DIRECT SYNTHESIS OF ACETIC ACID FROM METHANE AND CARBON DIOXIDE OVER SiO_2 AND TiO_2 SUPPORTED Pd AND Rh CATALYSTS

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Introduction

Based on the beneficial experience in synthesis of acetic acid from CO_2 and H_2, the pioneer noticed of two pieces of information in support of this research. One was the level 435.43 kJ/mol of bond energy of H–H bond in H_2, which is equivalent to that of C–H in CH_4; the other was the same intermediate CH_x involved in both CH_4 activation and CO_2 hydrogenation. And this led to a novel and interesting route to conversion of greenhouse gases, CH_4 and CO_2, directly to acetic acid by a two-step sequence employing heterogeneous catalysts like Cu-Co oxides[1]. In this work, we have investigated the supported transition metal catalysts and found that Pd and Rh catalysts exhibited a better performance.

Experimental

The catalysts were prepared by incipient wetness impregnation of silica from an aqueous solution of their chlorides. The slurry was dried at 110 °C for 16 h and then calcined at 500 °C for another 5 h. The reaction was implemented in a micro-reactor at atmospheric pressure with 400 mg catalyst (sized 40-60 mesh). A flowing argon (at a flow rate of 100 cm^3/min) was first used for 10 min to purge out the impurity gases in the reactor. The catalyst was then reduced from the room temperature to 400 °C. The reactor was maintained at this temperature for 2.5 h. The catalyst was then cooled in argon (or nitrogen) stream to the desired temperature. After that, a two-step sequence began with exposing the catalyst to a flow of CH_4 (85 cm^3/min) for 5 min and CO_2 (85 cm^3/min) for 10 min in turn. More CO_2 was fed to increase the yields on the basis of the consumed CH_4. The products were collected at ice-water mixture temperature by a bubbling absorber filled with caustic soda solution (50 ml). After reaction for 20 turns around 5 h, the products were analyzed by IC20 gas chromatography.

Results and Discussion

Figure 1 shows the yield of acetic acid synthesized directly from CH_4 and CO_2 over Pd/SiO_2 catalysts, while Figure 2 presents the results obtained from Rh/SiO_2 catalysts.

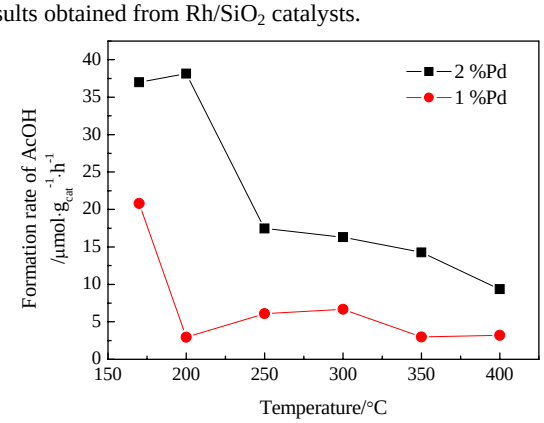

Figure 1. The formation rate of AcOH over Pd/SiO_2 at different temperatures

One can observe an apparent decline and a slight decline vibrated in acetic acid yield along with the temperature rises from 170 to 400 °C in the presence of catalyst 2%Pd/SiO_2 and 1%Pd/SiO_2.The maximum yield of acetic acid is 37.0 and 38.2 μmol/g_{cat}·h at 170 °C and 200 °C of the former, and the latter is 20.8 μmol/g_{cat}·h. An interesting point we noticed is that some formic acid was also formed for reaction carried out at 300 °C over both 2%Pd/SiO_2 and 1%Pd/SiO_2.

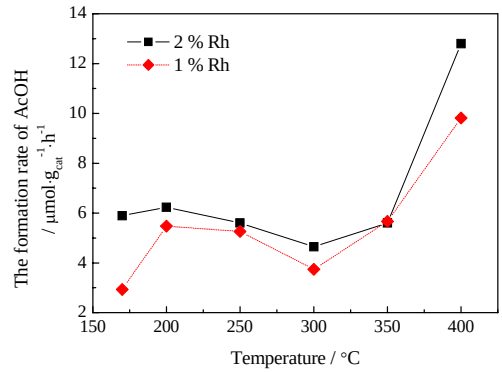

Figure 2. The formation rate of HCOOH over Rh/SiO_2 at different temperatures

The catalysts Rh/SiO_2 can also give to acetic acid. However, its catalytic activity was not as good as we expected. As represented in Figure 2, the yield of acetic acid does not exhibit a marked decline, but ascend as the temperature rises. The best results we obtained in our experiments are 12.8 μmol/g_{cat}·h for 2%Rh/SiO_2 and 9.8 μmol/g_{cat}·h for 1%Rh/SiO_2 at 400 °C. And no formic acid was observed. Unsurprisingly, a higher yield can be achieved by using more supported amount of metal.

TiO_2-supported Rh, Pd catalysts give results similar to SiO_2. The yield of acetic acid over Pd catalyst is higher than Rh catalyst, as shown in Figure 3. And, only Pd catalyst can lead to a formation of formic acid too. The yield of formic acid is shown in Figure 4.

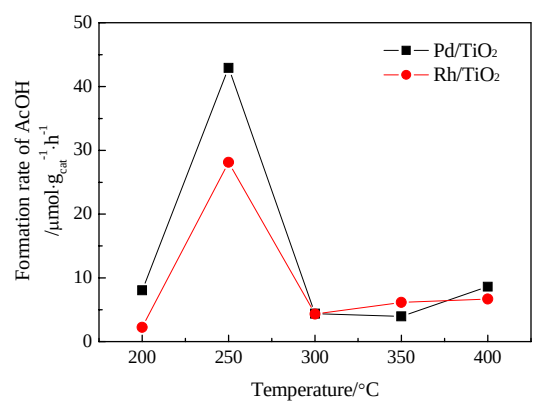

Figure 3. The formation rate of AcOH over Pd, Rh/TiO_2 at different temperatures

The present investigation has confirmed the effectiveness of the direct synthesis of acetic acid directly from methane and carbon dioxide. This route provides a potentially valuable means to convert directly greenhouse gases, CH_4 and CO_2, to acetic acid, a useful target molecule for methane conversion[2]. Further study is being conducted.

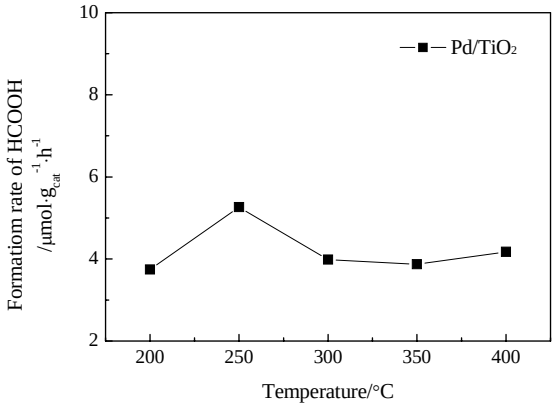

Figure 4. The formation rate of HCOOH over Pd /TiO_2 at different temperatures

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References

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(2) Lin, M.; Sen, A. *Nature*, **1994**, *368*, 613.