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Transfer hydrogenation of CO₂ into formaldehyde from aqueous glycerol heterogeneously catalyzed by Ru bound to LDH⁺

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Aqueous glycerol was used in this study as a liquid-phase hydrogen source for the hydrogenation of CO₂. It was found that hydrogen could be efficiently evolved from aqueous glycerol upon highly dispersed Ru on layered double hydroxide (LDH), inducing the transformation of CO₂ into formaldehyde under base-free conditions at low temperature.

Catalytic hydrogenation of CO₂ with H₂ has been extensively studied as a sustainable means to utilize CO_2 .¹⁻³ This rational treatment could not only reduce CO₂ emission, but also recycle CO₂ as a C₁ building block and reduce fossil-resource depletions. However, the low solubility of H2 in most solvents generates high H₂ pressure necessary to achieve desired conversions and yields. These high pressures incur safety concerns and a hefty infrastructure cost on the industrial scale.4,5

Liquid-phase alcohols have been applied as hydrogen donors in various hydrogenation reactions because they are safer and entail a more convenient management and usage than H₂.⁶ More interestingly, such liquid H₂ agents also create high local concentrations of H₂ generated in the liquid phase, which could enhance the intrinsic kinetics of the hydrogenation reaction.⁷⁻⁹ Antonchick et al. Used the biomass-derived carbohydrates, starch and lignin as liquid H₂ carriers, to successfully perform an efficient catalytic transfer hydrogenation (CTH) of alkynes, alkenes and carbonyl compounds.¹⁰ A Ru/C catalyst served as the catalyst for both H₂ formation from 2-propanol and the hydrogenation of furfural.¹¹ Glycerol is abundant because it is a major by-product of the biodiesel manufacturing process.

Its chemical structure (including three hydroxyl groups) allows glycerol to serve as a hydrogen-donor solvent in reduction reactions.^{12,13} Pescarmona et al. exploited the hydrogen liberated in the dehydrogenative oxidation of glycerol to in situ hydrogenate various unsaturated organic compounds such as levulinic acid, benzene, nitrobenzene, 1-decene and cyclohexene, from which lactic acid and the corresponding hydrogenated products were obtained in one pot in the presence of either a Pt/ZrO_2^{14} or Ni-Co/CeO₂¹⁵ heterogeneous catalyst.

Using glycerol in the CTH of CO₂, however, has not been extensively exploited. To date, only a few attempts, mainly using homogeneous catalysts have been reported. Aresta et al. used aqueous glycerol as the hydrogen source to produce formic acid from CO₂ and glycolic acid via the decarbonylation of glycerol using [RuCl₂(PPh₃)₃].¹⁶ Voutchkova-Kostal et al. used a homogeneous water-soluble Ru N-heterocyclic carbene complex to carry out the CTH of CO2, which executed 1685 and 1065 turnovers, respectively, of lactate and formate in alkaline hydrothermal media at 453 K.¹⁷ They further reported highly robust Ir-based homogeneous catalysts for the CTH of carbonate salts from glycerol, affording lactate and formate salts under basic conditions with high TONs (72 245 for LA and 52 032 for FA) under 2.6 MPa N₂ at 423 K.¹⁸ Although these sparsely reported homogeneous catalysts displayed high activities, they suffered from the disadvantages of difficult recovery and regeneration. In comparison, heterogeneous catalysis has several advantages in terms of separation, recycling and reactor designs. Lin et al. used heterogeneous Pd/C for the CTH of bicarbonate from glycerol, while there was almost no yield of formic acid at 513 K with CO₂ gas charge.¹⁹ The CTH of CO₂ using glycerol still lacks highly efficient heterogeneous catalysts, and urgently needs the related fundamental understanding of the reaction.

In this study, we have developed a layered double hydroxide supported Ru (Ru/LDH) heterogeneous catalyst to perform the CTH of CO₂ gas in aqueous glycerol media at mild temperatures without adding strong bases (Scheme 1).

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Scheme 1 An illustration of a conversion of carbon dioxide and waste glycerol into value-added products.

A Ca–Al LDH support was first prepared based on a previously reported procedure,²⁰ and is described in the ESI.† Briefly, LDH were prepared from an aqueous solution of high concentrations of metal salts through a homogeneous alkalization reaction triggered by propylene oxide. The final crystalline was characterized as mostly thin plates that possessed a regular hexagonal structure with an approximate grain size around 5 μ m. Its scanning electron microscopy (SEM) image suggests the formation of some agglomerated structures, which were overlapping with each other (Fig. S1, ESI†). Fig. 1(A) shows the XRD pattern of a Ca–Al LDH, which contained the characteristic peaks of Ca_{0.8}Al_{0.2}(OH)₂Cl_{0.2} with good crystallinity.²¹ The presence of a reasonable amount of impurities in the Ca–Al material could be attributed to the discrepancy in the ionic size of Ca (0.100 nm) and Al (0.054 nm).²²

Treatment of the LDH with a solution of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ in water at 323 K overnight afforded Ru/NLDH as a gray powder. The N₂ adsorption–desorption isotherm of Ru/LDH with 0.5 wt% of Ru is compiled in Fig. S2 (ESI†). The specific surface area and total pore volume that were obtained by BET and BJH methods are 25.6 m² g⁻¹ and 0.08 cm³ g⁻¹, respectively. Ru/LDH exhibited a combination between IV and V isotherms type, as commonly observed in microporous adsorbents.^{23,24} The pores of Ru/LDH are mostly distributed over the range of 0–20 nm. Its XRD pattern



Fig. 1 (A) XRD patterns of LDH and Ru/LDH, (B) Ru K-edge FT-EXAFS spectra of Ru/LDH and standard samples (Ru foil, RuCl₃ and RuO₂). (C) Schematic illustration of Ru/LDH.

shown in Fig. 1 exhibited the characteristic peaks of $Ca_{0.8}A-l_{0.2}(OH)_2Cl_{0.2}$ with relatively higher crystallinity than the LDH. No other crystal phases (such as Ru, RuO₂) were observed on Ru/LDH.

To further characterize the Ru species on the Ru/LDH, the samples were examined by transmission electron microscopy (TEM) and X-ray absorption fine structure (XAFS). As shown in Fig. S1(b) and S3 (ESI⁺), Ru species were not obviously observed on LDH. As proven by energy dispersive X-ray element mapping (Fig. S4, ESI[†]), no Ru aggregates could be observed in Ru/LDH. These results indicate the highly dispersion of Ru on LDH. Extended X-ray absorption fine structure (XAFS) is one of the most powerful techniques for characterizing the electronic state and local structure of Ru species. The shape and edge position in the Ru K-edge EXAFS spectrum of the Ru/LDH shown in Fig. 1(C) was similar to those of RuO₂, but differed from those of Ru foil and RuCl₃·nH₂O. The Fourier transform (FT) and inverse FT of the main peaks was well-fitted by the use of two longer Ru–O (2.05 Å) and two shorter Ru–O (1.93 Å) shell parameters, as summarized in Fig. S5 and Table S1 in the ESI.† X-ray photoelectron spectroscopy (XPS) was also carried out. As seen in the XP spectra of Ru in Fig. S6 (ESI[†]), Ru/LDH and oxidized Ru/LDH exhibit similar spectra with a BE (binding energy) of about 462.4 eV which is assigned to RuO_2 (462.4 eV). Thus, the oxidation state of Ru should be +4. Conclusively, an highly dispersed Ru species bears one hydroxyl grafted onto a triad of O atoms originating from the basic hydroxyl groups on the LDH surface, posing an especial metal-support interaction.

Unlike the previous studies, when the Ru/LDH catalyst was applied in the CTH of CO_2 , formaldehyde rather than formic acid was detected as the product of CO_2 reduction. Formaldehyde is a highly versatile platform chemical, and generally requires further reduction of formic acid. In order to indicate formaldehyde in aqueous media, the colorimetric 3-methyl-2-benzothiazolinone hydrazone (MBTH) method was used in addition to high performance liquid chromatography (HPLC).^{25,26} The typical blue-green color was observed in the reaction solution using the MBTH (Fig. S7, ESI†), indicating the formation of HCHO. HPLC was further employed to quantify the amount of HCHO.

Fig. 2 plots the yield of formaldehyde as a function of Ru loading amount (A) and reaction temperature (B). As the same catalyst was used in the direct hydrogenation of CO_2 by H_2 (1 MPa) and transfer hydrogenation of CO_2 with glycerol, respectively, regardless of Ru loading amount, the latter method produced higher HCHO yields, indicating a higher hydrogenation capability of liquid glycerol compared to H_2 gas. Moreover, there were no obvious activity changes when the loading amount of Ru was varied over the range of 0.1–3 wt%. The high yield of HCHO on 0.1 wt% Ru/LDH could be attributed to the special interactions between the highly dispersed Ru species and LDH. The products of glycerol oxidation such as Lactic acid (LA, $C_3H_6O_3$) and pyruvic acid (PA, $C_3H_4O_3$) were detected in the reaction solution (Fig. S8, ESI†).

In contrast, the effect of temperature on the yield of HCHO in the CTH system became complicated. The low reaction



Fig. 2 The yield of formaldehyde as a function of Ru loading amount (A) and reaction temperature (B) for the two reaction systems—direct hydrogenation of CO₂ by H₂ and hydrogenation of CO₂ with glycerol. (Conditions: 50 mg of catalyst, 10 mL of 0.2 M aqueous glycerol, 1 MPa CO₂, 1 MPa H₂ (in the case of direct hydrogenation of CO₂ by H₂), 323 K for Fig. 1(A), 0.5 wt% Ru for Fig. 1(B), 300 rpm, 12 h).

temperature (298 K) induced a low glycerol conversion (Fig. S9, ESI[†]). It has been reported that Ru exhibited low activity in glycerol oxidation, and the conversion of glycerol was less than 5% even at 353 K and under a pure O_2 atmosphere.²⁷ In our studies, O₂ was replaced by CO₂ with a lower oxidation ability. The conversion of glycerol was less than 10% over the temperature range of 298-398 K, and increased significantly when the reaction temperature was increased to 423 K. Besides the predominant formation of lactic acid, other substances such as pyruvic acid, glyceric acid and glyoxylic acid were also detected in the reaction solution, indicating that C-C cleavage in glycerol occurred in addition to C-H cleavage at 423 K. Consequently, the yield of HCHO at 423 K was higher than at 398 K. It was also confirmed by the experiments shown in Fig. 2(B) that higher temperatures were unfavourable for the direct hydrogenation of CO₂ by H₂ gas because the overall yield of HCHO was reduced from 446 to 138 mmol $L^{-1} g_{cat}^{-1}$ when the reaction temperature was increased from 323 to 373 K. The HCHO yields in the CTH reactions also decreased when the reaction temperature was increased from 323-398 K, indicating HCHO yield was influenced by both glycerol oxidation and CO₂ hydrogenation.

Given that CO_2 is in equilibrium with HCO_3^- and CO_3^{2-} in aqueous media, we performed the hydrogenation of bicarbonate/ carbonate ions with the Ru/LDH catalyst. The reaction atmosphere was consequently switched to either N₂ or air (for comparison), and the results are shown in Table 1. When the reaction atmosphere was air and Na₂CO₃ was used to replace CO₂ gas(entry 2), the conversion of glycerol obviously increased.

Table 1 Results of glycerol oxidation and CO_2 hydrogenation over 0.5 wt%Ru/LDH catalyst

	Yield of formaldehyde			Yield (mmol $L^{-1} g_{cat}^{-1}$)		
Entry	Yield ^f	TON	Glycerol conv. (%)	PA	GLA	LA
1^a_{h}	360	72	9	35	0	35
20	405	81	46	5	28	107
3 [°] ,	263	53	52	26	10	61
4^a	303	61	10	1	0	37
5^e	462	93	11	0	0	35

Reaction conditions: 50 mg of 0.5 wt% Ru/LDH, 0.2 M aqueous glycerol, 323 K, 12 h. ^{*a*} 1 MPa CO₂. ^{*b*} Na₂CO₃, air atmosphere. ^{*c*} Na₂CO₃, N₂ atmosphere. ^{*d*} NaHCO₃, N₂ atmosphere. ^{*e*} NaHCO₃, 1 MPa CO₂. ^{*f*} The unit is mmol L^{-1} g_{cat}⁻¹.

About 46% of glycerol was converted into LA (mainly), PA, GLA (glyceric acid, $C_3H_6O_4$) and other products undetected, and the yield of HCHO was slightly increased. In the case of the N₂ atmosphere and Na₂CO₃, the yield of HCHO was not improved even with a high conversion of glycerol (about 52%). The reason was probably due to the decreased selectivity toward LA. This result indicated that not only the conversion of glycerol, but also the selectivity towards C-H cleavage in glycerol is also important for hydrogenation of CO2. Entry 4 and 5 in Table 1 show the results of the CTH reactions in the cases using the aqueous glycerol solution containing NaHCO₃. Compare with entry 1-3, the selectivity towards LA during glycerol conversion increased, most of converted glycerol was transformed into LA. The yield of HCHO was also improved a lot. There was about 462 mmol $L^{-1} g_{cat}^{-1}$ of formaldehyde when NaHCO₃ was used and CO₂ (1 MPa) was charged into the reactor. Our experiments were consistent with the report about thermodynamics of bicarbonate hydrogenation in water, which are slightly more favourable than that of CO₂ ($\Delta G_{aq}^0 = 4.4 \text{ kcal mol}^{-1}$ for HCO₃⁻ vs. 13.4 kcal mol⁻¹ for CO₂).^{17,18} Furthermore, the products' distributions were similar in the cases with NaHCO₃ or CO₂ as the source, but were much different when Na₂CO₃ was used (Fig. S10, ESI[†]), indicating that bicarbonate was likely the actual species to undergo transfer hydrogenation when CO₂ was charged into the aqueous glycerol.

When RuCl₃ was used in the aqueous glycerol solution, we also detected the formation of HCHO (Fig. S12, ESI⁺), indicating that RuCl3 can be used as the homogeneous catalyst in transfer hydrogenation of CO2. Dispersion of Ru in LDH support affords much higher activity in CTH of CO₂ than RuCl₃. To assess the stability and reusability of this heterogeneous catalyst, we performed five repeated reaction runs, each followed by catalyst recovery after 24 h of reaction. The second run exhibited much loss of the yield of HCHO (Fig. S12, ESI⁺), while the recycled Ru/LDH showed the similar catalytic activity during the following catalytic cycles. It was worthy to note that the yields of HCHO over both fresh Ru/LDH and recycled ones were higher than that over RuCl₃, demonstrating the efficacy of the reversible switching and recycling properties of the Ru/LDH. The loss of activity in the second cycle are probably attributed to dissolution of the basic LDH in



Scheme 2 Proposed catalytic cycle for the transfer hydrogenation of CO_2 with aqueous glycerol by Ru/LDH.

 $\mathrm{H}_{2}\mathrm{O},$ which can be effectively avoided by alkaline addition in water.

Based on our experimental and theoretical studies on previously reported reaction mechanisms of metal complexes,²⁸ we proposed a plausible mechanism for the transfer hydrogenation of CO₂ with aqueous glycerol over Ru/LDH (Scheme 2 and Scheme S1, ESI†). The reaction is initiated by the dehydrogenation of glycerol to dihydroxyacetone (DHA) or glyceraldehyde, which is transferred to LA *via* dehydration and H₂O rearrangement (step 1). Next, CO₂ is inserted into the Ru-hydride species (step 2), followed by the isomerization *via* the attack of hydride H species onto C atoms, affording a Ru-no C—O intermediate (step 3). Then the dehydrogenation of glycerol or further dehydrogenation of LA to PA occurs, obtaining two H atoms in the periphery of the Ru center (step 4), which forms HCHO and H₂O, accompanied by the regeneration of the initial active species(step 5).

In summary, the anchoring of a Ru precursor onto the surface of LDH successfully generated the highly dispersed Ru catalyst surrounded by hydroxide ligands with a strong local basicity. Over the Ru/LDH catalyst, catalytic transfer hydrogenation of CO_2 from aqueous glycerol into formaldehyde occurred at low temperature, and low CO_2 pressure without any base additive. The yield of HCHO could be influenced by the reaction temperature and the usage of HCO_3^- . The metal-support interaction over Ru/LDH affords high turnover of hydrogen transferring between C_3 species and CO_2/HCO_3^- , generating HCHO in aqueous media. Our work and further improvement of the catalytic performance under mild reaction conditions is expected to be helpful for the realization of an environmental-friendly CO_2 -mediated sustainable system.

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Conflicts of interest

There are no conflicts to declare.

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