methanol; Nickel; Silica; Supported catalysts

1. Introduction

Methanol is expected to become a new energy resource and the methanol decomposition to hydrogen and carbon monoxide is applicable to a methanol fueling system for a vehicle to increase the fuel efficiency and reduce by-production of formaldehyde [1]. Since the reaction is endothermic, it will be also available for chemical storage of heat while significant improvement of catalysts for the methanol decomposition is desired.

Catalysts containing nickel have been reported to be active to the reaction [2–5]. The activity of supported nickel catalyst should depend on the content of nickel because a reaction over a supported metal catalyst relates essentially to the surface area of metal particles on a support. However, other physical and chemical properties of the particles cannot be ignored, and the activity does not always relate to the amount of the metal [6–9]. Hence, the relationship between the activity and the metal content is fundamental information for development of the effective catalytic system while it is often affected by the preparation method of catalysts.

In this work Ni/SiO$_2$ catalysts with different nickel contents were prepared by the impregnation or the sol–gel method. Somewhat surprisingly the samples synthesized by the latter method have exhibited high catalytic activity to the methanol decomposition when the nickel contents are high, although it is supposed that the major part of nickel atoms are incorporated in the bulk of the solids.

* Corresponding author.

Y. Matsumura et al. / Journal of Molecular Catalysis A: Chemical 99 (1995) 183–185

2. Experimental

Mixtures of nickel and silica gel were prepared by the hydrolysis and polymerization of tetraethyl orthosilicate (Kanto Chemical Corp.) whose solution consisted in nickel nitrate (Kanto Chemical Corp.), water, ethanol and nitric acid. After drying in air at 120°C they were heated in air for 5 h at 400°C for removal of NO_3^- anions and residual organic compounds. The samples contained 5–50 wt% of nickel if perfectly reduced in the solids (designated as 5S-Ni, 10S-Ni etc., where the numerical parts represent the metal contents). Other samples of nickel supported on silica were prepared by impregnation of nickel nitrate on a silica synthesized by the sol–gel method. They were heated in air at 400°C for 5 h after the impregnation. The samples contained 5–30 wt% of nickel as a metal (5I-Ni, 10I-Ni, etc.).

The catalytic experiments were performed in a fixed-bed continuous flow reactor operating under atmospheric pressure. The catalyst was sandwiched with quartz wool in a tube reactor made of stainless steel whose contribution to the reaction was negligible. After reducing the sample (1.0 g) in a flow of hydrogen diluted with argon (H_2, 1.8 dm^3 h^{-1}; Ar, 9.0 dm^3 h^{-1}) for 1 h at 500°C, the catalyst was kept at 250°C under a stream of argon (9.0 dm^3 h^{-1}); then, 3.0 dm^3 h^{-1} of methanol gas was added to the argon stream.

The reactant and products were analyzed with an on-stream Ohkura 802 gas chromatograph equipped with a TC detector. Two columns, one activated carbon (2 m, Ar carrier) and the other Porapak T (2 m, He carrier), were employed in the analyses.

The surface areas of the catalysts were measured by the conventional BET nitrogen adsorption method. The samples were taken out from the reactor after the reactions of 2 h on-stream.

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Rotaflex 20 diffractometer using nickel-filtered CuKα radiation. Patterns were recorded over the range $2\theta = 3$–60°. The mean crystalline size of nickel metal or nickel oxide in the sample was determined from width of the XRD peak using the equation of Sherrer [10].

3. Results and discussion

Methanol was decomposed mainly to carbon monoxide and hydrogen over the catalysts containing nickel at a reaction temperature of 250°C (Table 1). Methane and water were also detected as by-products. Although 30I-Ni, which was prepared by the impregnation technique, contained a large amount of nickel, the conversion produced was not significantly higher than that with 20I-Ni or 10I-Ni. The surface area of the catalyst prepared by the impregnation method decreased with increase in the nickel content, suggesting that nickel particles choke the micropores of silica when the nickel content is high. Peaks attributed to metallic nickel were recorded in the XRD patterns at 44.3° [Ni(1,1,1)] and 51.7° [Ni(2,0,0)] in 2θ for the catalysts prepared by the impregnation method taken out from the reactor after the reaction of 2 h on-stream [11]. The mean particle sizes of nickel in 20I-Ni and 30I-Ni were ca. 30 nm while those for 5I-Ni and 10I-Ni were less than 6 nm. Hence, the dispersion of nickel particles on 20I-Ni and 30I-Ni are not so good as on 5I-Ni or 10I-Ni. In the XRD patterns for the samples just after the preparation, only the peaks attributed to nickel oxide were observed at 37.3° [NiO(1,1,1)] and 43.3° [NiO(2,0,0)] [11]. Although the particle sizes of nickel in 5I-Ni and 10I-Ni were appreciably smaller than those of nickel oxide in those samples as prepared, the sizes of nickel for 20I-Ni and 30I-Ni were significantly larger than those of nickel oxide (see Table 1), suggesting that sintering of the particles takes place when the particles are reduced.

The methanol conversion produced with 5S-Ni was almost half of that with 5I-Ni while both values for the particle size and the surface area for the former were smaller than those for the latter. Although the activity of catalysts prepared by the impregnation method almost reached a plateau at the nickel content of 20 wt%, the methanol con-

Table 1
Methanol decomposition over nickel catalysts at 250°C

Catalyst	Conversion/%	Selectivity/%		Surface area/ m² g⁻¹	Particle size/ nm	
		CO	CH₄		Ni [a]	NiO [b]
5I-Ni	23.5	98.0	2.0	553.1	4.3	5.4
10I-Ni	31.5	96.2	3.8	492.5	5.8	7.1
20I-Ni	34.1	95.7	4.3	437.5	29.7	14.3
30I-Ni	34.8	95.5	4.5	328.5	33.6	26.8
5S-Ni	12.8	98.3	1.7	316.7	2.1	–
10S-Ni	37.4	96.0	4.0	420.7	5.2	5.4
20S-Ni	52.7	93.5	6.5	458.1	7.3	7.9
30S-Ni	55.4	92.1	7.9	471.2	10.0	11.6
40S-Ni	64.1	90.7	9.3	376.9	13.9	16.7
50S-Ni	51.3	92.8	7.2	352.0	15.9 [c]	17.5

[a] Particle size of Ni in the sample taken out after reaction determined from the XRD peak at 44.3° unless otherwise noted.
[b] Particle size of NiO in the sample as prepared determined from the XRD peak at 37.3°.
[c] Determined from the XRD peak at 51.7°.

version produced with the samples synthesized by the sol–gel method increased with increase in the nickel content up to 40 wt% and the conversion for 40S-Ni was almost double of that for 30I-Ni. Peaks attributed to metallic nickel were recorded in the XRD patterns for the catalysts prepared by the sol–gel method while peaks associated with nickel oxide were also observed in the pattern for 50S-Ni whose activity was considerably lower than that of 40S-Ni. The ratio of the peak intensities, 37.3° (NiO)/51.7° (Ni), was 0.36. The particle size of nickel oxide in 50S-Ni was calculated as 12.9 nm from the width of the peak at 37.3°. As in Table 1, the particle size of nickel metal was increased with the content of nickel in the samples prepared by the sol–gel method. Suzuki et al. prepared Ni/SiO₂ by the sol–gel method using Ni(OH)₂ dissolved in ethylene glycol as a source of nickel ions [12]. The particle sizes of nickel determined by small angle X-ray scattering were 2.0 nm for 2.2 wt% of nickel content, 3.0 nm for 4.3 wt%, 7.0 nm for 9.2 wt%, 8.5 nm for 12.4 wt%, and 10.5 nm for 25.8 wt%. These values correspond to the particle sizes of the nickel

catalysts prepared by the sol–gel method without ethylene glycol, suggesting that ethylene glycol is not always necessary for the preparation of the solid in which nickel particles are fairly well dispersed. The particle sizes of nickel oxide in the samples before the reduction treatment were appreciably larger than those of nickel after the reduction, suggesting no occurrence of sintering during the reduction treatment (see Table 1). The particle size of nickel for 50S-Ni was the maximum (15.9 nm) in the series the samples prepared by the sol–gel method. However, it was significantly smaller than that for 20I-Ni (29.7 nm, see Table 1), thus, the preparation of Ni/SiO₂ by the sol–gel technique allows a high nickel content in the catalyst with fairly high nickel dispersion. It is noteworthy that the activity of 10S-Ni was higher than that of 10I-Ni whose particle size was similar to that for 10S-Ni although almost all nickel particles in 10I-Ni exist on the surface and a considerable part of nickel in 10S-Ni is probably incorporated in the bulk [7].

References

[1] National Research Council, Catalysis Looks to the Future, National Academy Press, Washington, DC, 1992.
[2] B. Chen and J.L. Falconer, J. Catal., 144 (1993) 214.
[3] O. Tokunaga, Y. Satoh, T. Fukushima and S. Ogasawara, Sekiyu Gakkaishi, 33 (1990) 173.
[4] H. Imamura, T. Takada, S. Kasahara and S. Tsuchiya, Appl. Catal., 58 (1990) 165.
[5] A. Tada, Y. Watarai, K. Takahashi, Y. Imizu and H. Itoh, Chem. Lett., (1990) 543.
[6] J.-P. Jacobs, L.P. Lindfors, J.G.H. Reintjes. O. Jylha and H.H. Brongersma, Catal. Lett., 25 (1994) 315.
[7] H. Tamagawa, K. Oyama, T. Yamaguchi, H. Tanaka, H. Tsuiki and A. Ueno, J. Chem. Soc., Faraday Trans. 1, 83 (1987) 3189.
[8] A. Ueno, H. Suzuki and Y. Kotera, J. Chem. Soc., Faraday Trans. 1, 79 (1983) 127.
[9] J.L. Carter, J.A. Cusumano and J.H. Sinfelt, J. Phys. Chem., 70 (1966) 2257.
[10] H.P. Klug and L.E. Alexander, X-ray Diffraction Procedures, John Wiley and Sons, Inc., New York, 1954.
[11] JCPDS file, 4-0850 and 4-0835.
[12] H. Suzuki, S. Takasaki, F. Koga, A. Ueno, Y. Kotera, T. Sato and N. Todo, Chem. Lett., (1982) 127.