

# A comparative study of liquid- and gas-phase methanol decomposition catalyzed over nickel supported on silica

Mahendra P. Kapoor, Yasuyuki Matsumura\*

National Institute of Advanced Industrial Science and Technology, Midorigaoka, Ikeda, Osaka 563-8577, Japan

Received 21 March 2001; accepted 2 July 2001

## Abstract

Methanol decomposition to hydrogen and carbon monoxide can be catalyzed in a liquid-phase at 180 °C over nickel supported on silica. By-production of formaldehyde suggests that the reaction mechanism is similar to that for the gas-phase reaction. The initial rate of the liquid-phase decomposition is about one third of that in the gas-phase, but the reaction is not very sensitive against presence of hydrogen and carbon monoxide which cause a decrease in the reaction rate. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Methanol decomposition; Liquid-phase; Nickel catalyst; Reaction rate; Reaction mechanism

## 1. Introduction

Methanol is a clean burning liquid, which can be produced from natural gas, coal, biomass, etc. and it can be used as a fuel for automobiles. Since the methanol decomposition to hydrogen and carbon monoxide is endothermic, the reaction is utilized for the heat recovery of the exhaust gas and the decomposition gas is fed to the engine [1]. The decomposition can be also applicable to the energy recovery from the waste heat of industries whose temperature is as low as 200 °C [2–5] while on-site production of hydrogen and/or carbon monoxide is practically carried out in chemical processes.

The reaction is a part of methanol steam reforming ( $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 3 \text{H}_2 + \text{CO}_2$ ) which can be modeled as a combination of the methanol decomposition

( $\text{CH}_3\text{OH} \rightarrow 2\text{H}_2 + \text{CO}$ ) and the water–gas shift reaction ( $\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$ ). The reforming is expected as a source of hydrogen to fuel cells especially for electric cars. On the standing point of reaction-heat supply, which is important in an endothermic reaction, a liquid-phase reaction is advantageous to a gas-phase reaction because of the high heat flux between a reactor wall and liquid. However, application of solid catalysts to the liquid-phase decomposition under the practical condition has not been reported as far as we know. In the present study nickel supported on silica [6,7], which is active in the methanol decomposition, was employed as the catalyst for the liquid-phase reaction and the activity has compared with that in the gas-phase reaction.

## 2. Experimental

Nickel supported on silica was prepared by hydrolysis and polymerization of tetraethyl orthosilicate (GR grade, Kanto Chemical Co. Ltd.) of which

\* Corresponding author. Present address: Research Institute of Innovative Technology for the Earth, Kizu-cho, Soraku-gun, Kyoto 619-0292, Japan. Tel.: +81-774-75-2305; fax: +81-774-75-2318. E-mail address: yasuyuki@rite.or.jp (Y. Matsumura).

solution contained nickel nitrate (GR grade, Kanto), ethanol, water, and citric acid. After drying in air at 50 °C the solid was heated in an argon stream at 170 °C for 2 h and in air for 2 h at 500 °C for removal of NO<sub>3</sub>-anions and residual organic compounds. The sample contained 40 wt.% of nickel as metal (Ni/SiO<sub>2</sub>). The BET surface areas of the sample was 402 m<sup>2</sup> g<sup>-1</sup> determined by the isotherms of nitrogen physisorption.

The liquid-phase methanol decomposition was performed in an autoclave (0.20 dm<sup>3</sup>). Prior to the reaction, the catalyst (0.50 g) was activated under evacuation followed by reduction with hydrogen (0.2 kPa) at 500 °C for 1 h and sealed in a glass capsule. The capsule was placed in the reactor with methanol (1.22 mol), and the air inside of the reactor was usually displaced with argon. The capsule was broken by pressurizing with the purge gas at room temperature, then the pressure was reduced to at a desired pressure and the reactor was heated up to 180 or 200 °C within 0.5 h with a vigorous stirring. No contribution of the reactor to the reaction was confirmed. After the reactor was cooled down to room temperature, the pressure inside was measured. The products were analyzed with a Shimadzu-8A gas chromatography (TCD) whose columns were Porapak T (2 m) and activated carbon (2 m).

The gas-phase reaction was performed in a fixed-bed continuous flow reactor operated under an atmospheric pressure. The catalyst (0.25 g) was sandwiched with quartz wool plugs in a tube reactor made of quartz glass (i.d. 6 mm). After reducing the sample in a flow of hydrogen (25 vol.%) in argon for 1 h at 500 °C, then methanol (50 vol.%) was fed with an

argon carrier at 180 °C. The reactant and products were analyzed with an on-stream Yanaco G2800 gas chromatography (Porapak T, 4 m; Ar carrier) equipped with TCD.

### 3. Results and discussion

Liquid methanol was decomposed with Ni/SiO<sub>2</sub> at 180 °C. The products detected were hydrogen, carbon monoxide, and formaldehyde (Table 1). The masses of the products were well balanced. Nickel carbonyl would be formed, but no deposition of nickel on the reactor wall was observed; this suggests that the formation of nickel carbonyl is negligible under the reaction conditions while metallic nickel is easily formed by decomposition of the carbonyl. The yield of carbon monoxide increased with the time period of the reaction (Fig. 1), while the selectivity to formaldehyde did not change significantly. The presence of formaldehyde and the absence of methyl formate in the products suggest that formation of carbon monoxide takes place via formaldehyde [7,8]. At a reaction temperature of 200 °C no formation of formaldehyde was detected, showing that the decomposition of formaldehyde is preferable at a higher temperature.

The methanol decomposition was suppressed in presence of 0.50 MPa of carbon monoxide or hydrogen as a purge gas. In the gas-phase methanol decomposition it is known that presence of hydrogen and/or carbon monoxide in the reaction mixture inhibits the reaction [7]. When 0.50 MPa of hydrogen was purged at room temperature, the rate of the liquid-phase

Table 1  
Liquid-phase methanol decomposition over Ni/SiO<sub>2</sub> catalyst at 180 °C

Reaction period (h)	Purge gas	Pressure (MPa) <sup>a</sup>		Methanol conversion (%)	Selectivity (%)	
		Initial	Final		CO	H <sub>2</sub> CO
2.5	Ar	0.10	0.42	0.87	91	9
7.0	Ar	0.10	0.73	1.76	89	11
15.0	Ar	0.10	1.12	2.88	89	11
15.0 <sup>b</sup>	Ar	0.10	1.46	3.40	100	0
2.5	H <sub>2</sub>	0.50	0.78	0.70	Major	Trace
2.5	CO	0.50	0.67	0.43	Major	Trace

<sup>a</sup> Pressure of the reactor at room temperature.

<sup>b</sup> Reaction temperature, 200 °C.

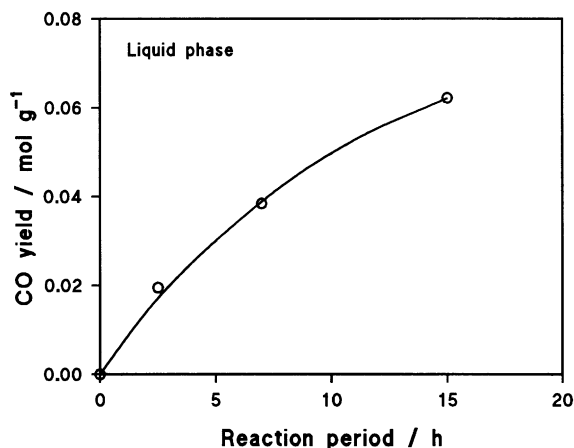


Fig. 1. Time course of liquid-phase methanol decomposition over Ni/SiO<sub>2</sub> catalyst at 180 °C. Purge gas: Ar, 0.10 MPa at room temperature.

reaction was appreciably decreased while the effect of carbon monoxide was larger (see Table 1).

Carbon monoxide and hydrogen were formed in the gas-phase methanol decomposition at 180 °C over Ni/SiO<sub>2</sub> with a slight amount of methane (Table 2). The yield of carbon monoxide depended on the contact time obtained from the F/W assuming that the apparent density of the catalyst is 1.2 kg dm<sup>-3</sup>. The initial rate of the reaction was 0.025 mol g<sup>-1</sup> h<sup>-1</sup>. On the other hand, the initial rate of the liquid-phase reaction was 0.008 mol g<sup>-1</sup> h<sup>-1</sup> and smaller than that of the gas-phase reaction (cf. Figs. 1 and 2).

The reaction in presence of carbon monoxide or hydrogen shows that the gases depress the liquid-phase methanol decomposition. However, the decrease in the apparent formation rate is not so large as estimated from the kinetic rate of the gas-phase decomposition although the pressure is high enough to poison

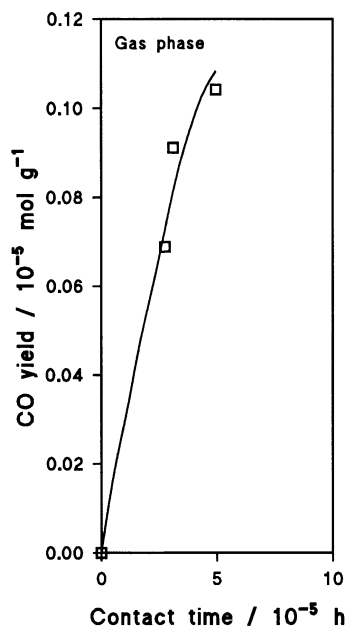
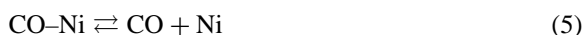
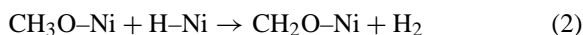


Fig. 2. Relationship between yield of carbon monoxide and contact time in gas-phase methanol decomposition over Ni/SiO<sub>2</sub> catalyst at 180 °C.

the surface of nickel in the gas-phase reaction almost completely [7]. In the gas-phase reaction on nickel, the following mechanism is proposed [7,8], that is



The methoxyl groups formed in step 1 is the intermediate of the decomposition and step 2 is rate-determining. Since the adsorption strengths of hydrogen and carbon monoxide are considerably higher than that of the methoxyl groups [7], the presence of hydrogen and carbon monoxide reduces the surface concentration of the intermediate although surface hydrogen is indispensable to promote the decomposition of the methoxyl groups (step 2). In the liquid-phase reaction adsorption of hydrogen and

Table 2  
Gas-phase methanol decomposition over Ni/SiO<sub>2</sub> catalyst at 180 °C<sup>a</sup>

F/W (dm <sup>3</sup> h <sup>-1</sup> g <sup>-1</sup> )	Methanol conversion (%)
16.8	5.6
26.7	4.9
30.2	3.7

<sup>a</sup> Reaction conditions: catalyst, 0.25 g; concentration of CH<sub>3</sub>OH, 50 vol.%.

carbon monoxide is supposed to be suppressed by the presence of methanol liquid, and it can account for the result that the reaction is not so sensitive against the presence of hydrogen and carbon monoxide as in the gas-phase reaction. However, the effect also reduces the surface concentration of hydrogen which promotes the decomposition of the methoxyl group. This may be a reason of the lower decomposition rate than in gas-phase.

In conclusion the methanol decomposition in liquid-phase proceeds as well as the gas-phase reaction while the interaction between the catalyst surface and the product gas is weaker than in the latter phase probably because methanol liquid covers the surface.

## References

- [1] National Research Council, *Catalysis Looks to the Future*, National Academy Press, Washington, DC, 1992.
- [2] W.H. Cheng, C.Y. Shiau, T.H. Liu, H.L. Tung, J.F. Lu, C.C. Hsu, *Appl. Catal. A* 170 (1998) 215.
- [3] W.H. Cheng, *Appl. Catal. A* 130 (1995) 13.
- [4] Y. Matsumura, M. Okumura, Y. Usami, K. Kagawa, H. Yamashita, M. Anpo, M. Haruta, *Catal. Lett.* 44 (1997) 189.
- [5] Y. Usami, K. Kagawa, M. Kawazoe, Y. Matsumura, H. Sakurai, M. Haruta, *Appl. Catal. A* 171 (1998) 123.
- [6] Y. Matsumura, K. Tanaka, N. Tode, T. Yazawa, M. Haruta, *J. Mol. Catal. A: Chem.* 152 (2000) 157.
- [7] Y. Matsumura, N. Tode, *Phys. Chem. Chem. Phys.* 3 (2001) 1284.
- [8] I. Yasumori, T. Nakamura, E. Miyazaki, *Bull. Chem. Soc. Jpn.* 40 (1967) 1372.