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Dehydrogenation of Methanol to Formaldehyde over Silicalite

YASUYUKI MATSUMURA,* KEIJI HASHIMOTO,* AND SATOHIRO YOSHIDA†

**Osaka Municipal Technical Research Institute, Joto-ku, Osaka, 536 Japan; and †Department of Hydrocarbon Chemistry, Kyoto University, Sakyo-ku, Kyoto, 606 Japan*

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Formaldehyde has been produced from methanol with high selectivity at 750 K in a continuous flow reactor over silicalites containing sodium ions. On the basis of the results obtained with the pulse reactor technique, it is concluded that the sodium ions in the silicalites are essential for the dehydrogenation of methanol, whereas the aluminum impurities play only a small role. The decomposition of formaldehyde has also been investigated at 670 K. Active sites for the decomposition would be transition metal impurities in the silicalites. These sites are assumed to be deactivated at the initial stage of the continuous flow reaction. © 1986 Academic Press, Inc.

INTRODUCTION

Formaldehyde is one of the key materials in the chemical industry, and at present, it is produced by oxidative dehydrogenation of methanol on an industrial scale. The process has been operated successfully; however, unavoidable production of water is a disadvantage and the production of formaldehyde by simple dehydrogenation of methanol is now being actively investigated. There are three main reactions in the dehydrogenation of methanol: (1) decomposition to carbon monoxide and hydrogen, (2) formation of methyl formate, and (3) formation of formaldehyde (*1*). Of the three reactions, the last one is thermodynamically unfavorable in the conventional temperature range (*2, 3*). Thus, ΔG of the reaction is positive at temperatures below 720 K, while ΔG of the reaction (1) is already negative at temperatures above 450 K. The precise thermodynamic data for methyl formate are not available, but we expect that reaction (2) is thermodynamically more favorable than reaction (3) and less favorable than reaction (1). By the thermodynamic limitation, the dehydrogenation of methanol to formaldehyde is usually operated at temperatures above 800 K. A typical catalyst is a Cu–Zn–Se alloy which is used in the temperature range 870–970 K (*4*). Such high reaction temperatures are not desirable because of the enhancement of formaldehyde decomposition and the deactivation of catalysts. It is assumed that the existence of selenium in the alloy lowers the catalytic activity below 800 K since selenium usually spoils catalytic activity. However, without selenium, the selectivity toward formaldehyde is very low at 923 K though the methanol conversion is very high (*4*).

In order to industrialize the simple dehydrogenation reaction, new substances which catalyze the formation of formaldehyde at temperatures below 800 K are required. It is known that alcohol dehydrogenation occurs over acid–base catalysts (*5–8*). Formaldehyde is believed to be formed in the alkylation of toluene with methanol over alkali metal cation-exchanged zeolite (*9*). However, the selective methanol dehydrogenation to formaldehyde over acid–base catalyst has not been reported because the reaction is considered to be overwhelmed by typical acid-catalyzed reactions such as dehydration.

Silicalite is an extremely aluminum-deficient crystalline silicate which has the same structure as ZSM-5 type zeolite (*10*). Because the acidity of ZSM-5 depends on the

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aluminum content (*11, 12*), the extremely aluminum-deficient silicalite does not have strong acid sites (*13*). Furthermore, alkali metal cations are usually used as a raw material for the synthesis of silicalite, and the cations remain in the silicalite as impurities (*14*). These can be removed by washing; however, if the cations are left in the silicalite they will modify the acid–base properties, which are important for the catalysis of alcohol dehydrogenation (*5–7*).

In the present work, methanol dehydrogenation over the sodium modified silicalite was studied. The reaction is accompanied by the decomposition to carbon monoxide and hydrogen which is thermodynamically more favorable than the simple dehydrogenation. Since formaldehyde is presumed to be a reaction intermediate in the decomposition reaction, the decomposition of formaldehyde was also studied. The silicalite samples examined here contain a slight amount of aluminum; therefore, the samples should be called "ZSM-5" (*15*). However, we will refer to them as "silicalite" because the aluminum impurities are confirmed to be inert with respect to the methanol dehydrogenation on the basis of the results described here.

EXPERIMENTAL METHODS

Methanol (purity 99.5%) was dehydrated by refluxing over magnesium just before use. Formaldehyde aqueous solution was prepared by dissolving paraformaldehyde in boiling water. The solution contained 23 wt% formaldehyde.

TABLE 1

Chemical Composition of Samples

Sample	Composition (wt%)				
	Si	Na	Al	Ni	Fe
Na(1.2)-SL-Al(0.01)	44	1.2	0.01	0.01	0.01
Na(1.1)-SL-Al(0.03)	44	1.1	0.03	0.01	0.01
Na(0.4)-SL-Al(0.01)	45	0.4	0.01	0.01	0.01
Na(0.03)-SL-Al(0.01)	45	0.03	0.01	0.01	0.01
Na(1.3)-SL-Ni(0.7)	44	1.3		0.7	
Na(0.13)-SL-Ni(0.7)	45	0.13		0.7	

Silicalite and nickel silicate, which gives the same structure as ZSM-5, were synthesized by the methods described in the patents (*14, 16*). The main starting materials of the synthesis were tetraethyl orthosilicate, sodium hydroxide or sodium nitrate, and tetra-*n*-propyl ammonium hydroxide. In the case of nickel silicate, nickel nitrate was added to these materials. Because aluminum existed in these raw materials as an impurity, the samples obtained contain a small amount of aluminum. After the hydrothermal reaction in a stainless-steel autoclave, the precipitate was heated in air at 770 K for 8 h to remove organic compounds. The samples contain sodium ions. The sodium ions in both the silicalite and the nickel silicate can be removed by reflux in water. The chemical composition of the samples was analyzed by atomic absorption spectroscopy (Na, Ni, Fe) and an usual titration method (Al). The results are summarized in Table 1. The samples, Na(0.03)-SL-Al(0.01) and Na(0.13)-SL-Ni(0.7), were respectively prepared by leaching sodium ions from Na(1.2)-SL-Al(0.01) and Na(1.3)-SL-Ni(0.7) by reflux three times for 5 h each, and Na(0.4)-SL-Al(0.01) was obtained from Na(1.2)-SL-Al(0.01) by reflux for 2 h. The samples were again heated in air at 770 K for 1 h. The difference in the amount of aluminum between Na(1.2)-SL-Al(0.01) and Na(1.1)-SL-Al(0.03) is caused by the difference in the raw materials. The X-ray diffraction patterns were in agreement with those reported by Olson *et al.* (*11*).

Reactions were carried out in a fixed-bed continuous flow reactor or a pulse microcatalytic reactor. In the case of the continuous flow reaction, a catalyst (50 or 100 mg) was heated under vacuum for 1 h at 770 K prior to a run. The catalyst was sandwiched with silica wool in a quartz reaction tube of 6-mm inner diameter. The reaction was carried out at atmospheric pressure. Methanol was fed via an oxygen-free helium or nitro-

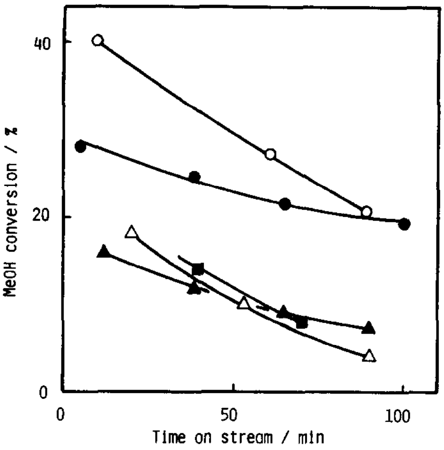

FIG. 1. Methanol dehydrogenation over Na(1.2)-SL-Al(0.01) in a continuous flow reactor. Reaction conditions: reaction temperature, 750 K; carrier gas, He. (○) Catalyst 100 mg, flow rate 20 ml min^{-1}, partial pressure of methanol 12 Torr; (△) 100 mg, 40 ml min^{-1}, 13 Torr; (●) 50 mg, 10 ml min^{-1}, 12 Torr; (▲) 50 mg, 20 ml min^{-1}, 12 Torr; (■) 50 mg, 20 ml min^{-1}, 18 Torr.

gen stream which was saturated with methanol vapor by passage through a bubbler. In the case of the pulse reaction, catalyst (10 mg) was preheated for more than 0.5 h at 770 K under a carrier gas prior to the reaction, and kept at the reaction temperature. The catalyst was then injected with a pulse of reactant (0.1–4 μl). The catalyst was sandwiched with silica wool in a Pyrex reaction tube of 2-mm inner diameter. Helium, nitrogen, or hydrogen at a flow rate of 10 ml/min was used as the carrier gas. The hydrogen carrier may reduce nickel ions. Measurement of hydrogen consumption confirmed that the nickel ions in Na(0.13)-SL-Ni(0.7) were almost reduced to their metal state by heating at 670 K under ca. 100 Torr hydrogen for less than 1 h, but the ions in Na(1.3)-SL-Ni(0.7) were scarcely reduced under the same conditions. The hydrocarbon balance of the reactants and products was well set up.

The reaction products were analyzed by gas chromatography. A Porapak Q (1 m) plus TSR-1 (3 m) column was used for normal analyses. For a precise separation of C_1 products, an activated carbon column (1 m) was also used.

RESULTS

Methanol Dehydrogenation

Dehydrogenation of methanol occurred over the Na(1.2)-SL-Al(0.01) catalyst at 750 K in the continuous flow system giving formaldehyde and hydrogen as the main products. The activity decreased gradually with time on stream as shown in Fig. 1. Carbon monoxide, carbon dioxide, and methane were also produced when the time on stream was less than 10 min. After the initial stage, the production of formaldehyde with high selectivity was above 98%. Small amounts of water and dimethyl ether were also detected. The catalyst withdrawn from the bed after 1.5 h had a black color and its activity was restored to the level just after the initial stage by calcination in an oxygen atmosphere at 750 K. This suggests that the deactivation is caused by carbon deposits on the catalyst. Under the same conditions, the activity of Na(0.4)-SL-Al(0.01) was about one-third of that of Na(1.2)-SL-Al(0.01), and the activity of Na(0.03)-SL-Al(0.01) was very low. The results strongly suggest the important role of sodium ions in the reaction. More detailed experiments were carried out to investigate the effects of the reaction conditions and the role of the cations.

The reaction was carried out with the pulse microcatalytic reactor in order to avoid the effects of carbon deposits on the catalyst and to investigate the initial stage of the reaction. The results are summarized in Table 2. It was confirmed by blank experiments that silica wool used for packing catalysts exhibits no activity with respect to methanol conversion even at 820 K. The catalytic activity depends almost entirely on the sodium content of the catalyst. As described in the table, the selectivity to formaldehyde decreased with an increase in the conversion in general, while a reverse tendency was observed for the selectivity

TABLE 2

Methanol Conversion over Silicalites in a Pulse Microcatalytic Reactor

Run	Catalyst	Reaction temp. (K)	MeOH (μmol)	Selectivity (%)				Conversion of MeOH (%)
				CO	$CO_2 + CH_4$	H_2CO	Me_2O	
1	Na(1.2)-SL-Al(0.01)	620	25	—	—	—	—	Trace
2	Na(1.2)-SL-Al(0.01)	670	25	8	12	73	6	5
3	Na(1.2)-SL-Al(0.01)	720	25	12	22	61	6	18
4	Na(1.2)-SL-Al(0.01)	770	25	49	6	45	—	47
5	Na(1.2)-SL-Al(0.01)	770	50	33	6	59	1	20
6	Na(1.2)-SL-Al(0.01)	820	25	72	1	27	—	83
7	Na(1.2)-SL-Al(0.01)	820	75	43	2	54	0.6	17
8	Na(1.1)-SL-Al(0.03)	770	25	45	5	50	—	40
9	Na(0.03)-SL-Al(0.01)	770	25	68	2	29	—	4
10	Na(1.3)-SL-Ni(0.7)	770	25	88	8	—	5	66
11	Na(0.13)-SL-Ni(0.7)	770	25	83	—	—	17	23
12	Na(1.2)-SL-Al(0.01)	770	25	75	—	25	—	57

Note. Carrier gas; He for Runs 1–11, H_2 for Run 12.

to carbon monoxide. This suggests that methanol is decomposed to carbon monoxide via formaldehyde. The decomposition of formaldehyde might be affected by water, a by-product of the reaction; however, the injection of a methanol–water mixture (H_2O, ca. 10 wt%) gave the same results as those with injection of methanol. Formaldehyde was not produced and carbon monoxide was the main product over Na(1.3)-SL-Ni(0.7) or Na(0.13)-SL-Ni(0.7). With a helium gas carrier, no significant change in both activity and selectivity of Na(1.2)-SL-Al(0.01) was observed for up to five pulses, and the products were in agreement with those of the continuous flow reaction though the selectivity toward formaldehyde was lower than that of the continuous flow reaction after the initial stage. According to patented methods, hydrogen is used as a carrier gas for methanol dehydrogenation to formaldehyde over catalyst containing copper (*4, 17, 18*). This suggests the possibility that coexistence with hydrogen gives good results in the methanol conversion; thus, the reaction was investigated with a hydrogen gas carrier. However, the selectivity toward formaldehyde decreased and that toward carbon monoxide, on the contrary, increased in comparison with the results under a helium stream, though a higher conversion was obtained. With a hydrogen gas carrier, the yield of carbon monoxide successively decreased with repeated pulses and that of formaldehyde changed in the reverse direction (Fig. 2); carbon dioxide and methane were not observed in the products. Figure 3 shows the dependence of the product distribution on the methanol dose over Na(1.2)-SL-Al(0.01). A maximum yield of carbon monoxide was observed at a methanol dose of about 15 μmol.

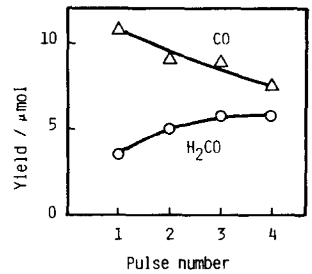

FIG. 2. Catalytic activity changes of Na(1.2)-SL-Al(0.01) for methanol conversion in a pulse microcatalytic reactor under a hydrogen stream. Reaction conditions: MeOH dose, 25 μmol; reaction temperature, 770 K.

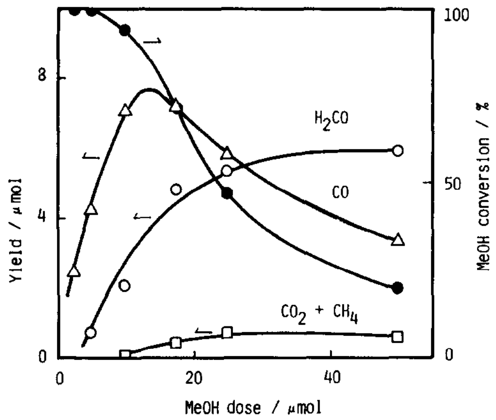

FIG. 3. Methanol conversion over Na(1.2)-SL-Al(0.01) in a pulse microcatalytic reactor. Reaction conditions: carrier gas, He; reaction temperature, 770 K.

Formaldehyde Decomposition

It is believed that carbon monoxide production from methanol occurs via formaldehyde or methyl formate (*1*). Because the change in the selectivity to formaldehyde with the conversion of methanol proceeds in a direction reverse of that for the selectivity to carbon monoxide, as described above, and because methyl formate was not observed in the reaction products, the conversion of formaldehyde was investigated. Aqueous formaldehyde solution (H_2CO, 23 wt%) was injected into the pulse reactor packed with the Na(1.2)-SL-Al(0.01) catalyst at 670 K. Silica wool was confirmed to be inactive to the reaction at 770 K; thus, the possibility of thermal decomposition or decomposition by silica wool can be excluded. The main products from the conversion of formaldehyde are carbon monoxide and hydrogen. Carbon dioxide, methane, and methanol were also observed as minor products along with a trace amount of dimethyl ether. The distribution of products is summarized in Table 3. The same results were obtained for a diluted formaldehyde solution (H_2CO: 9 wt%). Thus, water does not influence the decomposition of methanol. Both Na(1.3)-SL-Ni(0.7) and Na(0.13)-SL-Ni(0.7) exhibited very high catalytic activity in the formaldehyde conversion. The product distribution under a hydrogen stream was quite different from that under a helium stream. The activity of Na(1.2)-SL-Al(0.01) or Na(0.03)-SL-Al(0.01) changed with successive injections (Fig. 4). All of the product yields decreased with repeated pulses. Deactivated catalysts were scarcely regenerated by calcination at 770 K in air. When methanol coexisted in the injected solution, the production of carbon monoxide over Na(1.2)-SL-Al(0.01) was suppressed (Fig. 5). Figure 6 shows the dependence of the product distribution over Na(1.2)-SL-Al(0.01) on the

TABLE 3

Formaldehyde Conversion over Silicalites in a Pulse Microcatalytic Reactor

Run	Catalyst	Carrier gas	Yield (μmol)			Conversion of H_2CO (%)
			CO	$CO_2 + CH_4$	MeOH	
1	Na(1.2)-SL-Al(0.01)	He	1.1	0.76	0.45	19
2	Na(0.4)-SL-Al(0.01)	He	0.71	0.72	0.17	13
3	Na(0.03)-SL-Al(0.01)	He	0.40	0.54	—	8
4	Na(1.3)-SL-Ni(0.7)	He	8.5	1.4	1.9	99
5	Na(0.13)-SL-Ni(0.7)	He	8.4	1.4	0.36	85
6	Na(1.2)-SL-Al(0.01)	H_2	2.4	0.18	0.84	29
7	Na(0.03)-SL-Al(0.01)	H_2	3.5	0.13	0.48	34
8	Na(1.2)-SL-Al(0.01)	He	5.4	0.84	1.1	61

Note. Reaction conditions: reaction temperature, 670 K for Runs 1–7, 770 K for Run 8; reactant, 2 μl of 23% formaldehyde aqueous solution (ca. 12 μmol as H_2CO): first pulse.

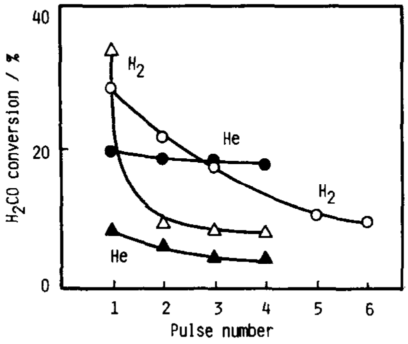

FIG. 4. Catalytic activity changes of silicalite for formaldehyde conversion in a pulse microcatalytic reactor. (△,▲) Na(0.03)-SL-Al(0.01); (○,●) Na(1.2)-SL-Al(0.01). Reaction conditions: H_2CO dose, 12 μmol (diluted in water); reaction temperature, 670 K.

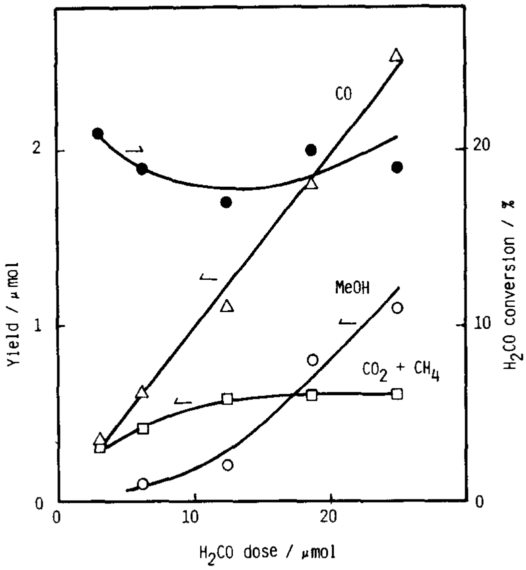

FIG. 6. Formaldehyde conversion over Na(1.2)-SL-Al(0.01) in a pulse microcatalytic reactor. Reaction conditions: reactant, 23% formaldehyde aqueous solution; carrier gas, He; reaction temperature, 670 K.

formaldehyde dose; the suppression effect of the methanol formed in the reaction on the formaldehyde conversion is supposed to be not significant because the amount of methanol is small compared with that of formaldehyde.

DISCUSSION

Effect of Aluminum Impurities

Though the synthesis was carried out without addition of aluminum ions, the silicalite examined here contains a slight amount of aluminum which existed as impurities in the raw materials. The formation of acid sites by the aluminum ions is possible, but the acid sites are supposed to be very weak because there exists an excess of sodium ions with respect to the aluminum ions in the silicalite. Actually, the formation of dimethyl ether, which is produced by dehydration of methanol, is very small.

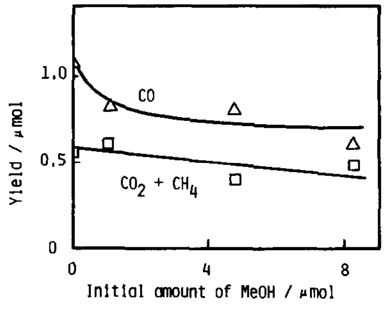

FIG. 5. Dependence of formaldehyde conversion over Na(1.2)-SL-Al(0.01) on amount of methanol added. Reaction conditions: reactant, H_2CO 12 μmol (diluted in water) + MeOH; carrier gas, He; reaction temperature, 670 K.

Yashima *et al.* have proposed that the aluminum ion and alkali-metal cation pairs in zeolites constitute basic sites and catalyze alcohol dehydrogenation (*7*). Consequently, a slight amount of the aluminum ion and sodium pairs existing in the silicalite examined here may be presumed to form active sites. However, the present results that the catalytic activity does not depend on the aluminum content (Runs 4 and 8 in Table 2) suggest that the pairs (if they do exist) do not have any effect on the dehydrogenation.

Thus, a small amount of aluminum ions in the silicalite would play a minor role in the methanol conversion.

Active Sites

Jacobs and Uytterhoeven discussed the participation of transition metal ion impurities in the catalytic dehydrogenation of isopropanol over alkali–metal cation-exchanged zeolites (*19*). Since Na(1.2)-SL-Al(0.01) contains nickel ions as in impurity (Table 1), the nickel ions might play a role in the catalysis. In fact, the activities of Na(1.3)-SL-Ni(0.7) and Na(0.13)-SL-Ni(0.7) were higher than those of Na(1.2)-SL-Al(0.01) and Na(0.03)-SL-Al(0.01) (Run 10 to Run 4 and Run 11 to Run 9 in Table 2); however, production of carbon monoxide was overwhelming over the former catalysts. Thus, the active sites for formaldehyde production are presumed to comprise sodium ions independent from nickel ions. This assumption is supported by the fact that both activity and selectivity toward formaldehyde of Na(1.2)-SL-Al(0.01) are much higher than those of Na(0.03)-SL-Al(0.01) (cf. Runs 4 and 9 in Table 2).

On the other hand, it is assumed that nickel ions participate in the active sites for the formaldehyde conversion over the silicalite. Thus, the activity decreases as sodium content of the silicalite increases, but the change in the activity is not as large as that in the sodium content of the silicalite (Runs 1–3 in Table 3). Very high activities were also observed for Na(1.3)-SL-Ni(0.7) and Na(0.13)-SL-Ni(0.7). The results suggest the participation of nickel ions in the conversion.

The formation of methanol in a helium stream is supposed to be caused by hydrogen transfer between formaldehyde molecules. The fact that the formation of methanol depends on the sodium content of the catalyst (Runs 1–3 in Table 3) suggests participation of the sodium ions in the reaction. Nickel ions are also assumed to participate in the reaction since Na(1.3)-SL-Ni(0.7) containing nearly as much sodium as Na(1.2)-SL-Al(0.01) catalyzes the methanol formation to a greater extent than Na(1.2)-SL-Al(0.01) (cf. Runs 4 and 1 in Table 3). In addition, the yield of methanol over sodium-poor Na(0.13)-SL-Ni(0.7) is less than that of Na(1.2)-SL-Al(0.01) (cf. Runs 5 and 1 in Table 3). On the basis of these results, the formation of methanol is assumed to be catalyzed by the cooperation between nickel and sodium ions.

With a hydrogen gas carrier, formaldehyde conversion over silicalite is enhanced in comparison with the results under a helium stream, by hydrogen (cf. Runs 6 and 1 or Runs 7 and 3 in Table 3), and the yields of both carbon monoxide and methanol increase. Aika *et al.* investigated the conversion of formaldehyde over nickel metal in a hydrogen stream in the temperature range 470–670 K (*20*), and reported that formaldehyde is decomposed mainly to carbon monoxide and hydrogen but methanol is also produced by formaldehyde hydrogenation. It is noteworthy that methanol was formed over sodium-poor Na(0.03)-SL-Al(0.01) in a stream of hydrogen (Run 7 in Table 3). Taking account of their results and the fact that nickel ions in Na(0.13)-SL-Ni(0.7) and some of the cations in Na(1.3)-SL-Ni(0.7) were reduced by hydrogen at 670 K, a portion of the nickel ions in Na(0.03)-SL-Al(0.01) and Na(1.2)-SL-Al(0.01) is assumed to be reduced to metal during the heating in a hydrogen stream at 770 K prior to the injection of formaldehyde. Considerable deactivation of Na(0.03)-SL-Al(0.01) and Na(1.2)-SL-Al(0.01) by successive injection of formaldehyde in a hydrogen stream (Fig. 4) would be brought about by aggregation of nickel particles because the deactivated catalysts cannot be regenerated by calcination in the air. The slow deactivation of Na(1.2)-SL-Al(0.01) compared with Na(0.03)-SL-Al(0.01) suggests the suppression of aggregation by sodium ions.

In order to evaluate the catalytic activity for the formaldehyde conversion except for methanol formation, it is necessary to exclude the contribution of methanol formation. In the case of a reaction with a helium gas carrier, it is assumed that formation of one molecule of methanol accompanies formation of one molecule of carbon monoxide. Assuming that the methanol is formed by a bimolecular reaction of formaldehyde and that the methanol produced does not react any more (the methanol conversion hardly advances over Na(1.2)-SL-Al(0.01) at 670 K), the formaldehyde conversion excluding the contribution of methanol formation, C, is obtained from the equation

$$C = C_T - 2C_M$$

where C_T = total formaldehyde conversion, C_M = conversion to methanol. The conversion, C, is respectively given 12% to Na(1.2)-SL-Al(0.01) (Run 1 in Table 3), 11% to Na(0.4)-SL-Al(0.01) (Run 2), and 8% to Na(0.03)-SL-Al(0.01) (Run 3). These values do not differ significantly compared with the difference in sodium content of the catalysts. Thus, the sodium ions are assumed to participate scarcely in the formaldehyde conversion except for the methanol formation.

Catalytic Activity of Sodium-Modified Silicalite in Continuous Flow System

It was observed that methanol is decomposed to carbon monoxide, etc., at the initial stage of the continuous flow reaction of methanol over Na(1.2)-SL-Al(0.01) but the selectivity to formaldehyde after the initial stage is very high while the catalytic activity gradually decreases. As discussed above, carbon monoxide is formed by formaldehyde decomposition, which is catalyzed mainly by transition metal impurities such as nickel species. The transition metal impurities would be cations at the start of the reaction; however, it is assumed that they are reduced by the reaction mixture including hydrogen and rapidly deactivated at the initial stage of the continuous flow reaction.

As shown in Fig. 3, the carbon monoxide yield of the methanol conversion over Na(1.2)-SL-Al(0.01) decreases with an increase in methanol dose from 15 μmol although the formaldehyde yield increases; Fig. 6 shows that the carbon monoxide yield depends on the amount of formaldehyde in the reaction. On the other hand, the formation of carbon monoxide is suppressed by methanol (Fig. 5), and the methanol conversion decreases with an increase in the methanol dose (Fig. 3); thus, the decrease in the carbon monoxide yield is assumed to be caused by the suppression effect of methanol. It is presumed that the change in the carbon monoxide yield corresponds approximately to that in the formaldehyde yield because the main products of the methanol conversion are formaldehyde, carbon monoxide, and hydrogen, and because carbon monoxide is formed by decomposition of the formaldehyde. However, Fig. 3 shows that the absolute change in the formaldehyde yield is quite smaller than that in the carbon monoxide yield. This suggests that all of the produced formaldehyde does not desorb to the gas phase and that part of the formaldehyde remains on the surface; therefore, polymerization of the adsorbed formaldehyde would cause deactivation of the catalyst with time on stream in the continuous flow system.

The rate of deactivation of Na(1.2)-SL-Al(0.01) in methanol dehydrogenation tends to increase with an increase in the rate of the methanol feed (Fig. 1). The impurities in the carrier gas are not responsible for the deactivation because the catalytic activity is kept in the pulse system in which the carrier gas continuously passes through the catalyst. Consequently, it is necessary to consider another deactivation mechanism in which methanol participates, such as formation of hemiacetal from methanol and formaldehyde (*21*); however, further research is necessary to elucidate such a mechanism.

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