Dehydrogenation of Methanol to Formaldehyde over Silicalite

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Formaldehyde is formed by catalytic dehydrogenation of methanol over silicalite containing sodium ions at 670—820 K.

Formaldehyde, when produced industrially by oxidative dehydrogenation of methanol contains a large amount of water, which is generally undesirable. Therefore, dehydrogenation of methanol at low temperatures, below *ca.* 800 K, would be an attractive industrial process.

It is known that alkali metal cation-exchanged zeolites catalyse the dehydrogenation of alcohols,[1,2] but selective methanol dehydrogenation to formaldehyde on zeolites has not been reported. Formaldehyde is thought to be formed as an intermediate in the alkylation of toluene with methanol on alkali metal cation-exchanged zeolites.[3] In methanol conversion, the dehydrogenation reaction is overwhelmed by, for example, dehydration to dimethyl ether which occurs on the acid sites of the zeolites.

Silicalite is an aluminium-free crystalline silicate which has the same structure as ZSM-5 type zeolite. Because the acidity of ZSM-5 depends on the aluminium content,[4] aluminium-free silicalite does not have any acid sites. Further, silicalite is able to contain alkali-metal cations[5] which might make silicalite basic; this may be pertinent since alcohol dehydrogenation has been assumed to occur at basic sites.[6] This paper reports methanol conversion into formaldehyde on the modified silicalite.

Silicalite was synthesized using a patented method.[5] Tetrapropylammonium hydroxide was used in the synthesis; the organic products were removed by heating in air at 770 K for 8 h. The sample (Na-SL) contained (wt. %): Na, 1.2; Si, 44; Al, 0.01; Fe, 0.01; Ni, 0.01. The sodium in Na-SL was removed by refluxing in water; this sample, denoted 0-SL, contained (wt. %): Na, 0.03; Si, 45; Al, 0.01; Fe, 0.01; Ni, 0.01. The *X*-ray diffraction patterns were in agreement with those reported by Olson *et al.*[7]

Table 1. Methanol dehydrogenation on Na-SL in a continuous flow reactor.[a]

Catalyst/mg	Flow rate/ ml min^{-1}	Partial pressure MeOH/Torr	Selectivity to H_2CO/%	Conversion of MeOH/%
50	10	12	98	16
50	20	12	100	9
50	20	17	99	9
100	20	13	99	27
100	40	12	98	8

[a] Reaction conditions: 750 K; He carrier gas; time on stream 1 h.

Reactions were carried out at 750 K in a fixed bed flow system or a pulse microcatalytic reactor. Dehydrogenation occurred and formaldehyde and hydrogen were the main products. The reaction was carried out under various conditions as shown in Table 1. The typical time course of the reaction is shown in Figure 1. The catalyst was quickly deactivated but was regenerated by calcination in an oxygen atmosphere at 750 K. Other reaction products were carbon monoxide, carbon dioxide, methane, and small amounts of water and dimethyl ether.

To investigate the initial stage of the reaction, the dehydrogenation was carried out in a pulse microcatalytic reactor. Conversion of methanol on Na-SL was detected at reaction temperatures above 620 K. Sodium ions in silicalite seem to be important in the reaction since 0-SL had little activity. The products obtained were in agreement with those obtained using the flow technique. Dehydration occurred as a side reaction, but only minor amounts of products were obtained. By decreasing the amount of methanol injected or increasing the reaction temperature, the conversion and selectivity to carbon monoxide were increased as shown in Table 2. When an aqueous solution of formaldehyde was injected onto Na-SL at 620 K, formaldehyde was converted into carbon monoxide and a small amount of methanol. This suggests that methanol

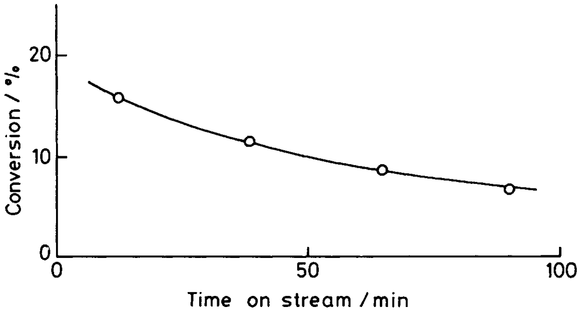

Figure 1. Methanol dehydrogenation on Na-SL in a continuous flow reactor. Reaction conditions: 50 mg catalyst, 750 K, He carrier gas 20 ml min^{-1}, partial pressure MeOH, 12 Torr.

Table 2. Methanol conversion on Na-SL in a pulse microcatalytic reactor.[a]

Reaction temperature/K	MeOH/µl	Selectivity/% CO	CO_2+CH_4	H_2CO	Me_2O	Conversion of MeOH/%
670	1	8	12	73	6	5
720	1	12	22	61	6	18
770	1	49	6	45	—	47
770	2	33	6	59	1	20
820	1	72	1	27	—	83
820	3	43	2	54	0.6	17

[a] Reaction conditions: He carrier gas 10 ml min^{-1}; 10 mg catalyst.

conversion into carbon monoxide occurs *via* decomposition of formaldehyde.

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References

1 Y. Matsumura, K. Hashimoto, S. Watanabe, and S. Yoshida, *Chem. Lett.*, 1981, 121.
2 T. Yashima, H. Suzuki, and N. Hara, *J. Catal.*, 1974, **33**, 486.
3 H. Itoh, A. Miyamoto, and Y. Murakami, *J. Catal.*, 1980, **64**, 284.
4 J. C. Vedrine, A. Auroux, V. Bolis, P. Dejaifve, C. Naccache, P. Wierzehowski, E. G. Derouane, J. B. Nagy, J. P. Gilson, J. H. C. van Hooff, J. P. van den Berg, and J. Wolthuizen, *J. Catal.*, 1979, **59**, 248.
5 U.S. Patent 4 061 724, 1977.
6 C. L. Kibby and W. K. Hall, *J. Catal.*, 1973, **29**, 144.
7 D. H. Olson, W. O. Haag, and R. M. Lago, *J. Catal.*, 1980, **61**, 390.