Novel Anion Exchange Resin-based Catalyst for Liquid-phase Methanol Synthesis at 373–393 K

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A thermo-stable anion exchange resin–Raney Cu system was found as the most effective solid catalyst for low-temperature liquid-phase methanol synthesis at 373 to 393 K under 5.0 MPa of syngas ($2H_2/CO$). With the catalyst (20 mL of the resin and 2.0 g of Cu) suspended in methanol solution 72% of CO was converted to methanol (70%) and methyl formate ($HCOOCH_3$) (30%) in 4 h.

Methanol is produced through gas phase reaction using copper–zinc based catalyst at 523–573 K under 5–20 MPa. Under these conditions, equilibrium limit of methanol yield is 20 to 40%. The separation and recycling process of the unreacted syngas requires large energy consumption.

Equilibrium conversion of methanol synthesis is high at low temperatures and high pressures as shown in Table 1. The group of italic number shows the condition under which methanol vapor pressure is lower than the equilibrium methanol pressure, so that methanol synthesized in the gas phase condenses automatically to liquid.[1] If any solid catalyst is developed and is active at such low temperatures, neither separation nor recycle process is necessary. The solved syngas and intermediate methyl formate ($HCOOCH_3$) are the possible impurities of the methanol product.

Several catalyst systems such as alkali alkoxide mixed with Ni compounds or Cu–Cr[2,3] and sodium methoxide–Ni[4] have been reported as the first success for the low temperature liquid phase methanol synthesis. The reaction proceeds through the following two steps:

$$CH_3OH + CO \rightarrow HCOOCH_3 \tag{1}$$

$$CH_3O^-(+Na^+) + CO \rightarrow CH_3OCO^-(+Na^+) \tag{1-a}$$

$$CH_3OCO^-(+Na^+) + CH_3OH \rightarrow HCOOCH_3 + CH_3O^-(+Na^+) \tag{1-b}$$

$$HCOOCH_3 + 2H_2 \rightarrow 2CH_3OH \tag{2}$$

Sodium methoxide catalyzes the first step (Eqs 1-a and 1-b are the mechanistic details), and metals (Ni or Cu) catalyzes the second. CH_3ONa–Raney Ni dissolved and suspended in methanol solution work even at 423 K under 5 MPa of syngas with the CO conversion of 95% and methanol selectivity of 99% in 4 h.[4] Excepting small amount of methyl formate, no other byproduct was formed.[4] These systems are being to be used for low-temperature liquid phase methanol synthesis in the future, too. However, the level of sodium methoxide in the reactor undergoes a continuous decrease because it is soluble in methanol. Thus, the separation process of catalyst (CH_3ONa–metal) from methanol is inevitable. Conventional Cu-Zn catalysts can work according to Eqs 1 and 2 (but not Eqs 1-a and 1-b) using an alcohol-based co-catalyst under temperatures as low as 443 K. However, the activity is not high enough.[5]

Table 1. Percentage CO conversion of methanol synthesis ($2H_2 + CO = CH_3OH$) under the equilibrium as functions of temperature and pressure

Temperature/K	Total Pressure/MPa					CH_3OH Vapor Pressure[a]/MPa
	0.1	0.5	2.0	5.0	10.0	
473	1.1	27	—	***84***	***90***	3.8
453	3.3	83	80	***89***	***93***	2.6
423	21	—	***89***	***94***	***96***	1.3
403	—	82	***93***	***96***	***98***	0.60
373	—	***92***	***97***	***98***	***99***	0.35

[a] Automatic product separation occurs if methanol vapor pressure is lower than the equilibrium pressure of the synthesized methanol.

The aim of our project is to replace sodium methoxide with solid bases or anion exchange resins to find an active solid catalytic system for methanol synthesis. Solid bases such as MgO or CaO did not catalyze the carbonylation reaction described by Eq 1, while anion-exchange resins such as Amberlyst® A26 (Rohm and Haas Co. Ltd., $-CH_2N(CH_3)_3{}^+Cl^-$, maximum operating temperature of 333 K) is known to be active to exchanging alkoxides (Eq 3) and to catalyze Eq 1.[6–8] Around 83% of CO was converted to methyl formate at 333 K under 5.0 MPa of CO using A26 exchanged with methoxide.[7]

$$Resin^+Cl^- + NaOCH_3 \rightarrow Resin^+CH_3O^- + NaCl \tag{3}$$

Carbonylation (Eq 1) is proved to be such an easy reaction over resin–alkoxide system working at low temperature. In this instance is needed any heat-resistant anion-exchanging resin working at high temperatures (373 to 423 K). Because the hydrogenation of methyl formate (Eq 2) is a slow reaction over metals, we intended to operate the two reactions above 373 K at the same time. Meanwhile, a heat-resistant anion-exchanging resin with $-(CH_2)_4-N(CH_3)_3{}^+Cl^-$ functional group (DIAION® TSA1200, Mitsubishi Chemical Co. Ltd., maximum operating temperature of 373 K) was newly developed,[9] and tested for carbonylation (Eq 1) at 373–393 K.

20 mL of the resin[10] was added to a solvent media composed of methanol (0.40 mol) and tri(ethylene glycol) dimethyl ether (triglyme) then subjected to the reaction. The reaction was carried out in a magnetically stirred autoclave (234 mL) with a batch operation. The reactant gas ($CO/Ar = 4/1$) was pressurized to 5.0 MPa. Then, the temperature was increased to 373–393 K. The extent of methanol carbonylation over TSA1200 reached about 80% of the equilibrium in 15 min (before reaching the set temperature) and then the equilibrium was attained in 40 min at 373–393 K. The CO was added again to the same batch. The initial reaction (CO decrease) rates were much the same for the 2 runs for TSA1200, suggesting that the resin was not deactivated at 373–393 K. On the other hand, the activity of A26 declined in several runs even at 373 K.

Next, we studied the hydrogenation of $HCOOCH_3$ (Eq 2) by

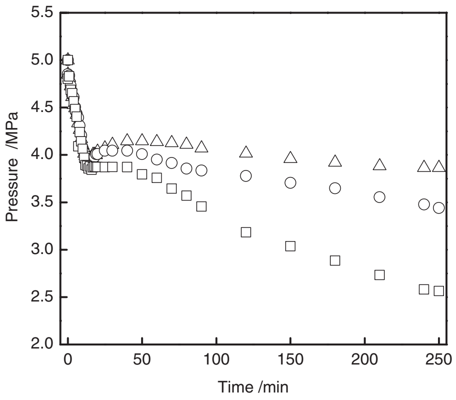

Figure 1. Time course of pressure of syngas ($H_2/CO/Ar = 8/4/1$) during methanol synthesis using Raney Cu (1.0 g (△), 2.0 g (○), or 4.0 g (□)) and TSA1200 (20 mL) in triglyme (70 mL) and methanol (406 mmol). Temperature was raised at 5 K·min^{-1} and kept constant at 393 K.

using Ni and Cu (both in Raney form[11]). Hydrogenation of methyl formate (13 mL, 97.5%) was carried out over 2.0 g of Ni (or Cu) in triglyme (87 mL) solution under 5.0 MPa of H_2/Ar (=8/1) in the same autoclave for 15 h. A comparable amount (24 mmol) of CH4 was produced in addition to methanol (29 mmol) for the case of Ni at 423 K. On the other hand, hydrogenation of $HCOOCH_3$ over Cu gave CH_3OH exclusively; 106 mmol at 423 K for 3 h, 39 mmol at 393 K for 5 h. indicating Raney Cu was active and selective for Eq 2.

Now the resin and Raney Cu were added together and methanol synthesis under 5.0 MPa of syngas ($CO/H_2/Ar = 4/8/1$) was tested using the same autoclave. The results obtained at 393 K for different amount of Cu are shown in Figure 1. The gas pressure drops rapidly for the first 15 min before reaching the set temperature of 393 K, independent from the Cu amount. In this period, the methanol carbonylation (Eq 1) proceeds over the resin. The slow pressure drop during the initial period depended on the Cu amount. Here, the hydrogenation of $HCOOCH_3$ (Eq 2) occurs. After the 4 h-run with 2.0 g of Cu, 72% of CO was reacted to produce 33 mmol of methanol and 6.9 mmol of methyl formate.

The same type of experiments were conducted for 3 times at 373 K. The results are shown in Figure 2. Here also, the first pressure drop is due to CO consumption (Eq 1) and the second due to H_2 reaction (Eq 2). Since the second reaction is slow, some methyl formate is left unconverted and thus the H_2/CO ratio is higher than 2 at the end of every run. However, syngas with the ratio of 2 (H_2/CO) was again added at the beginning of 2nd and 3rd runs. Thus, the consumption of CO was smaller (41 mmol) in the 2nd run and much smaller (26 mmol) in the 3rd run than in the 1st run (57 mmol), due to the equilibrium limitations (methyl formate is left unconverted).

The total hydrogen consumption (126 mmol) after 3 runs was estimated from the pressure drop and gas analysis. The half of this amount (63 mmol) must be equal to produced methanol (Eqs 1 and 2). The measured value of 59 mmol corresponded to the above mentioned value. The left methyl formate after third run was 71 mmol. The sum of the two products (130 mmol) corresponded to CO consumption (124 mmol). About 5% discrepancy of carbon mass balance may be brought by the vague methanol analysis due to low methanol increment (59/406 mmol = 15%). Under the same reaction condition Raney Ni-TSA1200 exchanged with CH_3O^- gave no methanol but only methyl formate from the syngas. Probably Cu (and Cu^+) activates H_2 heterolytically (to $H^+ + H^-$), while Ni does it in homolytic way (to H• + H•).

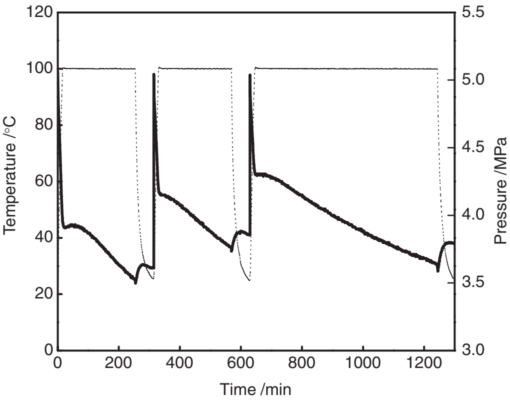

Figure 2. Time course of temperature (dotted line) and pressure (solid line) of syngas ($H_2/CO/Ar = 8/4/1$) using Raney Cu + TSA1200 (2.0 g + 20 mL) in triglyme and methanol (406 mmol). After 4-h run, the syngas was added to 5.0 MPa and the next run started. Consecutive three runs were recorded.

From these experiments the followings were concluded. 1) Methanol was catalytically produced with TSA1200/Cu at 373–393 K with an appreciable rate. 2) The second step (Eq 2) was slower (rate-determining step) than the first (Eq 1). However, the hydrogenation rate can be accelerated by increasing the amount of Cu or by increasing the reaction temperature. (At present the temperature limit of the resin is 373–393 K.) Thus, the amount of intermediate $HCOOCH_3$ can be controlled. 3) This is the first example of active solid catalyst for low-temperature liquid-phase methanol synthesis from syngas at 373–393 K.

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10 The resin was treated with HCl aq solution, NaOH aq solution, and CH_3ONa (1 mol·L^{-1}) methanol solution. Cl^- in the resin was confirmed to be exchanged almost completely with methoxide by SEM-EDX.
11 Raney Ni or Cu were prepared by leaching 4.0 g of an Al–Ni (50/50 wt %) or Al–Cu (50/50 wt %) alloy in 50 mL of 5 N NaOH at 353 K. The surface area of the Raney Ni (Cu) was 84 (92) m^2·g^{-1}.