[Letter]

Methanol Synthesis from Carbon Dioxide and Hydrogen via Formic EsterYoshitada Sakaiya, Li Fan ^{*}, Kaoru FujimotoDepartment of Applied Chemistry, School of Engineering,
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A new route of methanol synthesis, at 473 K and 30 bar, from carbon dioxide and hydrogen through formic ester was reported, by using active carbon supported palladium catalyst and coexisting weak base. This one-pot reaction consisted of 3 steps: (1) formic acid synthesis from CO₂ and H₂, (2) esterification of formic acid by ethanol to ethyl formate, (3) hydrogenolysis of ethyl formate to methanol and ethanol, the rate-determining step. Longer reaction time favored methanol synthesis and high CO₂ conversion.

1. Introduction

As carbon dioxide is the main source of green house effect, it is very important to fix it or to change it to other chemicals. Because of its low reactivity, it is difficult to synthesize oxygenates such as methanol and methyl formate from carbon dioxide. Generally high temperature and high pressure are necessary for oxygenate synthesis from hydrogenation of carbon dioxide. Jessop et al. reported that supercritical-phase CO₂ can be hydrogenated to formic acid by a coordinated ruthenium catalyst, with the aid of amine and/or further additive ¹⁾. On the other hand, methanol synthesis from CO and H₂ via methyl formate has been widely studied, where carbonylation of methanol, hydrogenation of methyl formate were included ²⁾⁻⁴⁾. But in this reaction, CO₂ and H₂O were poisonous to the catalyst and must be completely removed from syngas. BNL method is an effective synthesis route for low-temperature methanol synthesis from syngas where the catalyst is derived from coexisting acetate, alcohol and sodium hydride ⁵⁾. Similarly CO₂ and H₂O can not be included in the reactant gas.

Based on the literature above, we propose a new reaction route, which is hydrogenation of carbon dioxide to methanol via formic ester. More concretely, it is composed of three steps as shown below: (1) carbon dioxide is hydrogenated to formic acid, (2) immediately it reacts with ethanol, accompanying

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solvent to form ethyl formate, (3) then methanol and ethanol are produced by further hydrogenolysis of ethyl formate. Thermodynamically, methanol synthesis from CO_2 and H_2 is favored at low temperature, indicating the feasibility of this new route. In fact, step (1) should be easily realized, as formate was the intermediate of water-gas shift reaction. Step (2) is well known to be a very fast reaction. Step (3) is industrially operated at 453 K and 30 bar on some solid catalysts³⁾. Theoretically, this new route seems not to be very difficult, if suitable catalyst is employed. We aim to accomplish these three reactions in one reactor. The supported Pd catalyst on active carbon showed highest activity among active carbon supported metal catalysts, while the weak base as additives (carbonate etc.) coexisted. The reaction conditions were investigated in use of these catalysts and additives. It is expected that methanol or formic ester can be formed from carbon dioxide at mild reaction conditions.

2. Experimental

Typical batch reactor was employed in the reaction. Loading of Pd for the Pd / active carbon (A.C.) catalyst (N.E.CHEMCAT) in this study was 5wt%. Before reaction, catalyst was reduced in H_2 gas at 673 K under atmospheric pressure. In the experiment the Pd / A.C. catalyst and additive was put into the reactor, and ethanol as a solvent was poured in, and the pressurized mixture gas of H_2 (75%) and CO_2 (25%) was introduced, then the reaction took place at the desired temperature. The standard reaction conditions were as follows: catalyst weight=0.20 g; additive (K_2CO_3) weight=0.10 g; solvent quantity=172 mmol; mixture gas quantity=63 mmol (CO_2), 21 mmol (H_2); initial pressure=30 bar.

All products were confirmed on GC-MS (Shimadzu GCMS 1600) and analyzed by gas chromatography (Shimadzu GC-8A).

3. Results and Discussion

The results in **Table 1** show the effect of the base addition. The catalyst used was Pd / A.C. catalyst. If the basic additive was not used, diethyl ether was produced, by the dehydration of two molecules of ethanol. Ethyl formate and methanol were not produced at this condition (at 473 K, for 2 h), without the base addition. At any case, CO selectivity was high, due to the reverse water-gas shift reaction of CO_2 and H_2 . It is well known CO_2 could hardly adsorb onto the supported Pd and Pt catalysts, without the aid of the support or additive^{6,7)}. It is considered that carbon dioxide could easily adsorb onto the catalyst by the aid of base; and the target reaction was possible to proceed.

It is clearly demonstrated in **Table 1** that, with the addition of weak base, ethyl formate formed

remarkably, indicating that reactions (1) and (2) proceeded smoothly. It should be noted here that the methanol did not form, as the reaction temperature or the reaction time was not enough, which will be discussed below.

Table 1 The effect of coexisted base

Additive	CO ₂ conv. (%)	CO sel. (%)	CH ₄ sel. (%)	C2+ sel. (%)	ethyl formate sel. (%)	ethyl ether yield (mmol)
None	0.42	44	16	40	0	1.8
Li ₂ CO ₃	1.2	29	65	0	6	0.02
K ₂ CO ₃	2.5	74	2	0	24	0
Na ₂ CO ₃	1.2	36	4	0	60	0
Cs ₂ CO ₃	1.8	50	10	0	40	0
CH ₃ COOK	2.2	50	30	0	20	0
CH ₃ COONa	1.9	54	11	0	35	0
HCOOK	4.7	79	1	0	20	0

Catalyst: 5 wt% Pd/A.C.; solvent: ethanol; reaction time: 2 h; temperature: 473K.

These bases could be supported onto Pd/A. C. catalyst and used for the reaction. But in this case, the yield of ethyl formate and/or methanol was lower than that of the directly-added case. The results in **Fig. 1** and **Fig. 2** exhibit the effect of the reaction temperature and reaction time in the reaction with Pd / A.C. and K₂CO₃. CO was produced in large amount, and it indicated that reverse water-gas shift reaction happened meanwhile. The selectivity of the produced ethyl formate was increased as the reaction

Reaction conditions: reaction time 2 h; catalyst 5 wt% Pd/ A.C.; additive K₂CO₃; solvent ethanol

Fig.1 The Effect of Reaction Temperature

Reaction conditions: reaction temp. 473 K; catalyst 5 wt% Pd/ A.C.; additive K₂CO₃; solvent ethanol

Fig.2 The Effect of Reaction Time

temperature rose up to 443 K, and it was decreased while the temperature was higher. Methanol was not produced if reaction temperature was below 473 K, in the case of 2 h reaction. But as exhibited in **Fig. 1**,

when the reaction temperature was higher than 473 K, methanol selectivity increased obviously, even if the reaction time was only 2 h.

On the other hand, if reaction time became longer than 2 h, methanol could be produced at 473 K, as shown in **Fig. 2**. It is estimated that even if at low temperature such as 473 K or lower, methanol can be still synthesized in high selectivity if the reaction time was prolonged. It is clear that in **Fig. 2** where Pd/A.C. and K_2CO_3 was used, CO_2 conversion was enhanced remarkably while the reaction time increased. Meanwhile CO selectivity was nearly the same and methanol selectivity was increased gradually, with the correspondent decrease of ethyl formate. These results suggested that methanol was produced from carbon dioxide and hydrogen via ethyl formate. And it seemed that the hydrogenolysis of ethyl formate was the rate-determination step in this series reaction. It was easy to form ethyl formate, slower to convert ethyl formate to methanol. Longer reaction time or slightly higher reaction temperature was favorable to reaction (3), methanol synthesis from hydrogenolysis of formic ester. Also, a large amount of coexisting ethanol was not favorable to reaction (3), due to the equilibrium limitation. As the overall reaction of these three steps is exothermic, rather high temperature should lead to the low formation rate of methanol. As both reactions (1) and (3) are molecule-reducing reactions, high reaction pressure would be helpful to the overall reaction.

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Keywords

Carbon dioxide, Hydrogenation, Hydrogenolysis, Methanol, Ethyl formate, Palladium catalyst