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Coupling Glucose Dehydrogenation with CO_2 Hydrogenation by Hydrogen Transfer in Aqueous Media at Room Temperature

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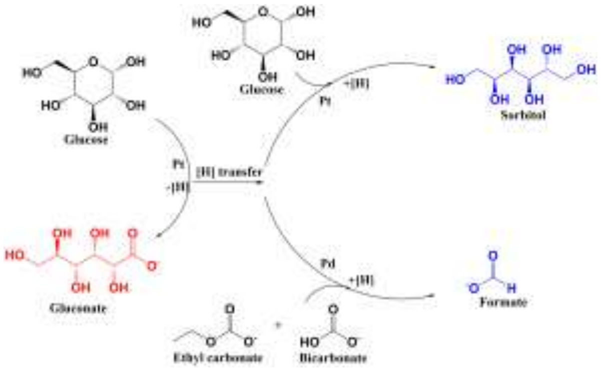
Dedication ((optional))

Abstract: Conversion of carbon dioxide into value-added chemicals and fuels provides a direct solution to reduce excessive CO_2 in the atmosphere. Herein, a novel catalytic reaction system is presented by coupling the dehydrogenation of glucose with the hydrogenation of a CO_2 derived salt, ammonium carbonate, in the ethanol-water mixture. For the first time, the hydrogenation of CO_2 into formate by glucose has been achieved under ambient conditions. Under the optimal reaction conditions, the highest yield of formate reached ~ 46 %. We find that the apparent pH value in the ethanol-water mixture plays a central role in determining the performance of the hydrogen transfer reaction. Based on the ^{13}C NMR and ESI-MS results, a possible pathway of the coupled glucose dehydrogenation and CO_2 hydrogenation reactions was proposed.

The concentration of atmospheric CO_2 increases dramatically in the recent several decades. Due to its strong connection to catastrophic global warming and climate change,[1,2] the utilization and conversion of carbon dioxide (CO_2) has received much attention recently. Although many value-added substances including methane, methanol, formaldehyde, formic acid, and organic carbonates can be produced by CO_2 hydrogenation,[3–17] few processes has been successfully realized in an industrial scale. Part of the reason is the limitation of sustainable and economically feasible hydrogen supply, which remains one of the biggest challenges for CO_2 hydrogenation. Based on the techno-economic analysis of the hydrogen production from water electrolysis, it has been highlighted that the cost of renewable hydrogen production has to decrease by at least 2.5 times to make it economically feasible for the hydrogenation of CO_2.[18]

Hydrogen generated from renewable resource such as biomass has been regarded as an promising alternative renewable energy resource to replace natural gas and petroleum.[19–22] However, hydrogen production from biomass, such as dark fermentation,[23] steam-reforming,[24] aqueous phase reforming,[25] and gasification[26] suffer from low hydrogen production rate and/or complicated processing requirements. More crucially, in these processes, CO_2 is produced in stoichiometric proportion with respect to H_2, which inherently demolish the possibility of creating a carbon negative scheme. In this respect, using biomass-derived compounds, such as alcohol,[27–31] polyol[32] or sugar,[33–36] as hydrogen donor for transfer hydrogenation of CO_2 is promising as external molecular H_2 is not needed.[37] Recently Beller's group used ruthenium pincer complexes to catalyze methanol dehydrogenation and bicarbonate hydrogenation simultaneously, providing a green synthesis route of production of formate in high yields (>90 %)[38]. However, it is well known that there are significant challenges related to the separation, reuse, deactivation, and regeneration of homogeneous catalysts. Several research groups have studied transfer hydrogenation of CO_2 with biomass-derived alcohol or polyol by transition metal catalysts, such as Fe, Zn, Ni, in high temperature (300-400 ºC) hydrothermal media.[39–43] Instead of acting as catalysts, the transition metals served as reducing agents and were oxidized simultaneously. However, the formate yield in these cases was pretty low (<10 %).[42] Recently, a novel approach to simultaneously produce value-added carboxylic acids and formate has been developed by our group via a "one-pot" aqueous-phase hydrogen transfer (APHT) process, in which the hydrogen in biomass molecules is transferred to bicarbonates over the carbon supported Pd nano-catalysts.[44] However in that study, a high reaction temperature was needed to facilitate the dehydrogenation of alcohols or polyols. Unfortunately, at the same time the decomposition of formate was also inevitably enhanced at elevated temperatures, which limited the formate yield. Therefore, low-temperature hydrogen transfer from biomass derived compounds as hydrogen donor to hydrogenate CO_2 is highly desirable and could be a sustainable strategy to produce formate.

Herein, for the first time, we present a new strategy for CO_2 reduction via a room-temperature APHT process using sugar as a hydrogen donor to reduce ammonium carbonate over



Scheme 1. The proposed primary pathways of the reactions in low temperature hydrogen transfer reaction system.

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heterogeneous Pt and Pd bimetallic catalysts. This process couples the dehydrogenation of sugar, especially glucose, with CO_2 hydrogenation in a one-pot process under ambient conditions. Under optimized experimental conditions, the yield of formate and sorbitol in the solution can be approximately 46% and 21%, respectively. We select carbohydrates such as glucose as the hydrogen source is due to its abundance as it occupies 75 % of the annual renewable biomass production.[35] At the same time, earlier work of the dehydrogenation of carbohydrate done by Bekkum et. al[33,34] also inspires us to search after the possibilities on its application. It turns out to be that the dehydrogenation of sugars such as glucose, can be suitably coupled with the hydrogenation of CO_2 in liquid phase reaction. A schematic illustration of this novel hydrogen transfer reaction is shown in Scheme 1. Glucose as a hydrogen donor can be dehydrogenated into gluconate to produce hydrogen species on Pt surface. Meanwhile part of the glucose can be hydrogenated into sorbitol by the produced hydrogen species from the dehydrogenation on Pt surface as well. It is worthwhile to point out that although the hydrogenation of glucose to sorbitol is intensively reported,[45–47] it is normally proceeded under rather high temperature and high pressure. Herein the production of sorbitol through partial hydrogenation of glucose in the ambient condition provides a new possibility of sorbitol acquisition. More importantly, formate is also obtained through the hydrogenation of CO_2 in its carbonate at the same time in an unprecedented manner in the presence of Pd catalyst. Thus three value added products can be acquired simultaneously in the present reaction system under ambient conditions.

As our previous study showed that involving ethanol as a co-solvent significantly improves the efficiency of CO_2 hydrogenation due to the creation of an active intermediate, ethyl carbonate.[48] Initially, we started present hydrogen transfer reaction from investigating the plausible effects of using ethanol-water mixture as the solvent. As shown in Table 1, ethanol as a co-solvent indeed significantly enhanced the yields of formate and sorbitol at room temperature. The formate yield increased steadily from less than 5 % to above 30 % upon the increase of ethanol content from 10 % to 50 %. At the same time, the yield of sorbitol was also doubled. Moreover, ethanol also influenced the conversion of glucose and H_2 concentration in the solvents. With 10% ethanol, the solubility of H_2 in the aqueous solvent increased. Higher local H_2 concentration around Pt might hinder the dehydrogenation of glucose, leading to the decrease of glucose conversion (64.3 % to 50.5 %). On the other hand, ethanol reacted with ammonium carbonate in the ethanol-water mixed solvent to generate ethyl carbonate which has been proved to be a highly active intermediate for CO_2 hydrogenation[48]. Therefore, the formate yield increased from 3.0 % to 4.4 %(Entries 1 and 2, Table 1). As the ethanol content further increased from 10% to 50 %, the concentration of ethyl carbonate increased. However, hydrogenation of ethyl carbonate consumed H_2 and thus the local concentration of H_2 in the solution might decreased, which indirectly enhanced the dehydrogenation of glucose and led to a higher glucose conversion (Entries 2 to 4, Table 1). Unfortunately, when ethanol was presented in excess (70%), the performance of the hydrogen transfer reaction deteriorates sharply (Entry 5, Table 1). This phenomenon can be attributed to the fact that the solubilies of glucose and ammonium carbonate in aqueous solvent with high ethanol contents are very low. For example, glucose is almost insoluble in pure ethanol.[49]

Table 1. Effect of solvent composition on room temperature hydrogen transfer.

Entry	Ethanol weight percentage wt %	Glucose Conversion /%	Product yield / mol%		
			Gluconate	Sorbitol	Formate
1	water	64.3	58.6	5.6	3.0
2	10% ethanol	50.5	43.8	5.6	4.4
3	30% ethanol	60.6	50.9	7.5	12.7
4	50% ethanol	72.6	59.5	10.7	32.3
5*	70% ethanol	56.5	49.8	7.5	22.1

Reaction conditions: Both Pd and Pt on AC is 5wt %, Pt/AC is 0.1 g, the ratio of Pd to Pt is 4, 30 mL solvent, 0.18 M glucose, 0.1 M $(NH_4)_2CO_3$, 0.2 M KOH, 20ºC, 24 hours. *The solubilites of glucose and ammonium carbonate were very low in the 70wt% ethanol solution. Thus the undissolved solutes after the reaction were re-dissolved for analysis by adding another 30mL water into the solution.

Previous studies also proved that higher pH favors the dehydrogenation of glucose as stronger base facilitates the deprotonation of glucose.[34] A detailed discussion on the pH effect were presented in the supporting information (Figures S1-S2). It should be noted here, the yields of formate and sorbitol in pure water were much more inferior to those in ethanol-water mixed solvents. As mentioned previously, ethanol has been proved to be able to improve the hydrogenation of CO_2 via the ethyl carbonate intermediate. The superior performance of the hydrogenation reaction in 50 wt % ethanol indeed facilitated the coupled dehydrogenation reaction and thus made the conversion of glucose comparable to that in the pure water. In our opinion, this is a clear and live example of interpreting how two cascade reactions synergize in a “one-pot” process.

Base on the outcomes of the examination on solvent effect, as well as the screening results of multiple combinations of CO_2 derived salts and sugars (supporting information Figures S3-S6), without special notification, the discussions on the room temperature hydrogen transfer reaction in the following studies will be focused on glucose (hydrogen donor)/ammonium carbonate (hydrogen acceptor) system with 50 wt % of ethanol solution as the solvent.

Step 1: $NH_4^+ + CO_3^{2-} + H_2O \leftrightarrow HCO_3^- + NH_3 \cdot H_2O$

Step 2: $HCO_3^- + NH_3 \cdot H_2O \leftrightarrow NH_2CO_2^- + 2\,H_2O$

Step 3: $NH_2CO_2^- + H_2O + CH_3CH_2OH$

$\leftrightarrow CH_3CH_2OCO_2^- + NH_3 \cdot H_2O$

Step 4: $HCO_3^- + OH^- \leftrightarrow CO_3^{2-} + H_2O$

Scheme 2. Postulated equilibriums between carbonate/bicarbonate, carbamate and ethyl carbonate ions in ethanol-water mixture under alkaline condition. Step 1 and Step 2 can be merged, assuming carbamate is an intermediate which can be rapidly converted.

To get more information about the reaction system, we began following investigations. Previous studies proved that ethyl carbonate ions could be formed in the ethanol solutions when ammonium carbamate/carbonate was presented, which resulted in the superior hydrogenation performance.[48,50] Therefore in order to explain the decrement of the formate yield caused by the pH change of the solution, the distributions of carbon species in the solution at various pH conditions are required to be investigated. The crucial ionic equilibriums in ethanol-water mixture are proposed in Scheme 2. In the cases referred in the discussions above, ammonium carbonate is used as carbon source thus it might be partly converted into ammonium hydroxide nd bicarbonate (Step 1). The formed bicarbonate can be in equilibrium with ammonium carbamate (Step 2), which will finally promote the formation of ethyl carbonate ions in the presence of ethanol (Step 3). However the formed ethyl carbonate can also be transformed back into bicarbonate or even carbonate (Step 4) especially under basic conditions.

To identify the distributions of carbon species under different pH conditions, the ^{13}C NMR spectra of 0.1 M ammonium carbonate solution (50wt % ethanol) with various KOH concentrations were collected. As shown in Figure 1, two major kinds of peaks are identified. The peak located at 160.2 ppm should be assigned to the carbonyl carbon in ethyl carbonate ion (donated as “b” in Figure 1). Another peak assigned to the bicarbonate/carbonate pair which is located between 161.1 and 169.0 ppm (donated as “a” in Figure 1). It should be pointed out that the position of ethyl carbonate peak in the spectra is rather fixed regardless of the increasing of pH. While the peak from bicarbonate/carbonate pair shifts to higher field upon the increasing of pH due to the proton scrambling. This kind of higher-field shift was also observed before in the NH_3-CO_2-water system.[51] Clearly, when the apparent pH value increases, there is an unambiguous transition of carbon species from ethyl carbonate to bicarbonate and carbonate. When the pH value reaches 13.90, no peak of ethyl carbonate can be found anymore. Under this conditions the active species such as ethyl carbonate and bicarbonate are substantially or even completely converted to inactive carbonate species, the hydrogenation of ammonium carbonate will be inhibited. The overall observations of the spectra are consistent with the postulated ionic equilibrium in Scheme 2. However, the peak of the predicted carbamate ion is presented in a negligible manner (around 166 ppm) in all pH conditions. That indicates carbamate is also an intermediate which can be rapidly converted into other species in the system, so Step 2 and Step 3 in Scheme 2 can be lumped. On the other hands, as higher pH value facilitates the dehydrogenation of glucose, it does not favor the preservation of active carbon species for hydrogenation of ammonium carbonate. Thus an optimized hydrogen transfer reaction should be a compromise of both dehydrogenation and hydrogenation, and thus the optimized pH condition is supposed to be achieved at 0.2 M KOH in this glucose-ammonium carbonate system.

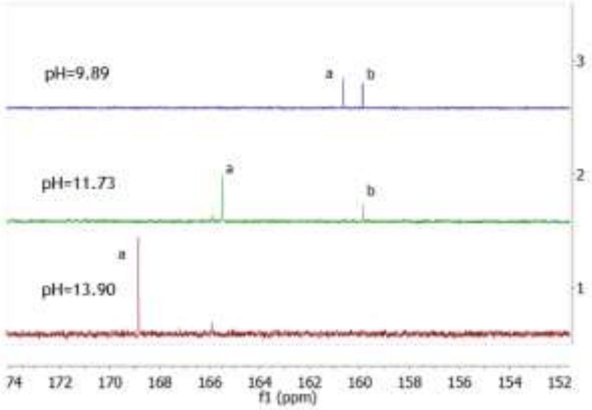


Figure 1. ^{13}C NMR spectra of 0.1M carbonate dissolved in 30 mL ethanol-water mixed solvent (50/50 wt%) under three different pH values.

Besides discussing the performances of dehydrogenation and hydrogenation reactions separately, it is also important to understand how well these two reactions are coupled as a cascade reaction. The related hydrogen transfer efficiency (THE) efficiencies of the cascade reactions are displayed in Figure S1 and Figure S2. In Figure S1b, both HTE formate and HTE total have optimal values when the concentration of KOH is in the range from 0.15 to 0.2 M. At the same time, this specific range also corresponds to a minimal net hydrogen production, indicating that 0.2 M (pH ca. 11.73) is indeed around the optimal KOH concentration. When the initial pH is fixed at the optimal value (Figure S2b), the HTE formate and HTE total just rise up upon the increase of glucose supply. This result suggests that at optimal initial pH condition, within the limit of glucose solubility, more glucose feed results in a better and more efficient cascade reaction. This property is rather ideal in aspects of both scaling up and atomic efficiency of reactants. As for the selectivity of formate, it decreases upon approaching the optimal pH condition from lower ones (Figure S1b). However as long as the optimal pH condition is assured, the selectivity of formate is always higher than 60%.

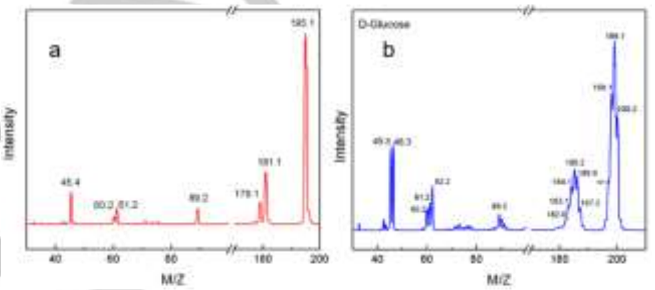
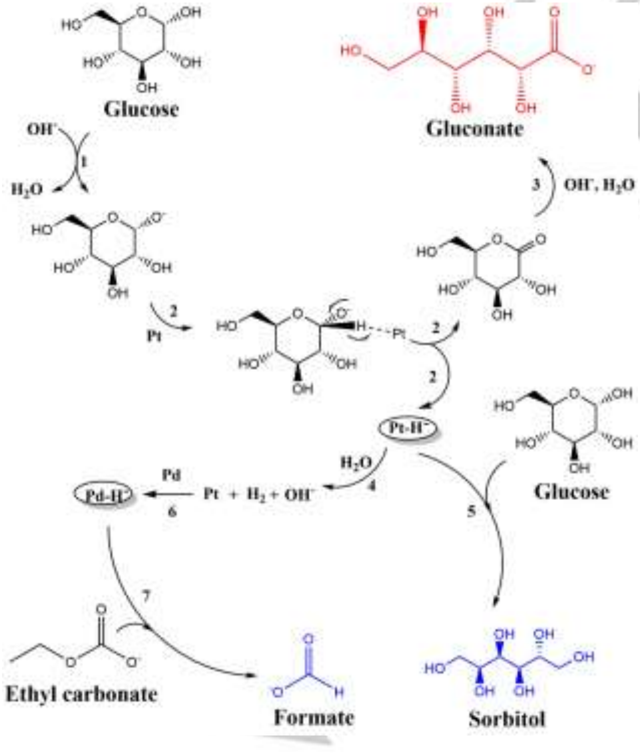


Figure 2. ESI-MS analysis: Reaction conditions: 0.4 gPd/AC (5wt%), 0.1 g Pt/AC (5wt%); 30 mL solvent (50wt% ethanol in aqueous solution), 0.2 M glucose, 0.1 M ammonium carbonate, 20 ºC, 24 h. (a) H_2O and 0.2 M KOH were used. (b) D_2O and 0.2 M KOD were used.

Deuterium labelling experiments were further employed to study the reaction pathways and confirm them by the comparison between ordinary experiments (Figure S7). Glucose or deuterated glucose is appeared to be completely deprotonated by 0.2M KOH. This phenomenon has been intensively discussed before. Here the ESI-MS results proves that the hypothetic deprotonation indeed happens under alkaline condition. The mass spectrum after a single run of normal reaction is shown in Figure 2a. The signals of formate ion (M/Z=45.4), carbonate ion (M/Z=60.2), bicarbonate ion (M/Z=61.2), ethyl carbonate ion (M/Z=89.2), glucose (M/Z=179.1), sorbitol (M/Z=181.1), and gluconate (M/Z=195.1) are observed. As has been mentioned in the ^{13}C NMR section before, carbonate ion (M/Z=60.2), bicarbonate ion (M/Z=61.2), and ethyl carbonate ion (M/Z=89.2) are the ions in equilibrium in ethanol/water solvent when ammonium carbonate is dissolved. Here, this is the first time of obtaining direct evidence of the formation of ethyl carbonate species. And gluconate (M/Z=195.1) can be firmly regarded as the product of glucose dehydrogenation, and sorbitol (M/Z=181.1) is the product of glucose hydrogenation. Figure 2b shows the signals of deuterium labelling experiment. Formate ion (M/Z=45.3 and 46.3), carbamate ion (M/Z=60.2), bicarbonate ion (M/Z=61.2 and 62.2), ethyl carbonate ion (M/Z=89.2), glucose and sorbitol (M/Z=182-187.2) and gluconate (M/Z=197.1-200.2) are shown in the spectra. In general, the peaks of the substances are split off due to the involving of deuterium-hydrogen fast exchange. Most critically, the split of the peak from formate indicates that glucose is not the only hydrogen donor in this low temperature hydrogen transfer reaction. Other hydrogen donor could be D_2O and KOD. More interestingly, the integrals of the peaks at M/Z=45.3 and 46.3 are rather close, which implies that glucose and liquid phase each provides roughly 50 % hydrogen, respectively.

Based on the above experiments, the proposed mechanism of the low temperature hydrogen transfer reaction is depicted in Scheme 3. The deprotonation of glucose into glucose ion in a basic condition is shown in Step 1. Step 2 is the dehydrogenation of the deprotonated glucose on the surface of Pt nano-particles, resulting in the creation of a negatively charged hydride species. It has been proved that this deprotonation only happens on the Pt surface (in supporting information Figure S8b). Step 3 is the production of gluconate via a base catalyzed hydrolysis process. Step 4 is the oxidation of the produced Pt hydride, in which the hydride atom coming from glucose reacts with water to produce hydrogen species and hydroxyl ion. The production of hydroxyl ion is unambiguous consumed by the deprotonation step and has to be given back. While as for the produced hydrogen species which is ready for the supply of hydrogenation, there is quite some room for discussion. It is well known that metal hydride is extremely sensitive to water or even moisture, therefore the hydrogen atom (hydride) on the Pt surface is very likely to be oxidized by water instantaneously. Meanwhile, we also prove that the hydrogenation of ammonium carbonate only occurs on the surface of Pd (in supporting information Figure S8a). Therefore dehydrogenation of glucose and hydrogenation of ammonium carbonate are spatially separated. Thus it is hard to imagine how the hydrogen species can be transported from Pt to Pd surface in the solution if it is not in the form of hydrogen. We also prove that the hydrogenation of glucose into sorbitol only occurs on Pt surface (in supporting information Figure S8b). In another word, Pd has no catalytic activity in both dehydrogenation of glucose and hydrogenation of glucose. The hydrogen transferred from Pt to Pd (Step 6), regardless of its form during the transferring, is utilized in the hydrogenation reaction of ethyl carbonate and bicarbonate into formate (Step 7). Note that carbonate has no activity on this step which has been discussed before.



Scheme 3. The proposed reaction process of low temperature hydrogen transfer reaction system.

In summary, we have shown that for the first time, the low temperature hydrogen transfer process can be combined with CO_2 reduction. This reaction system couples two reactions: dehydrogenation of glucose and hydrogenation of ammonium carbonate. With the Pd/AC and Pt/AC bimetallic catalyst, a 46 % yield of formate and a 21 % yield of sorbitol were obtained at the same time from ammonium carbonate and glucose in ethanol-water mixed solvents at room temperature. In this cascade reaction system, the formation of the key intermediate, ethyl carbonate, in the basic aqueous ethanol solutions plays a central role in the hydrogenation reaction. The amounts of glucose and ammonium carbonate as reactants, as well as the KOH additives, affected the initial pH value of the system significantly and therefore predominately determine the yields of the main products. The optimal pH value to maximize the formate yield was approximately 11.73. The efficiency of hydrogenation transfer was a compromise of the dehydrogenation and hydrogenation reactions. However, a complete and fulfilled explanation on the intrinsic mechanism of the transfer hydrogenation on Pd and Pt surface still needs further investigation.

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Keywords: Hydrogen transfer • Gluconic acid • Formate • CO_2 reduction • Dual Pt/Pd catalyst

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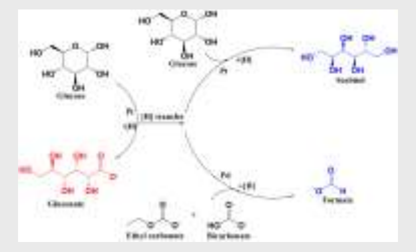
COMMUNICATION

A novel catalytic reaction system is presented by coupling the dehydrogenation of glucose with the hydrogenation of a CO_2 derived salt in the ethanol-water mixture at room temperature. Based on the ^{13}C NMR and ESI-MS results, the possible mechanism was also proposed.



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