

Letter

Selective formation of methanol over nickel carbonyl with potassium methoxide

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Abstract

Carbon monoxide (CO) hydrogenation in the liquid medium was carried out at 373 K and 423 K with an initial pressure of 5 MPa using a catalyst composed of a metal carbonyl and potassium methoxide. Among the metal carbonyls tested, nickel tetracarbonyl showed a peculiarly high production of methanol, and its performance largely depended on the amount of alkoxide. The role of alkoxide in the reaction was discussed. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Methanol synthesis from carbon monoxide (CO) and hydrogen is highly exothermic and is thermodynamically favorable at low temperatures. Thus, if a catalyst, highly active at low temperatures, was available and the heat of reaction was efficiently removed, methanol production with a high per-pass conversion could be achieved. Recently, liquid-phase methanol synthesis at low temperatures of around 373 K has been claimed by several patents [1–5] as the process to overcome existing problems in the conventional methanol production process. A metal compound or a metal carbonyl with an alkali metal alkoxide was employed as the cata-

lyst in the patents. However, information on catalytic performance and behavior is scarce and kinetic data are not provided in the literature. In this study, the authors examined the catalytic activity of several metal carbonyls with and without alkoxide for liquid-phase CO hydrogenation.

2. Experimental

Catalysts were composed of transition metal (Cr, Mo, W or Ni) carbonyl and potassium methoxide (CH₃OK). The metal carbonyls employed were mononuclear, that is, Cr(CO)₆, Mo(CO)₆, W(CO)₆ and Ni(CO)₄. Nickel tetracarbonyl was obtained from Strem Chem. Nickel carbonyl is highly toxic and flammable, so it was handled with the greatest of care in a glove

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box under an inert atmosphere. Potassium methoxide was employed in the form of 30% CH₃OK solution in methanol (Wako Pure Chemical Industries), 10 cm³ of which contained 40 mmol of CH₃OK and 210 mmol of methanol. The catalyst, a mixture of 10 mmol of metal carbonyl and 10 cm³ of CH₃OK solution, was added to triethylene glycol dimethyl ether (triglyme), forming 100 cm³ of the solution. The reagents described here were obtained from Aldrich Chem. unless otherwise stated.

The reaction was carried out in batch operation in a magnetically stirred autoclave. The details of the experiment have been given elsewhere [6]. The feed gas (H₂/CO = 2) was introduced into the reactor at the reaction temperature (373 K or 423 K) and pressurized to 5 MPa. The reaction was conducted for 1 h or 3 h. The gas-phase and the liquid-phase components after the experiment were withdrawn from the reactor and analyzed by gas chromatography. The conversion of CO and the selectivity to products were evaluated on the carbon basis. The space time yield (STY) was determined from the amount of product, the reaction time continuing a pressure decrease during the run, and the total volume of the catalyst system (100 cm³, including the solvent).

3. Results and discussion

One of the patents reported that the coexistence of the group VI metal carbonyls (Cr, Mo and W) enhanced the catalytic activity of the Ni compound with alkoxide for methanol synthesis [2]. Since the liquid-phase CO hydrogenation over a single component carbonyl of the group VI metals has not been investigated so far, the experiments were conducted over a single metal carbonyl of group VI metals and Ni with and without CH₃OK at 423 K. The product yields are shown in Fig. 1. All the metal carbonyls without CH₃OK exhibited little activity with only traces of methyl formate (MF) and dimethyl ether (DME), confirming that the metal car-

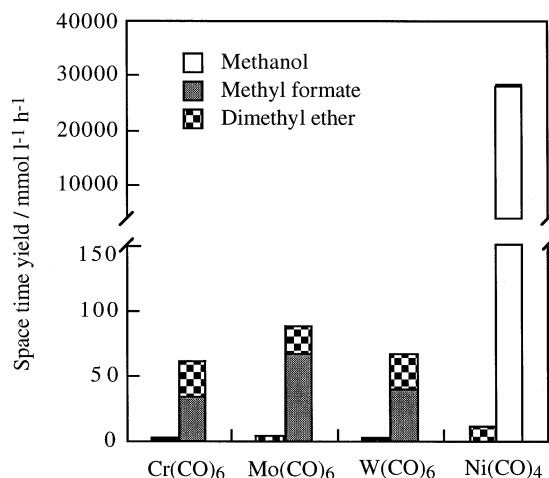
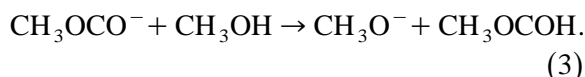
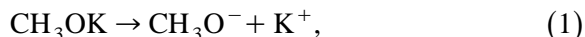


Fig. 1. Productivity for CO hydrogenation on metal carbonyls with and without CH₃OK. Reaction condition: 423 K, 5 MPa (initial pressure), reaction time: 3 h (1 h in case of Ni(CO)₄). The left bar for each catalyst indicates the value without CH₃OK; the right bar the one with CH₃OK.

bonyls alone virtually displayed no catalytic activity for CO hydrogenation under these conditions. On the other hand, a considerable amount of MF and DME was produced over the metal carbonyls with CH₃OK except Ni(CO)₄. The amount of methanol consumed, which was initially present with the catalyst, was approximately equal to the amount of MF and DME formed on the carbon basis, indicating that MF and DME were produced from methanol. Although DME seemed to be formed by the dehydration of methanol, the details were not clarified. As for the formation of MF, alkali metal alkoxides are known to promote the carbonylation of alcohols to alkyl formates [7]. In this study, CH₃OK was regarded as a catalyst promoting the carbonylation of methanol according to the following reaction scheme [7]:



W(CO)₆ is known to enhance the activity of CH₃OK in the carbonylation of methanol to MF

under similar conditions although $W(CO)_6$ itself shows no activity for the reaction [8,9]. Darensbourg et al. [8,9] reported that the catalytic activity over CH_3OK with $W(CO)_6$ was seven times that of CH_3OK alone. Since CH_3OK with the other metal hexacarbonyls (Mo and Cr) also showed the activities comparable to that of CH_3OK with $W(CO)_6$ as shown in Fig. 1, synergy was observed over these metal carbonyls as well. As a consequence, the catalytic activity for the carbonylation of methanol over the $M(CO)_6/CH_3OK$ system (M: Cr, Mo, W) was obtained in the following order: Mo > W > Cr.

Compared with the group VI metal carbonyls, $Ni(CO)_4$ with CH_3OK showed a peculiarly high methanol yield. In the experiment, when the feed gas was charged at 423 K, the reactor pressure decreased immediately with no induction period, suggesting that a combination of $Ni(CO)_4$ and CH_3OK served as an effective catalyst for the production of methanol. Also, the pressure decrease due to the reaction was completed within 5 min, and the STY value of $27.9 \text{ mol MeOH l}^{-1} \text{ h}^{-1}$, i.e., $0.89 \text{ kg MeOH l}^{-1} \text{ h}^{-1}$, was obtained with a selectivity of over 99%. In the past, some metal carbonyls of group VII and group VIII (Co [10,11], Rh [12–14], Ru [15], Ir [16] and Re [16]) were reported to show a slight production of methanol (20–30 mol MeOH mol metal⁻¹ h⁻¹ at most) even under the severe conditions of 503–553 K and 35–200 MPa, although they were employed without alkali alkoxide. Hence, the catalytic activity over the $Ni(CO)_4/CH_3OK$ system was quite enormous for the selective formation of methanol ($280 \text{ mol MeOH mol Ni}^{-1} \text{ h}^{-1}$) under much milder conditions.

The ICI process, a typical industrial methanol production process, shows an STY of $0.5\text{--}0.77 \text{ kg l}^{-1} \text{ h}^{-1}$ (average $0.66 \text{ kg l}^{-1} \text{ h}^{-1}$) under the conditions of 500–523 K and 5–10 MPa [17]. It is apparent that $Ni(CO)_4$ with CH_3OK shows a productivity comparable to that of the conventional methanol process, but under mild conditions.

Since the performance of $Ni(CO)_4$ changed drastically depending on the presence of alkoxide, it is obvious that CH_3OK would play an important role in the formation of methanol. CO hydrogenation was carried out at 373 K and 5 MPa employing $Ni(CO)_4$ with various amounts (0–40 mmol) of CH_3OK . In the experiments, the amount of methanol in the catalyst was adjusted to 210 mmol, while the quantities of CH_3OK were varied. The pressure drop profiles during the runs are shown in Fig. 2 and the catalytic performance is summarized in Table 1. In the run with $Ni(CO)_4$ alone, no pressure drop was observed in the course of the run (Fig. 2) and no products were detected (Table 1). In contrast, $Ni(CO)_4$ with CH_3OK showed an immediate pressure drop on charging the feed gas, and the pressure profiles became steeper with an increasing amount of CH_3OK . This indicates that the conversion and the reaction rate increased with the CH_3OK content. In fact, as shown in Table 1, the conversions increased with the added quantities of CH_3OK , and the

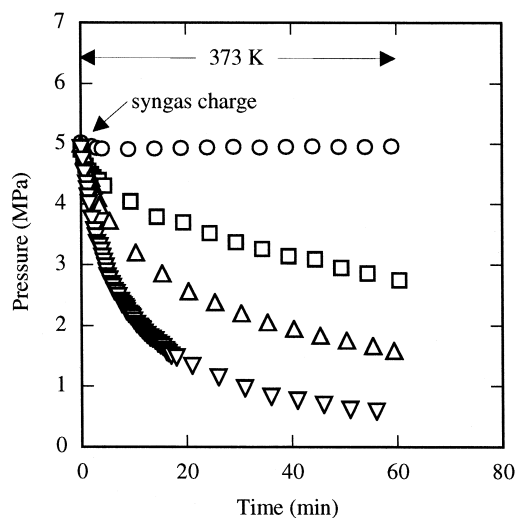


Fig. 2. Time courses of pressure during the run over $Ni(CO)_4/CH_3OK$. Catalyst: (O) $Ni(CO)_4$ with none of CH_3OK ; (□) $Ni(CO)_4$ with 20 mmol of CH_3OK ; (Δ) $Ni(CO)_4$ with 32 mmol of CH_3OK ; (▽) $Ni(CO)_4$ with 40 mmol of CH_3OK . Solvent: triglyme + MeOH (210 mmol); total volume = 100 cm^3 . Reaction conditions: initial pressure = 5 MPa (charged at 373 K), reaction temperature = 373 K.

Table 1
The CO hydrogenation over Ni(CO)₄/CH₃OK

Catalyst ^a	Product yields ^b (mmol)				Conversion (%)	Selectivity (%)		TOF ^c (h ⁻¹)	
	MeOH	MF	DME	CH ₄		MeOH	MF	MeOH	MF
Ni(CO) ₄	–	–	–	–	–	–	–	0.0	0.0
Ni(CO) ₄ /CH ₃ OK (20 mmol)	38.5	38.9	0.1	trace	57.7	33.1	66.9	3.8	3.9
Ni(CO) ₄ /CH ₃ OK (32 mmol)	120.6	17.3	0.2	trace	75.6	77.5	22.3	12.1	1.7
Ni(CO) ₄ /CH ₃ OK (40 mmol)	173.3	0.1	0.5	0.1	86.3	99.2	0.1	17.3	0.0

Reaction conditions: temperature = 373 K; initial pressure = 5 MPa (at 373 K); reaction time = 1 h.

^aNi(CO)₄: 10 mmol; CH₃OK: 0–40 mmol. Solvent: triglyme + MeOH (210 mmol). Total volume = 100 cm³.

^bMeOH: methanol; MF: methyl formate; DME: dimethyl ether.

^cTurnover frequency based on moles of Ni(CO)₄.

turnover frequency (TOF) of methanol also increased in a similar manner.

Fig. 3 illustrates the effect of CH₃OK on the STYs of methanol and methyl formate over Ni(CO)₄ at 373 K. The STY of methanol increased with the addition of CH₃OK, whereas that of MF decreased through the maximum at 20 mmol of CH₃OK. If CH₃OK had only functioned as a carbonylation catalyst and Ni(CO)₄ itself had promoted the hydrogenation of MF to two molecules of methanol, MF would have increased with an increase of the CH₃OK content and the selectivity to methanol, on the

contrary, would have decreased. However, the obtained results were reverse (Table 1; Fig. 3). This suggests that CH₃OK was involved in the formation of active species with Ni(CO)₄ to promote methanol synthesis, as well as functioning as a carbonylation catalyst. Another possibility is that the addition of CH₃OK to the catalyst solution might stabilize ionic active species or ionic intermediates, which are responsible for the production of methanol.

Marchionna et al. [18] reported that nickel carbonyl anion ([HNi(CO)₃]⁻) would be an active species for the hydrogenation of MF to methanol, and alkoxide would take part in the formation of the anion. In this study, as proposed by them, CH₃OK would have participated in the formation of some complexes with Ni(CO)₄. This speculation is strengthened by our results that the hydrogenation of MF hardly proceeded with Ni(CO)₄ alone under H₂ atmosphere. In addition, the color change of the catalyst was observed (from light yellow to red) upon the addition of CH₃OK to the Ni(CO)₄ solution during the preparation of the catalyst, which suggests the formation of some species related to Ni(CO)₄ and CH₃OK.

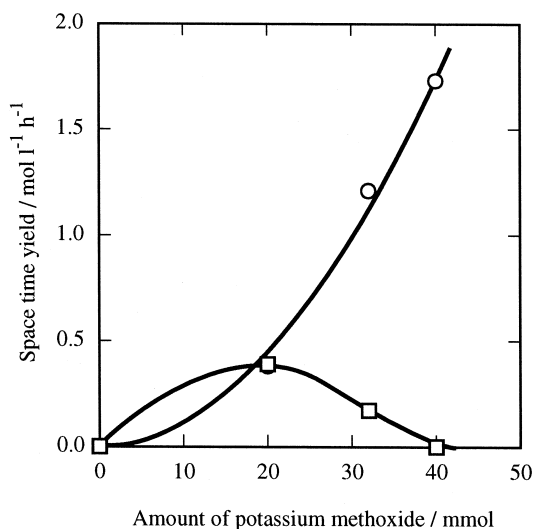


Fig. 3. Effect of potassium methoxide on the space time yields of methanol (○) and methyl formate (□). Catalyst: Ni(CO)₄. Reaction conditions: 373 K, 5 MPa (initial pressure), reaction time: 1 h.

4. Conclusion

The Ni(CO)₄ with CH₃OK showed peculiarly high activity for the methanol production at

373–423 K in the liquid-phase CO hydrogenation, and its performance was largely dependent on the amount of alkoxide, suggesting that CH_3OK was involved in the formation of the active species and/or stabilized the ionic species that were responsible for the production of methanol, as well as functioning as a carbonylation catalyst.

References

- [1] H. Nakamura, K. Saeki, M. Tanaka, Jpn. Patent 88/51,129 (1988).
- [2] R.S. Sapienza, W.A. Slegeir, T.E. O'Hare, D. Mahajan, U.S. Patent 4,614,749 (1986).
- [3] D. Mahajan, R.S. Sapienza, W.A. Slegeir, T.E. O'Hare, U.S. Patent 4,992,482 (1991).
- [4] M. Marchionna, M. Lami, F. Ancillotti, U.S. Patent 5,032,618 (1991).
- [5] S.T. Sie, E. Drent, W.W. Jager, U.S. Patent 4,812,433 (1989).
- [6] S. Ohyama, *React. Kinet. Catal. Lett.* 61 (1997) 331.
- [7] S.P. Tonner, D.L. Trimm, M.S. Wainwright, N.W. Cant, *J. Mol. Catal.* 18 (1983) 215.
- [8] D.J. Darensbourg, R.L. Gray, C. Ovalles, M. Pala, *J. Mol. Catal.* 29 (1985) 285.
- [9] D.J. Darensbourg, R.L. Gray, C. Ovalles, *J. Mol. Catal.* 41 (1987) 329.
- [10] D.R. Fahey, *J. Am. Chem. Soc.* 103 (1981) 136.
- [11] R.B. King, A.B. King Jr., K. Tanaka, *J. Mol. Catal.* 10 (1981) 75.
- [12] J.S. Bradley, *J. Am. Chem. Soc.* 101 (1979) 74191.
- [13] B.D. Dombek, *J. Am. Chem. Soc.* 102 (1980) 6855.
- [14] J.S. Bradley, in: M. Tsutsui (Ed.), *Fundamental Research in Homogeneous Catalysis*, Vol. 3, Plenum Press, New York, 1979, p. 165.
- [15] B.D. Dombek, *Adv. Catal.* 32 (1983) 325.
- [16] W. Keim, M. Anstock, M. Roper, *J. Schlupp, C1 Mol Chem.* 1 (1984) 21.
- [17] R.G. Hermann, K. Klier, G.W. Simmons, B.P. Finn, J.B. Bulko, T.P. Kobylinski, *J. Catal.* 56 (1979) 407.
- [18] M. Marchionna, L. Basini, A. Aragno, M. Lami, F. Ancillotti, *J. Mol. Catal.* 75 (1992) 147.