Heterogeneous Catalysis

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Water-Enhanced Synthesis of Higher Alcohols from CO_2 Hydrogenation over a Pt/Co_3O_4 Catalyst under Milder Conditions

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Abstract: *The effect of water on CO_2 hydrogenation to produce higher alcohols (C_2–C_4) was studied. Pt/Co_3O_4, which had not been used previously for this reaction, was applied as the heterogeneous catalyst. It was found that water and the catalyst had an excellent synergistic effect for promoting the reaction. High selectivity of C_2–C_4 alcohols could be achieved at 140°C (especially with DMI (1,3-dimethyl-2-imidazolidinone) as co-solvent), which is a much lower temperature than reported previously. The catalyst could be reused at least five times without reducing the activity and selectivity. D_2O and $^{13}CH_3OH$ labeling experiments indicated that water involved in the reaction and promoted the reaction kinetically, and ethanol was formed via CH_3OH as an intermediate.*

CO_2 is a greenhouse gas. Meanwhile, it is an abundant, nontoxic, and renewable carbon resource.[1] Transformation of CO_2 into highly valuable chemicals is of great importance.[1] It has been used as a C1 building block to produce various chemicals, such as carboxylic acids, esters, 2-oxazolidinones, methylamines, alcohols, hydrocarbons, and olefins.[2]

Alcohols are very useful chemicals in industry. Synthesis of methanol from CO_2 hydrogenation has attracted extensive attention in recent years.[3] The higher alcohols ($C_{2+}OH$), which are well-known commodity chemicals and have higher energy densities than methanol, have wide applications.[4] Compared to methanol, the synthesis of $C_{2+}OH$ from CO_2 and H_2 is a more difficult, but it is a very important topic.[5] Some work on $C_{2+}OH$ synthesis over heterogeneous and homogeneous catalysts has been reported. Many heterogeneous catalysts have been used for this kind of reaction. For example, Rh/SiO_2 catalysts promoted by Fe[6] and Li[7] generated ethanol with a selectivity of about 40% at 260°C and 70% at 240°C, respectively. The $[Rh_{10}Se]/TiO_2$ catalyst produced 83% selectivity to ethanol at 350°C.[8] Other catalysts, such as CoMoS (35.6% selectivity of $C_{2+}OH$ at 340°C),[9] physically mixed Fe- and Cu-based (74.8% selectivity of $C_{2+}OH$ at >330°C),[10] and K/Cu-Zn-Fe catalysts (87.1% selectivity of $C_{2+}OH$ at 300°C),[11] were also reported. The reaction could be carried out at lower temperatures under homogeneous catalysis. It was reported that $Ru_3(CO)_{12}$-$Co_2(CO)_8$-KI[12] and $Ru_3(CO)_{12}$-$Rh_2(CO)_4Cl_2$-LiI[13] catalytic systems could catalyze the reaction effectively at 200°C. Although the hydrogenation of CO_2 to produce $C_{2+}OH$ has been studied extensively, it is common that the heterogeneous catalysts suffer from the high temperature and/or low efficiency, and the homogeneous catalysts are limited by the difficulties in recovery and separation. It has no doubt that design of heterogeneous catalysts that are highly efficient at lower temperature is of great significance, but is a challenge.

Water as solvent or promoter can accelerate different types of reactions, such as organic synthesis,[14] Fischer–Tropsch synthesis,[15] CO methanation,[16] and the methanol synthesis from CO_2 and H_2.[17] However, the study of the effect of water on $C_{2+}OH$ synthesis by hydrogenation of CO_2 has not been reported. Herein, we carried out the first work to study the effect of water on CO_2 hydrogenation to produce $C_{2+}OH$. Pt/Co_3O_4 was applied as the catalyst, which has not been used in this reaction. It was found that water could improve the activity and selectivity of the catalyst significantly. D_2O labeling experiments indicated that water took part in the reaction by providing hydrogen source. A $^{13}CH_3OH$ labeling experiment showed that ethanol could be formed from a CH_3OH intermediate in the heterogeneous catalysis.

The catalytic performances of different metals, including Pt/Co_3O_4, Ru/Co_3O_4, Rh/Co_3O_4, Pd/Co_3O_4, Pt/ZrO_2, and Pt/CeO_2, were studied, and the results are given in Table 1. It is well-known that Co-based catalysts are effective in CO_2 and CO hydrogenation to alkanes.[18] However, in alcohol synthesis, particularly for $C_{2+}OH$, the pure Co_3O_4 catalyst exhibited much low catalytic efficiency (Table 1, entry 1). Clearly, the catalytic activity of Pt/Co_3O_4 was obviously higher than that of other catalysts (entries 2 vs. 5–9). High $C_{2+}OH$ selectivity (82.5%) and total alcohols (ROH) time-yield ($0.509\ \mathrm{mmol\,g_{cat}^{-1}\,h^{-1}}$) were obtained under the catalyzing of 1 wt% Pt/Co_3O_4 in mixed solvent (1,3-dimethyl-2-imidazolidinone (DMI) and water) at 200°C. The alcohol products included mainly methanol, ethanol, propanol, and butanol. A low or high loading of Pt (0.2 wt% or 5 wt%) on Co_3O_4 resulted in a decrease in $C_{2+}OH$ selectivity and ROH time-yield, demonstrating that the 1 wt% Pt loading was suitable for the formation of $C_{2+}OH$ (entries 3 and 4).

The characterization of the Pt/Co_3O_4 catalyst was conducted by various methods. X-ray diffraction (XRD) patterns showed that in the Pt/Co_3O_4 catalyst, Co^0 metal, CoO, and Co_3O_4 species co-existed (Supporting Information, Fig-

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Table 1: CO_2 hydrogenation over different heterogeneous catalysts.[a]

Entry	Catalyst	ROH time-yield[b]					$C_{2+}OH$ sel. [%]
		C_1	C_2	C_3	C_4	Total	
1	Co_3O_4	2.7	0.4	0	0	3.1	12.9
2	1 wt%Pt/Co_3O_4	8.9	29.0	7.8	5.2	50.9	82.5
3	0.2 wt%Pt/Co_3O_4	6.2	6.8	0.6	0	13.6	54.4
4	5 wt%Pt/Co_3O_4	5.6	12.8	2.0	0	20.4	72.5
5	1 wt%Ru/Co_3O_4	8.7	5.4	1.0	0	15.1	42.4
6	1 wt%Rh/Co_3O_4	9.7	14.1	3.3	0.9	28.0	65.4
7	1 wt%Pd/Co_3O_4	11.7	0.7	0	0	12.4	5.6
8	1 wt%Pt/ZrO_2	2.0	0.2	0	0	2.2	9.1
9	1 wt%Pt/CeO_2	2.7	0.4	0	0	3.1	12.9

[a] Reaction conditions: catalyst 20 mg, H_2O/DMI solvent (15:85, v/v) 1.0 mL, initial pressure 8.0 MPa ($H_2/CO_2 = 3:1$), 200 °C, 15 h. [b] Both $C_{2+}OH$ selectivity and ROH time-yield [$100 \times \text{mmol}\ g_{cat}^{-1}\ h^{-1}$] are based on moles of carbon. sel. = selectivity, DMI = 1,3-dimethyl-2-imidazolidinone.

Table 2: CO_2 hydrogenation over 1 wt% Pt/Co_3O_4 catalyst in different solvents.[a]

Entry	Solvent	T [°C]	ROH time-yield[b]					$C_{2+}OH$ sel. [%]
			C_1	C_2	C_3	C_4	Total	
1	none	200	0	0	0	0	0	–
2	water	200	6.8	13.4	2.5	1.6	24.3	72.0
3	water	160	6.7	6.2	2.1	0	14.9	55.3
4	water	180	6.0	12.0	2.3	0.6	20.9	71.3
5	water	220	7.3	26.1	4.6	1.9	39.9	81.7
6	DMI	200	29.6	9.4	1.6	1.1	41.7	29.0
7	NMP	200	30.3	2.5	0.5	0.3	33.6	9.8
8	Cy	200	4.5	0.3	0	0	4.8	6.3
9	n-decane	200	5.3	0.4	0	0	5.7	7.0
10[c]	NMP/water	200	10.3	24.0	5.3	3.3	42.9	76.0
11[c]	Cy/water	200	15.0	2.5	0	0	17.5	14.3
12[c]	n-decane/water	200	13.1	1.8	0	0	14.9	12.1
13[d]	DMI	200	10.3	2.1	0.1	0	12.5	17.6
14[e]	DMI	200	15.6	3.2	0.4	0	19.2	18.8
15[f]	DMI	200	9.6	0.3	0	0	9.9	3.0
16[g]	DMI	200	2.3	0.2	0	0	2.5	8.0
17[h]	DMI	200	2.5	0.3	0	0	2.8	10.7
18	DMI	140	4.9	0.1	0	0	5.0	2.0
19	DMI	160	12.7	2.1	0	0	14.8	14.2

[a] Reaction conditions: catalyst 20 mg, solvent 1.0 mL, initial pressure 8.0 MPa ($H_2/CO_2 = 3:1$), 15 h. Cy = cyclohexane. [b] Both $C_{2+}OH$ selectivity and ROH time-yield [$100 \times \text{mmol}\ g_{cat}^{-1}\ h^{-1}$] are based on moles of carbon. [c] The water volume fraction was 15 vol%. [d] The catalyst was 1 wt% Ru/Co_3O_4. [e] The catalyst was 1 wt% Rh/Co_3O_4. [f] The catalyst was 1 wt% Pd/Co_3O_4. [g] The catalyst was 1 wt% Pt/ZrO_2. [h] The catalyst was 1 wt% Pt/CeO_2.

ure S1 b). Pt was mainly reduced to Pt^0, which was confirmed by an X-ray photoelectron spectroscopy (XPS) study (Supporting Information, Figure S2 d). The XRD and/or XPS results showed that both Co and Pt species in the unreduced catalyst were oxidized forms (Supporting Information, Figures S1 and S2; details of analysis for XRD and XPS data are given in Supporting Information). The results indicated that in the Pt/Co_3O_4 catalyst, the Co oxide species was partly reduced to Co^0, and the Pt^0 and Co^0 species were both supported on Co_3O_4. A transmission electron microscopy (TEM) image showed that the Pt nanoparticles were mainly in the range of 2–6 nm, and were well-dispersed on the support (Supporting Information, Figure S3). It is known that the Co_3O_4 support could form oxygen vacancies after reduction under a reducing gas. The vacancies and supported metal then could dissociate H_2O into H and OH at the oxide–metal interface.[19] The H could act as a hydrogen source in CO_2 hydrogenation, which will be further discussed in the following paragraphs.

Table 2 presents the results of CO_2 hydrogenation in different solvents. Under solvent-free conditions, the amount of alcohols generated was negligible (entry 1). Interestingly, water favored the formation of $C_{2+}OH$ significantly. For example, 72.0 % selectivity of $C_{2+}OH$ was obtained at 200 °C (entry 2), even at 160 °C and 180 °C, the $C_{2+}OH$ selectivity was 55.3 % and 71.3 % (entries 3 and 4). When the reaction was carried out at 220 °C, the $C_{2+}OH$ selectivity increased up to 81.7 % (entry 5). DMI and *N*-methyl-2-pyrrolidone (NMP) also gave satisfactory ROH time-yield, but showed much lower selectivity of $C_{2+}OH$ (entries 6 and 7). In contrast, the hydrocarbon solvents, such as cyclohexane and n-decane, gave both low $C_{2+}OH$ selectivity and ROH time-yield (entries 8 and 9). In general, the polar solvents, such as water, DMI and NMP were better solvents for the alcohol synthesis. In particular, the $C_{2+}OH$ was obtained with high selectivity in water. Nonpolar solvents, such as cyclohexane and n-decane, however, exhibited poor performance. We also studied the reaction in the binary solvents containing water. Adding water to other solvents could improve the reaction efficiency considerably, as can be known from Table 2, entries 10–12 and Table 1, entry 2. Furthermore, we also studied the effect of water on the reaction in DMI catalyzed by Ru/Co_3O_4, Rh/Co_3O_4, Pd/Co_3O_4, Pt/ZrO_2, and Pt/CeO_2 with water (Table 1, entries 5–9) and without water (Table 2, entries 13–17). The results indicated that water could also enhance the $C_{2+}OH$ selectivity on the catalyst of Rh/Co_3O_4 and Ru/Co_3O_4 effectively. However, water improved the selectivity of the reaction less effectively over Pd/Co_3O_4, Pt/ZrO_2, and Pt/CeO_2. In general, the Pt/Co_3O_4 catalyst in DMI/water yielded much better results.

The yields of the other products at all the conditions in Table 1 and Table 2 are given in the Supporting Information, Table S1 and Table S2, respectively. CO, methane, and trace amount of higher hydrocarbons were produced. The highest selectivity to total alcohols was 33.1 % obtained in DMI/water using Pt/Co_3O_4 as the catalyst, which is comparable with the highest values reported.[6,7,9–11] However, temperature to generate higher alcohols was much lower in the catalytic system of this work because water promoted the formation of the larger alcohols effectively, which will be discussed below.

As can be seen from Table 2, entries 2–5, water itself was an excellent solvent for the reaction. Furthermore, it could

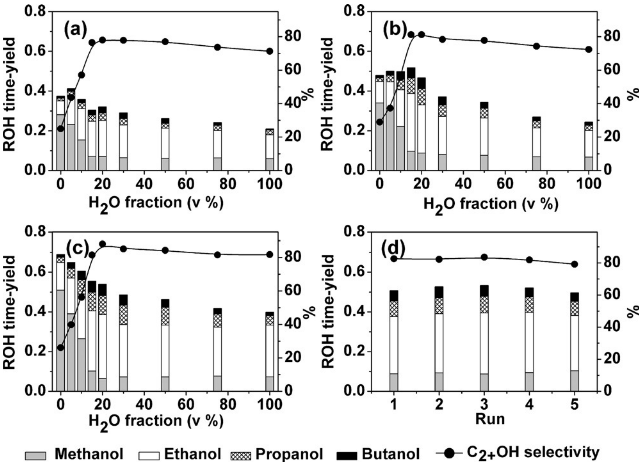

Figure 1. a)–c) Effect of H_2O volume fraction in H_2O/DMI mixed solvent on the ROH time-yield and the distribution of ROH products: a) 180 °C, b) 200 °C, c) 220 °C, and d) the reusability of the Pt/Co_3O_4 catalyst under the conditions of Table 1, entry 2. Reaction conditions: catalyst 20 mg, initial pressure 8.0 MPa ($H_2/CO_2 = 3{:}1$), 15 h. The unit of ROH time-yield is mmol $g_{cat}^{-1}\,h^{-1}$. DMI = 1,3-dimethyl-2-imidazolidinone.

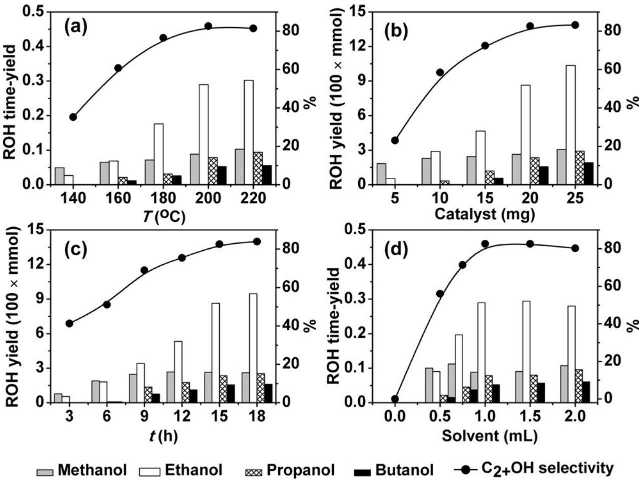

Figure 2. Effects of the reaction conditions over 1 wt % Pt/Co_3O_4 in H_2O/DMI mixed solvent (15:85, v/v) under 8.0 MPa of the initial pressure ($H_2/CO_2 = 3/1$): a) effect of temperature, catalyst 20 mg, 15 h; b) effect of catalyst amount, 200 °C, 15 h; c) effect of reaction time, catalyst 20 mg, 200 °C, and d) effect of solvent volume, catalyst 20 mg, 15 h. The unit of ROH time-yield is mmol $g_{cat}^{-1}\,h^{-1}$.

improve the performances of other solvents, especially DMI. In this work, we also studied the effect of the composition of DMI/water mixed solvent on the reaction systematically at 180 °C, 200 °C, and 220 °C, and the results are given in Figure 1. At all the temperatures, the $C_{2+}OH$ selectivity increased with the increase of water volume fraction dramatically at the beginning and then decreased slightly upon adding further water; the mixed solvent with 15–20 vol % yielded the highest selectivity to $C_{2+}OH$. At 180 °C and 200 °C, addition of small amount of water enhanced the ROH time-yield notably, but the yield decreased continuously after water fraction exceeded certain value (Figure 1 a,b). However, the ROH time-yield decreased with increasing water fraction in the entire composition range of the mixed solvent at 220 °C (Figure 1 c). One of the reasons was that in DMI, methanol was produced with a high rate at this temperature. The reactions in water/DMI mixed solvent of suitable composition were very efficient and $C_{2+}OH$ selectivities at 180 °C, 200 °C, and 220 °C are 77.0 % (15 vol % of H_2O), 82.5 % (15 vol % of H_2O), and 88.1 % (20 vol % of H_2O), respectively.

We also studied the effects of temperature, amount of the catalyst used, reaction time, and the amount of solvent used on the reaction using water/DMI mixed solvents (15:85 v/v) over 1 wt % Pt/Co_3O_4 catalyst, and the results are shown in Figure 2. The ROH time-yield increased with increasing temperature in the range of 140 °C to 220 °C (Figure 2 a). An increase in temperature also enhanced the selectivity of the $C_{2+}OH$, but the selectivity was not changed as temperature varied from 200 °C to 220 °C. The main reason was that generation of methanol from CO_2 hydrogenation is easier than forming larger alcohols. It is very interesting that the $C_{2+}OH$ selectivities with water at 140 and 160 °C could be 35.2 % and 60.7 %, respectively (Figure 2 a). The selectivity of $C_{2+}OH$ was extremely low without water at these temperatures (Table 2, entries 18 and 19), further indicating that water could promote the formation of higher alcohol. Figure 2 b shows that the major alcohol product was methanol when the catalyst amount was 5 mg. The $C_{2+}OH$ selectivity and ROH time-yield were enhanced with increasing the amount of the catalyst. After the amount of catalyst used exceeded 20 mg, $C_{2+}OH$ selectivity increased slightly. The effect of reaction time on the catalytic performance is shown in Figure 2 c. The selectivity of $C_{2+}OH$ increased with prolonging the reaction time, and reached 83.9 % with a reaction time of 18 h. The solvent volume had an important influence on the reaction (Figure 2 d). The ROH time-yield and the selectivity to $C_{2+}OH$ increased with the increase of the solvent dosage. However, the yield and the selectivity became independent of the amount of the solvent as it was larger than 1 mL.

Above results demonstrated that the synergistic effect between Pt/Co_3O_4 catalyst and water leaded to the formation of $C_{2+}OH$ with a high selectivity. To further study the water effect, D_2O was used instead of H_2O to find out whether it took part in the reaction under the conditions of entry 2 in Table 1, and the GC-MS spectra are given in the Supporting Information, Figure S4. The molecular ion peak of m/z 47, which is assigned to C_2H_6OD or C_2H_4DOH, was detected. However, this could not make conclusion that D_2O was a participating reactant because the D in D_2O could be exchanged with H in the OH group of CH_3CH_2OH. Interestingly, we also detected the m/z 48 and 49, noted as $C_2H_4D_2O$ and $C_2H_3D_3O$, respectively (Supporting Information, Figure S4), demonstrating that D_2O was indeed involved in the catalytic reaction.[17] It should be mentioned that water was not the reactant (feedstock) of the reaction because it is produced in the total reaction. In other words, water only promoted the reaction kinetically. The hydrogen source of alcohols was proved to be derived partly from the water. We further investigated whether the methanol was consumed by labeling experiment in the presence of water at the condition of entry 2 in Table 1. $^{13}CH_3OH$ was added into the reactor before reaction. Except for the m/z 46 assigned to be ethanol, the peaks at m/z 47 assigned to be $^{13}CH_3CH_2OH$ or $CH_3{}^{13}CH_2OH$ was also found (Supporting Information, Figure S5), showing that the C atom of methanol could be transferred into ethanol under the given conditions.

It is generally considered that formation of $C_{2+}OH$ involved C–C coupling and OH formation.[2j,10] Taking the synthesis of ethanol as an example, it is commonly accepted that CO_2 is firstly hydrogenated to CH_3* species (the asterisk indicates that the species is adsorbed on the surface of the catalyst), and then followed by a CO insertion which was obtained from the reverse water-gas shift reaction to form CH_3CO*. The CH_3CO* species is further hydrogenated to ethanol.[7,8] The CH_3* plays a very important role for the ethanol synthesis.[20] According to our ^{13}C labeling test above, CH_3OH could act as a carbon source for the synthesis of ethanol in the present catalytic system. Previous reports indicated that the water could promote CH_3OH dissociation on the surface of Cu(111).[21] As shown by the experimental results, water involved in the reaction could promote the formation of the $C_{2+}OH$. Herein, we speculate that the promoting effect of water on $C_{2+}OH$ synthesis was probably because water could protonate methanol to form a protonated methanol, which was easily dissociated into CH_3*, OH*, and H* (or H_2O) species. The CH_3* species could further couple with CO to CH_3CO*, which was then hydrogenated to ethanol at the active sites of Pt/Co_3O_4 catalyst. Therefore, it can be deduced that one of the main reasons for water to improve the selectivity of $C_{2+}OH$ was to assist dissociation of methanol into CH_3*, which could be more readily used in forming ethanol. It has been reported that the CH_3OH could dissociate into CH_3* and OH* or CH_3O* and H*, depending on the catalyst and operating conditions.[22] The high temperature favors the dissociation of methanol to CH_3* and OH*, while the low temperature leads to CH_3O* and H*.[22b] This is very consistent with our results that the low temperature ($< 140\,°C$) was not favorable to ethanol formation. One of the main reasons may be that the low temperature could not dissociate the CH_3OH into CH_3*. As for the $C_{3+}OH$, it could also be synthesized via the dissociation of ethanol; however, the conditions may be more severe than that of methanol, and thus the $C_{3+}OH$ selectivity was low. Therefore, the entire catalytic processes of $C_{2+}OH$ synthesis should start from the formation of CH_3OH via CO_2 hydrogenation. The CH_3OH could be homologated to ethanol. The other $C_{3+}OH$ were synthesized in the similar way.

The reusability of the Pt/Co_3O_4 catalyst was tested, and the results are illustrated in Figure 1 d. The catalyst could be reused at least five times without considerable loss in activity. As can be known from the Supporting Information, Figures S1 and S2, the XRD pattern and XPS spectra of the catalyst after it was used five times were nearly the same as those of the fresh catalyst. Besides, inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis showed that Pt leached into the solvent after reaction was only 1 ppm. All these results indicate that the catalyst was very stable in the reaction.

In summary, we have investigated $C_{2+}OH$ synthesis from CO_2 hydrogenation over Pt/Co_3O_4 catalyst in different solvents. It has been shown that solvent plays a crucial role in the reaction. Water as the solvent can enhance the reaction significantly, and it also promotes selectivity of the reaction in other solvents effectively. In water, the selectivities at 160 °C, 180 °C, 200 °C, and 220 °C are 55.3 %, 71.3 %, 72.0 %, 81.7 %, respectively, and the reaction rates are satisfactory. The reaction in water/DMI mixed solvent of suitable composition is more efficient, and the selectivity at 140 °C, 160 °C, 180 °C, 200 °C, and 220 °C can be 35.2 %, 60.7 %, 77.0 %, 82.5 %, and 88.1 %, respectively. The results of labeling experiments indicate that the water takes part in the reaction by providing a hydrogen source, and the $C_{2+}OH$ are formed with methanol as the intermediate. We believe that the Pt/Co_3O_4/water (or aqueous solution) catalytic systems that are effective at low temperature have a great potential of application in the reaction, and the strategy to use the synergistic effect of water and metallic catalysts can also be used to explore other catalytic systems for efficiently producing $C_{2+}OH$ at mild conditions.

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