

# Low-temperature methanol synthesis in liquid-phase with a Raney Nickel–alkoxide system: effect of Raney Nickel pretreatment and reaction conditions

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## Abstract

The CO hydrogenation in liquid-phase was carried out using a set catalyst composed of Raney-Ni and CH<sub>3</sub>ONa in an autoclave of 234 ml under the reaction condition of 5 MPa, 423 K and 2 h. A high productivity (CO conversion of 92.4% with methanol selectivity of 99.8%) was achieved by eliminating the water after leaching of the Raney-Ni catalyst and by using CH<sub>3</sub>ONa rather than CH<sub>3</sub>CH<sub>2</sub>ONa. Ni(CO)<sub>4</sub> was observed in the liquid-phase after the reaction under the condition of high CO content (CO/H<sub>2</sub> > 2). However, the formation of Ni(CO)<sub>4</sub> was not observed, when stoichiometric gas ratio (H<sub>2</sub>/CO = 2) was used with Raney-Ni and CH<sub>3</sub>ONa at 423 K, 5 MPa, and 2 h. Carbonylation of CH<sub>3</sub>OH (CH<sub>3</sub>ONa catalysis) seems to be faster than the carbonylation of Raney-Ni to Ni(CO)<sub>4</sub> under these conditions. Hydrogenolysis of methyl formate (MeF) on the Raney-Ni yielded both methanol and methane at 443 K. However, the by-product methane was never obtained when using Raney-Ni with CH<sub>3</sub>ONa under the stoichiometric gas ratio (H<sub>2</sub>/CO = 2) at 423 K, 5 MPa, and 2 h. The essential pathway must be the carbonylation of methanol to MeF with the CH<sub>3</sub>ONa catalyst followed by the hydrogenolysis of MeF to methanol with the Raney-Ni; however, the synergy effect between Raney-Ni and CH<sub>3</sub>ONa are suggested in the mechanism. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Low-temperature methanol synthesis; Methanol synthesis in liquid-phase; Raney-Ni; CH<sub>3</sub>ONa

## 1. Introduction

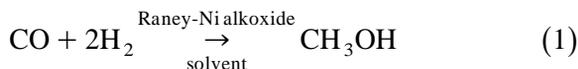
Recently, a low-temperature (353–433 K, initial pressure: 1–5 MPa) methanol synthesis process from carbon monoxide (CO) and dihydrogen in the liquid phase has been claimed in several patents [1–8]. Methanol synthesis from CO and H<sub>2</sub> is quite an exothermic and thermodynamically favorable reaction at lower temper-

atures. If the heat of reaction is efficiently removed, methanol production with high per-pass conversion may be achieved. The catalyst proposed by Brookhaven National Laboratory consists of NaH–RONa–M(OAc)<sub>2</sub> in which M = Ni, Pd or Co and R = tertiary amyl [1] (for example: CO conversion 86.9%, MeOH selectivity 99.4% under the reaction condition of 5 MPa, 373 K, 1 h, H<sub>2</sub>/CO = 2 in case of M = Ni [2]). That is a well-known reagent which has been used in hydrogenation reactions of halides, ketones, alkenes and alkynes in the past studies by Brunet and coworkers [9–12]. They have

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reported that complex reducing agents (CRA) such as  $\text{NaH-RONa-M(OAc)}_2$  are described as sources of new, atmospheric pressure, heterogeneous hydrogenation catalysts and M-H bond formation is postulated as one of the key steps in the catalytic hydrogenations. The active species of the system is believed to be  $\text{Ni(CO)}_4$  and a complex base (intermediate) from  $\text{NaH-RONa-M(OAc)}_2$  in case of  $\text{M} = \text{Ni}$ . Marchionna et al. [8] have reported that nickel carbonyl anion ( $[\text{HNi(CO)}_3]^{-1}$ ) would be an active species for the methanol production, and alkoxide would take part in the formation of the anion. Thus, the  $\text{Ni(CO)}_4$  and alkoxide system was studied and was found to show a high activity [6–8]. But this system is difficult to be used practically in industry because  $\text{Ni(CO)}_4$  is highly toxic, highly volatile and flammable.

In this work, it is our goal to develop a less harmful and highly active catalyst instead of  $\text{Ni(CO)}_4$ . Therefore, CO hydrogenation in liquid-phase was carried out using a catalyst composed of a Raney-Ni and  $\text{CH}_3\text{ONa}$  as follows (Eq. (1)). It was studied how the activity was influenced by the catalyst preparation and the reaction conditions.



## 2. Experimental

Catalysts were composed of Raney-Ni and 16.3%  $\text{CH}_3\text{ONa}$  solution of methanol (from Wako Pure Chemical Industries, 99.5%). The

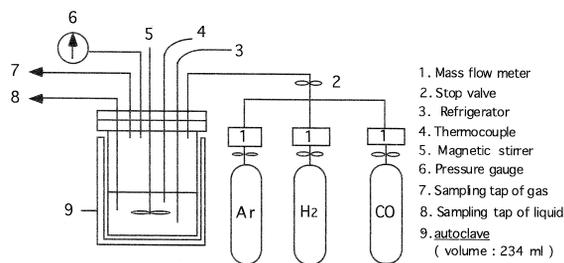


Fig. 1. Diagram of the apparatus.

Table 1  
Range of experimental operating conditions

Temperature	353–453 K
Total pressure	1–5 MPa
Reactant ratios ( $\text{H}_2/\text{CO}$ )	0.5–2
Stirrer speed	1000 rpm

Raney-Ni was prepared by leaching Al (50 wt.%) and Ni (50 wt.%) alloy (from Kanto Pure Chemical Industries) in 50 ml of 5 N NaOH at 346–363 K over 2–38 h, then washed to give pH 7, and finally dried with an evaporator. The catalysts were added to triethylene glycol dimethyl ether (DME) (triglyme) and subjected to the reaction. The reaction was carried out in batch operation in a magnetically stirred autoclave (Fig. 1). The reactant gas composition ( $\text{Ar}/\text{H}_2/\text{CO}$ ) is controlled by flow meters ( $\text{ml min}^{-1}$ ) for each gas, which was introduced into the batch reactor autoclave at the room temperature, and pressurized to 5 MPa and maintained for 2 h (Table 1).

The gas-phase and the liquid-phase components were analyzed gas chromatographically after the experiment. The produced amount of methanol was calculated from the quantity of

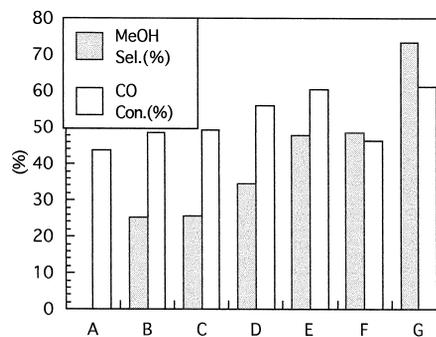


Fig. 2. Effect of washing methods on activity of Raney-Ni catalyst. Reaction condition: 5 MPa, 423 K, 4 h. Ratio of reactant gas:  $\text{Ar}/\text{H}_2/\text{CO} = 20/160/80$ . Catalysts: Raney-Ni 17 mmol,  $\text{CH}_3\text{CH}_2\text{ONa}$  41 mmol,  $\text{CH}_3\text{CH}_2\text{OH}$  210 mmol. Solvent: triglyme 88 ml. (A and B) Blank runs without further washing (A stood overnight before the reaction), (C): washing with EtOH, (D): washing with EtOH and drying in the vacuum, (E): washing with EtOH and washing with THF, and drying in the evaporator, (F): washing with EtOH and drying in the evaporator, (G): washing with THF and drying in the evaporator.

Table 2  
Effect of alkoxides on methanol synthesis

Alkoxide	MeOH selectivity (%)	Product yields (mmol)				
		MeOH	MeF <sup>a</sup>	DME <sup>a</sup>	CH <sub>4</sub>	EtF <sup>a</sup>
MeONa	82.7	67.3	0.1	6.9	0.1	–
EtONa	82.7	29.5	–	2.7	0.3	0.2

Reaction condition: 5 MPa, 423 K, 4 h.

Ratio of reactant gas: Ar/H<sub>2</sub>/CO = 20/160/80.

Catalysts: Raney-Ni 17 mmol, CH<sub>3</sub>CH<sub>2</sub>ONa or CH<sub>3</sub>ONa 41 mmol, CH<sub>3</sub>CH<sub>2</sub>OH or CH<sub>3</sub>OH 210 mmol.

Solvent: triglyme.

<sup>a</sup>MeF: methyl formate; DME: dimethylether; EtF: ethyl formate.

methanol before and after reaction. The quantity of soluble nickel was measured with the inductively coupled plasma method (ICP: SPS 4000). The selectivity was determined on the carbon basis. The apparent space time yield (STY) was calculated from the product amount, the reaction time during which a rapid pressure decrease was observed, and the total volume of the catalyst system (100 ml, including the solvent) for comparison with the other data.

### 3. Results

#### 3.1. Effect of drying method on activity of Raney-Ni catalyst

After pretreatment of Raney-Ni, various drying methods were used to investigate the effect of water elimination. Raney-Ni and CH<sub>3</sub>CH<sub>2</sub>ONa were used as catalysts to distinguish the effects well. Because CH<sub>3</sub>CH<sub>2</sub>ONa is easily decomposed by water, water should be removed well before the reaction for the effective use of the alkoxide. The Al–Ni alloy was leached with 50 ml of 5 N NaOH for 30 min at 323 K, for 15 h at 353 K and for 1 h at 363 K, then washed with water to give pH 7, and finally washed with various methods shown in Fig. 2. A higher activity was achieved by eliminating water after leaching of Raney-Ni catalyst. The most effective method to eliminate water in the Raney-Ni was the one using tetrahydrofuran (THF) rather than ethanol (Fig. 2).

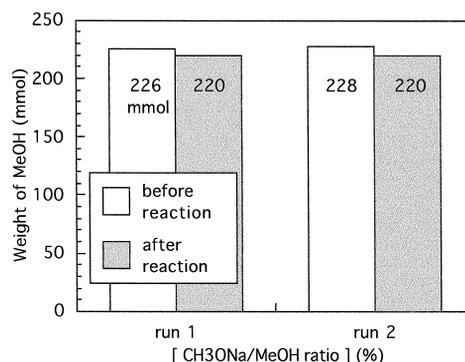


Fig. 3. The blank tests of methanol change without supplying H<sub>2</sub>/CO. Reaction condition: 5 MPa, 423 K, 4 h. Reactant gas: Ar (50 ml/min). Catalysts: Raney-Ni 17 mmol, CH<sub>3</sub>ONa 16.3% (CH<sub>3</sub>ONa 41 mmol, CH<sub>3</sub>OH 210 mmol). Solvent: triglyme.

#### 3.2. Effect of alkoxide

The effect of alkoxide was investigated. The Al–Ni alloy was leached with 50 ml of 5 N NaOH for 30 min at 323 K, for 17 h at 346 K, then washed with water to give pH 7, washed with THF and finally dried with an evaporator. Two kinds of alkoxides were compared as a counter part of the Raney-Ni. The results are shown in Table 2. Between the two alkoxides, CH<sub>3</sub>ONa showed more effectiveness in the activity than the CH<sub>3</sub>CH<sub>2</sub>ONa did although the selectivities were similar.

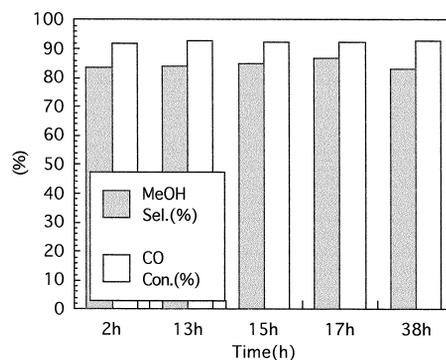


Fig. 4. Effect of leaching time on activity of Raney-Ni catalyst. Reaction condition: 5 MPa, 423 K, 4 h. Ratio of reactant gas: Ar/H<sub>2</sub>/CO = 20/160/80. Catalysts: Raney-Ni 17 mmol, CH<sub>3</sub>ONa 41 mmol, CH<sub>3</sub>OH 210 mmol. Solvent: triglyme 91.5 ml.

Table 3  
Effect of reaction temperature on methanol synthesis

Reaction temperature	MeOH selectivity (%)	CO concentration (%)	Product yields (mmol)				STY of MeOH (kg MeOH l <sup>-1</sup> h <sup>-1</sup> )
			MeOH	MeF	DME	CH <sub>4</sub>	
353 K	94.2	71.3	55.0	1.7	–	trace	0.12
393 K	99.8	91.8	67.1	trace	–	0.1	0.26
423 K	99.8	92.4	70.9	trace	–	trace	0.46
453 K	98.5	91.5	60.0	0.4	–	0.1	0.39

Reaction conditions: 5 MPa, 2 h, 353–453 K.

Ratio of reactant gas: Ar/H<sub>2</sub>/CO = 20/160/80.

Catalysts: Raney-Ni 17 mmol, CH<sub>3</sub>ONa 41 mmol, CH<sub>3</sub>OH 210 mmol.

Solvent: triglyme 91.5 ml.

### 3.3. Role of alkoxide, the blank test

The higher activity was achieved by eliminating water after the pretreatment of Raney-Ni catalyst in the early stage of this study. The presence of small amount of water might react with alkoxide to give methanol. For this reason, we carried out two blank test runs using Raney-Ni and CH<sub>3</sub>ONa 30% (CH<sub>3</sub>ONa 41 mmol: CH<sub>3</sub>OH 210 mmol) under the Ar gas only. The quantity of methanol before and after the blank run was analyzed by a gas chromatography. This experiment was repeated twice and both of them showed almost the same results. The quantity of methanol after the reaction did not increase as shown in Fig. 3. Therefore, CH<sub>3</sub>ONa is not decomposed under the reaction condition and is considered to play an active catalyst.

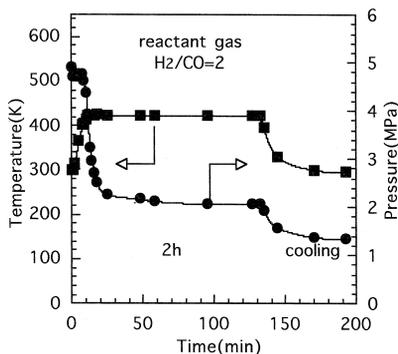


Fig. 5. Time courses of reaction temperature and pressure during methanol synthesis.

### 3.4. Effect of leaching condition on activity of Raney-Ni catalyst

We changed either the leaching time or the temperature of Al (50%)–Ni (50%) alloy, and the leached Raney-Ni was mixed with CH<sub>3</sub>ONa and used for the reaction under the condition of 423 K, 5 MPa and 4 h. Leaching condition may change the surface area and the content of residual Al of Raney-Ni. The product yield of methanol was increased a little by increasing the leaching time from 2 to 17 h (Fig. 4). But when the leaching time was increased to 38 h, the selectivity of methanol was decreased because of an increase in the product yield of DME. Also when the leaching temperature was increased from 346 to 363 K. As a whole, when

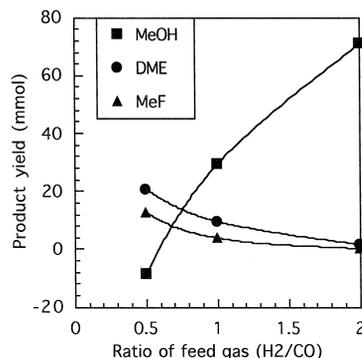


Fig. 6. Effect of feed composition on product yields of methanol. Reaction condition: 5 MPa, 423 K, 2 h. Ratio of reactant gas: H<sub>2</sub>/CO = 2, 1, 0.5. Catalysts: Raney-Ni 1 g, CH<sub>3</sub>ONa 41 mmol, CH<sub>3</sub>OH 210 mmol. Solvent: triglyme 91.5 ml.

Table 4  
The blank tests of catalyst activity by introducing only H<sub>2</sub> or CO

Ratios of reactant gas (Ar/H <sub>2</sub> /CO)	Reaction condition (KMPa <sup>-1</sup> h <sup>-1</sup> )	Charge of CO (mmol)	CO concentration (%)	MeOH selectivity (%)	Product yields (mmol)			
					MeOH	MeF	DME	CH <sub>4</sub>
20/160/0	423/5/2	–	–	–	–	–	–	0.50
20/160/80	423/5/2	84.9	92.4	95.2	70.9	trace	1.8	trace
20/0/80	423/5/2	222.3	67.0	–	–	14.0	8.7	0.02

Catalysts: Raney-Ni 17 mmol, CH<sub>3</sub>ONa 41 mmol, CH<sub>3</sub>OH 210 mmol.

Solvent: triglyme 91.5 ml.

changing leaching condition of Raney-Ni catalyst as above, no great difference in the activity of the catalyst was found.

### 3.5. Effect of reaction temperature

The effect of the reaction temperature on the catalyst activity was investigated. The results are shown in Table 3. The experiment was carried out using Raney-Ni and CH<sub>3</sub>ONa from 353 K to 453 K. The selectivity of methanol obtained was over 95% at 423 K. When the reactant gas (H<sub>2</sub>/CO = 2) was introduced into the reactor at the room temperature and raised to 423 K, the pressure immediately decreased after this reaction temperature was attained. An example of the time course of the temperature and pressure during the reaction are shown in Fig. 5. The slope of the initial pressure drop was taken to calculate the reaction rate (STY).

### 3.6. Effect of reactant gas ratio

The experiments were carried out using Raney-Ni and CH<sub>3</sub>ONa with the reaction condition of 423 K, 5 MPa and 2 h, while only the ratio of reactant gas was changed. The product yield of methanol was increased by increasing the ratio of reactant gas (H<sub>2</sub>/CO = 0.5–2), but DME and methyl formate (MeF) were decreased as shown in Fig. 6. The negative values of methanol production at H<sub>2</sub>/CO = 0.5 means that methanol solvent is converted to DME and MeF.

### 3.7. Carbonylation of methanol

Generally, it is known that Ni(CO)<sub>4</sub> could be formed from CO gas and Ni. Ni(CO)<sub>4</sub> is hard to be handled because it is highly toxic, highly volatile and flammable. According to the patents [5–7], CO conversion of more than 90% and

Table 5  
The ICP analysis of soluble Ni

Code number	Reaction conditions			Ratio of reactant gas (Ar/H <sub>2</sub> /CO)	Catalysts	Quantity of Ni (mg)	
	Temperature (K)	Pressure (MPa)	Time (h)			Before reaction (Raney metal)	After reaction (in the liquid)
1	423	5	4	20/0/0	R-Ni, CH <sub>3</sub> ONa	1000	0.03
2	423	5	2	20/160/0	R-Ni, CH <sub>3</sub> ONa	1000	0.07
3	423	5	4	20/160/80	R-Ni, CH <sub>3</sub> ONa	1000	0.03
4	423	5	2	20/160/80	R-Ni, CH <sub>3</sub> ONa	1000	0.08
5	423	5	2	20/40/80	R-Ni, CH <sub>3</sub> ONa	1000	24.45
6	423	5	2	20/0/80	R-Ni, CH <sub>3</sub> ONa	1000	64.16
7	423	5	2	20/160/80	R-Ni	1000	489.91
8	423	5	4	20/160/80	R-Ni, CH <sub>3</sub> CH <sub>2</sub> ONa	1000	0.20

Table 6  
The hydrogenolysis of methyl formate

Code number	RRG <sup>a</sup> (Ar/H <sub>2</sub> )	Catalyst (Raney-Ni)	Reagent (MeF)	Solvent (triglyme)	RC <sup>b</sup> (K MPa <sup>-1</sup> h <sup>-1</sup> )	MeOH selectivity (%)	Product yields (mmol)			
							MeOH	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	CO
1	20/160	1 g	13 ml	87 ml	423/5/2	21.0	4.8	18.0	0.02	0.5
2	20/160	1 g	13 ml	87 ml	443/5/2	62.5	11.1	6.5	0.08	0.2
3	20/160	2 g	13 ml	87 ml	423/5/15	54.0	28.9	24.1	0.25	0.4
4	20/160	3 g	13 ml	87 ml	443/5/15	47.0	149.1	155.9	5.30	0.1

<sup>a</sup>Ratio of reactant gas.

<sup>b</sup>Reaction conditions.

methanol selectivity of more than 95% were obtained when a catalyst composed of Ni(CO)<sub>4</sub> and alkoxide was applied in the liquid-phase. In this study, we also obtained CO conversion of more than 90% and methanol selectivity more than 95% by using Raney-Ni and alkoxide under the reaction condition of 423 K, 5 MPa, and 2 h with the reactant gas (H<sub>2</sub>/CO = 2). Here, a question arises whether Ni(CO)<sub>4</sub> is formed from Raney-Ni and CO gas during the reaction condition or not. The blank experiments were carried out by introducing only H<sub>2</sub> or CO and the results are shown in Table 4. H<sub>2</sub> gave almost no product, while CO alone was consumed much more than that with H<sub>2</sub>. The CO consumption suggests the formation of MeF and Ni(CO)<sub>4</sub>.

### 3.8. ICP analysis

If Ni(CO)<sub>4</sub> is formed, the solvent must contain Ni, which can be analyzed by the ICP method. The soluble Ni in the solvent after the reaction are shown in Table 5. The reactant gas ratio (H<sub>2</sub>/CO) and the catalyst composition were changed (Table 6), and several new findings were obtained.

1. Under the standard reaction condition, no Ni(CO)<sub>4</sub> is formed (code no. 3 and 4).
2. A part of Ni (6.4%) is turned to Ni(CO)<sub>4</sub> if no H<sub>2</sub> is present (code no. 6) and H<sub>2</sub> retarded the Ni(CO)<sub>4</sub> formation (code no. 5, 4).
3. But, if alkoxide is not applied a half of Ni (49%) was turned to Ni(CO)<sub>4</sub> even in the

presence of H<sub>2</sub> (code no. 7). This means that alkoxide prevents the formation of Ni(CO)<sub>4</sub> (code no. 4, 8).

### 3.9. Hydrogenolysis of MeF

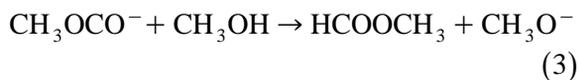
Alkoxide is known to be a quite effective catalyst of methanol carbonylation to form MeF. Then the second step must be the formation of methanol through hydrogenolysis of MeF. The question is whether Raney-Ni catalyzes this process independently or is accelerated by alkoxide. Hydrogenation experiment of MeF was carried out using Raney-Ni under the H<sub>2</sub> gas only. The results are shown in Table 6. Increasing the reaction time and the quantity of Raney-Ni, a higher product yields of methanol and methane were obtained (code no. 1–3, at 423 K, code no. 24 at 443 K).

## 4. Discussion

### 4.1. Role of alkoxide

Water and carbon dioxide have been reported to have negative effects on the carbonylation catalyst by Tonner et al. [13], Liu et al. [14], Maatschappij [15], Imyanitov et al. [16] and UCB [17], because they react with the alkali metal methoxides to form inactive products (alkali formates, alkali methyl carbonates, or alkali hydroxide). In this study, Raney-Ni and alkoxide were used as a set catalyst. Alkoxide can be

turned to hydroxide-forming methanol by water existing in the catalyst, solvent, or reactant gas. Therefore, after leaching the Raney-Ni, various drying methods were used to investigate the effect of eliminating water at the first part of this study (Fig. 2). Among them, the most effective method was the washing with THF, because the boiling point of THF is lower than ethanol. Another blank experiment was carried out to investigate the effect of water as shown in Fig. 3. According to the result, the quantity of solvent methanol (210 mmol) increased only a little by mixing with Raney-Ni at the beginning of the reaction; however, the quantity of methanol (226 mmol) was not increased during the blank test period without H<sub>2</sub>/CO. Therefore, alkoxide is considered to be unchanged during the reaction and to play a role as a catalyst. The formation of MeF in the carbonylation reaction is known to occur through the two-step mechanism: the addition of CO to the methoxide anion (Eq. (2)) and the reaction with the proton (Eq. (3)) [18].

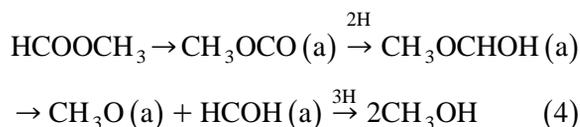


Alkoxide ion (RO<sup>-</sup>) can react as a nucleophile in a substitution reaction or as a base in an elimination. As the size of the R group is increased, the reactivity decreases. Methoxide ion is a stronger base and a better nucleophile than ethoxide ion. Therefore, in this study, a higher activity was obtained by using CH<sub>3</sub>ONa rather than CH<sub>3</sub>CH<sub>2</sub>ONa as is shown in Table 2.

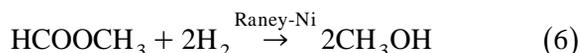
#### 4.2. Role of Raney-Ni

Hydrogenolysis of MeF has been studied in the gas phase [19] and in the slurry phase [13,20,21] at the temperature of 393 to 473 K using copper–chromite catalysts. The concurrent synthesis of methanol has been studied in a single mechanically agitated slurry reactor using

CH<sub>3</sub>OK as the usual homogeneous formate synthesis catalyst and a heterogeneous catalyst of copper–chromite under the mild conditions of 413–453 K and 38–65 bar by Liu et al. [22]. Palekar et al. proposed an overall reaction model in which MeF is formed by homogeneous carbonylation (Eq. (2)) near the copper–chromite surface and in the bulk methoxide liquid, coupled with regeneration of the methoxide catalyst (Eq. (3)) on the copper–chromite surface. This is followed by heterogeneous hydrogenolysis of MeF to yield methanol (Eq. (4)) [23], a part of which had been proposed by Sorum and Onsager [21], as shown in Eq. (4).



In this study, we found that Ni(CO)<sub>4</sub> formation from CO and Raney-Ni was prevented by another catalyst component, alkoxide, under the synthesis condition. For this reason, we can propose that Raney-Ni acts as a solid catalyst like the copper–chromite and does not act as a homogeneous molecular catalyst, Ni(CO)<sub>4</sub>. The main role of alkoxide must be the carbonylation to form MeF as the first step (Eq. (5)). The main role of Raney-Ni surface must be the hydrogenolysis of MeF to form methanol (Eq. (6)). However, the second step is not simple. If MeF is treated with H<sub>2</sub> on Raney-Ni, a side reaction, methanation, occurs (Table 6). The side reaction is prevented by the presence of CO and alkoxide.



## 5. Conclusions

By using a catalyst composed of Raney-Ni and CH<sub>3</sub>ONa, we obtained the CO conversion

of over 90% and the methanol selectivity of over 95% at 423 K, 5 MPa, 2 h, with the stoichiometric reactant gas ( $H_2/CO = 2$ ). The high reaction rate was achieved by eliminating water after leaching the Raney-Ni and by using  $CH_3ONa$  rather than  $CH_3CH_2ONa$ . Methanol was rapidly and selectively formed by adding  $CH_3ONa$  to the Raney-Ni. It was concluded that the  $CH_3ONa$ , a carbonylation catalyst, was not decomposed during the reaction, because methanol was not formed from  $CH_3ONa$  in the blank run. When using the catalyst of Raney-Ni and  $CH_3ONa$  under the reaction condition of 423 K, 5 MPa ( $H_2/CO = 2$ ), and 2 h, any amount of soluble Ni in the liquid-phase was not detected after the reaction by the ICP method. The formation of  $Ni(CO)_4$  was effectively prevented by  $H_2$  gas and by the presence of alkoxide, the latter effect was extraordinary. Methanol and methane were obtained by hydrogenolysis of MeF over Raney-Ni; however, the presence of CO and alkoxide retarded the methane formation.

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### References

- [1] R.S. Sapienza et al., US Patent 4,614,749 (1986).
- [2] S. Ohyama, *Petrotechnology* (Japan) 18 (1) (1995) 29.
- [3] H. Nakamura, K. Saeki, M. Tanaka, *Jpn. Patent* 88/51129 (1988).
- [4] S.T. Sie, E. Drent, W.W. Jager, US Patent 4,812,433 (1989).
- [5] D. Mahajan et al., US Patent 4,935,395 (1990).
- [6] D. Mahajan, R.S. Sapienza, W.A. Slegeir, T.E. O'Hare, US Patent 4,992,482 (1991).
- [7] M. Marchionna, M. Lami, F. Ancillotti, US Patent 5,032,618 (1991).
- [8] M. Marchionna, L. Basini, A. Aragno, M. Lami, F. Ancillotti, *J. Mol. Catal.* 75 (1992) 147.
- [9] J.J. Brunet, L. Mordenti, P. Caubere, *J. Org. Chem.* 43 (25) (1978) 4804.
- [10] L. Mordenti, J.J. Brunet, P. Caubere, *J. Org. Chem.* 44 (13) (1979) 2203.
- [11] J.J. Brunet, P. Gallois, P. Caubere, *J. Org. Chem.* 45 (1980) 1937.
- [12] P. Gallois, J.J. Brunet, P. Caubere, *J. Org. Chem.* 45 (1980) 1946.
- [13] S.P. Tonner, D.L. Trimm, M.S. Wainwright, N.W. Cant, *J. Mol. Catal.* 18 (1983) 215.
- [14] Z. Liu, J.W. Tierney, Y.T. Shah, I. Wender, *Fuel Processing Technol.* 18 (1988) 185.
- [15] N.V., Maatschappij, British Patent, 1,047,408 (Nov. 2) (1966).
- [16] N.S. Imyanitov, B.E. Kuvayev, D.M. Rudkovsky, *Gidroformilirovanie*, 1972, p. 152.
- [17] UCB, Belgium, British Patent, 1,511,961 (May 24) (1978).
- [18] J.R. Christiansen, US Patent 1,302,011 (April 29) (1919).
- [19] J.W. Evan, P.S. Casey, M.S. Wainwright, D.L. Trimm, N.W. Cant, *Appl. Catal.* 7 (1983) 31.
- [20] D.M. Monti, M.A. Kohler, M.S. Wainwright, D.L. Trimm, N.W. Cant, *Appl. Catal.* 22 (1986) 123.
- [21] P.A. Sorum, O.T. Onsager, in: *Proc. 8th Int. Congr. Catal.*, Vol. 2, West Berlin, Verlag, Chemie Weinheim, 1984, p. 133.
- [22] Z. Liu, J.W. Tierney, Y.T. Shah, I. Wender, *Fuel Processing Technol.* 23 (1989) 149.
- [23] V.M. Palekar, H. Jung, J.W. Tierney, I. Wender, *Appl. Catal. A* 102 (1993) 13.