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Letter

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ACS Catal., **Just Accepted Manuscript** • DOI: 10.1021/acscatal.7b00312 • Publication Date (Web): 22 Mar 2017

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Isolated Single-Atomic Ru Catalyst Bound on a Layered Double Hydroxide for Hydrogenation of CO_2 to Formic Acid

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KEYWORDS: Single-site catalyst • Layard double hydroxide • Ruthenium • CO_2 hydrogenation • formic acid

ABSTRACT: In order to achieve an economical CO_2-mediated hydrogen energy cycle, the development of heterogeneous catalysts for CO_2 hydrogenation to formic acid is an urgent and challenging task. In this study, a stable and well-defined single-site Ru catalyst on the surface of a layered double hydroxide (LDH) in a basic medium is proven to be efficient for selective hydrogenation of CO_2 to formic acid under mild reaction conditions (2.0 MPa, 100°C). The electron-donating ability of triads of basic hydroxyl ligands with a particular location is crucial for an active electron-rich Ru center. There is a strong correlation between catalytic activity and adjustable CO_2 adsorption capacity in the vicinity of the Ru center. Such electronic metal-support interactions and a CO_2 concentration effect result in a significant positive influence on the catalytic activity.

The precise design of supported metal nanostructures is a key challenge in controlling the activity and specificity of heterogeneous catalysts to achieve particular target reactions.[1] The downsizing of metal assemblies to clusters, or ultimately isolated single-atomic state, with well-defined metal atoms atomically dispersed or anchored on supports, offers unrivalled opportunities to maximize atom efficiency.[2-4] In contrast to heterogenization of existing homogeneous organometallic complexes on insoluble matrices, the anchoring of single-site catalysts directly to metal oxides has also led to geometric and electronic effects induced by improvements in strong metal-support interactions (SMSI) originating from particular locations and chemical bonding between metals and the associated interfaces.[5-7] Recent remarkable progress in the development of such isolated single-atomic catalysts has resulted in an exciting research field involving the creation of novel catalysts and their application in a variety of industrial chemical reactions.

The chemical fixation of carbon dioxide (CO_2) into synthetically beneficial compounds is of great interest in industrial chemistry because it can be considered an inexpensive, nontoxic, and abundant C1 feedstock.[8-10] The hydrogenation of CO_2 to produce formic acid (FA; HCOOH), which is a liquid at room temperature and contains 4.4 wt% hydrogen, is a promising approach to establishing FA as a renewable hydrogen storage material, since the chemically stored H_2 in the FA can be liberated in controllable fashion in the presence of appropriate catalysts even at room temperature.[11-14] Thus, the design of novel catalysts for CO_2 hydrogenation to form FA is a crucial task in the realization of economical CO_2-mediated hydrogen energy cycles.

Homogeneous transition metal complexes in basic media have proven to be efficient catalytic systems.[15,16] Recent design strategies have been principally focused on the synthesis of electron-rich metal centers through the use of electron-donating organic ligands, which exhibit satisfactory reaction rates even under mild reaction conditions.[17,18] However, the development of heterogeneous catalysts lags significantly behind that of homogeneous catalysts, in spite of their practical utility,[19-25] and, to make matters worse, their use frequently requires a high catalyst concentration, organic solvents, and extremely high pressures.

Here we present an isolated single-atomic Ru catalyst on the surface of layered double hydroxides (LDHs) for the exploitation of a heterogeneous CO_2 hydrogenation system. The general formula of LDHs are represented as $M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2)^{x+}(A^{n-})_{x/n}\cdot mH_2O$, where M^{2+} and M^{3+} are di- and tri-valent metal cations and A^{n-} represents interlayer anions such as $CO_3{}^{2-}$.[26] LDHs are known to act as efficient base catalysts owing to the six-fold coordinated OH^- groups with di- and tri-valent cations.[27] It was expected, and is herein demonstrated, that an electron-rich mononuclear Ru species could be successfully created with the aid of strong Brønsted OH^- ligands, which further boost CO_2 adsorption in the vicinity of the active Ru center, ultimately enhancing CO_2 hydrogenation even at relatively low pressure.

Various LDHs were prepared by a literature procedure.[28] Treatment of a LDH, $Mg_{10}Al_2(OH)_{24}CO_3$, with a solution of $RuCl_3\cdot nH_2O$ in 0.2 M aqueous NaOH at 50°C for 8 h afforded Ru/LDH as a gray powder (Ru content: 0.36 wt%, as determined inductively coupled plasma (ICP) analysis. Other Ru catalysts were also synthesized by the same method with different supports (Ru contents: 0.38 -0.40 wt% by ICP). The reason for treating the acidified Ru chloride with an alkaline solution is to create an electron-rich ruthenium hydroxide precursor such as $[Ru(OH)_6]^{3-}$,[29] as well as avoiding dissolution of the basic LDH during the deposition step. In the UV-vis spectrum, a peak assigned to the Ru–OH bond was observed at around 400 nm upon addition of $NaOH_{aq}$ to the aqueous $RuCl_3\cdot nH_2O$ solution (**Fig. S1**). The addition of $NaOH_{aq}$ induced a change in the Ru K-edge XANES spectrum of the aqueous $RuCl_3\cdot nH_2O$ solution, indicating a change in the local coordination environment (**Fig. S2A**). Fourier transform (FT) of a k^3-weighted Ru K-edge EXAFS spectrum revealed the disappearance of a peak associated with the Ru–Cl bond, expected to be around 1.9 Å, upon addition of $NaOH_{aq}$ to the aqueous $RuCl_3\cdot nH_2O$ solution (**Fig. S2B**), coincident with the appearance of a new scattering peak due to an Ru–O bond at around 1.6 Å, demonstrating the formation of ruthenium hydroxide species.

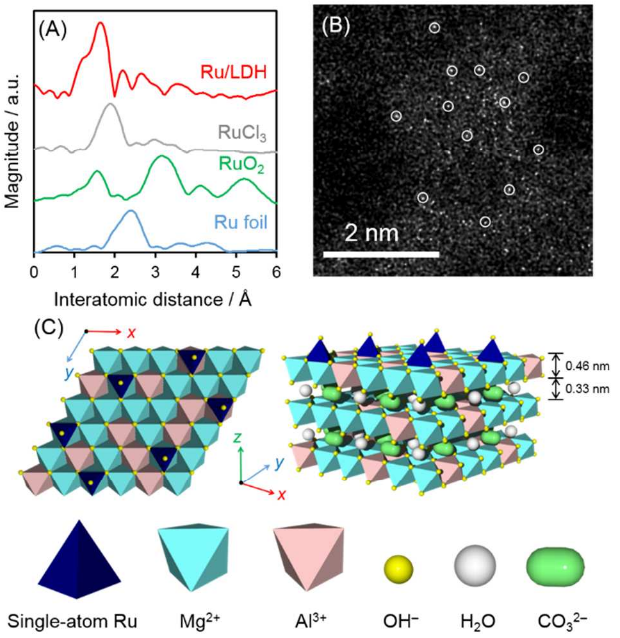


Figure 1. (A) Ru K-edge FT-EXAFS spectra, (B) HAADF-STEM image of Ru/LDH (the circles are drawn around a part of isolated Ru atoms), and (C) schematic illustration of Ru/LDH (top and side view).

The Brunauer Emmett Teller surface areas (S_{BET}) calculated from N_2 adsorption-desorption were 81.6 and 84.3 $m^2 \cdot g^{-1}$ for Ru/LDH and the parent LDH, respectively (**Table 1**). The XRD pattern of Ru/LDH did not show any d_{001} peak shift in comparison with that of the original LDH (**Fig. S3**). These facts demonstrated predominant deposition of Ru species on the surface of LDH, while the interlayer space was maintained (0.79 nm) without exfoliation or segregation. The absence of chlorine in the Ru/LDH was confirmed by XPS analysis (**Fig. S4**). The shape and edge position in the Ru K-edge XANES spectrum of Ru/LDH (22124.6 eV) was similar to those of $RuCl_3 \cdot nH_2O$ (22125.2 eV) and RuO_2 (22125.9 eV), but differed from that of Ru foil (22118.2 eV) (**Fig. S5**), indicating that Ru exist in the +4 oxidation state.[30,31] In the FT-EXAFS spectrum of Ru/LDH, there were no peaks due to metallic Ru–Ru and contiguous Ru–O–Ru bonds, expected to be around 2.5 and 3.3 Å (**Fig. 1A**). The absence of a Ru–Cl bond, detectable in the spectrum of $RuCl_3 \cdot nH_2O$ at around 2.0 Å, was also confirmed. The two peaks observed at 2.2 and 2.8 Å may be assigned to the Ru-Mg or Ru-Al in the second coordination spheres,[32] which indicate that Ru species is located on the surface of Brucite layer of the LDH, not within the interlayer space. The maximum in the envelope of the inverse FT spectrum for Ru/LDH was located at around $k = 7$ Å^{-1}, which was lower than the equivalent result for Ru foil (11 Å^{-1}), RuO_2 (9 Å^{-1}), and $RuCl_3$ (8 Å^{-1}) (**Fig. S6**). The appearance of maxima in the envelope at smaller k values suggests a second shell interaction with lighter atoms. The inverse FT of the main peaks was well fitted by the use of five longer Ru–O (2.05 Å) and one short Ru–O (1.82 Å) shell parameters, as summarized in **Table S1** and **Fig. S6**. In a separate experiment, the sample was desorbed under vacuum conditions, and further subjected to XAFS analysis. The inverse FT of this Ru/LDH after desorption treatment was well fitted by the use of three longer Ru–O (2.04 Å) and one short Ru–O (1.81 Å) shell parameters, indicating that Ru center contains two adsorbed water ligand. A high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image also indicated white points suggestive of an isolated single-atomic structure (**Fig. 1B**) without the significant agglomeration. Conclusively, an isolated single-atomic Ru species with octahedral coordination geometry bearing one hydroxyl and two water ligands was grafted onto a triad of oxygen atoms originating from the basic hydroxyl groups on the LDH surface (**Fig. 1C**).

As summarized in **Table 1**, hydrogenation of CO_2 to give formic acid was carried out using various Ru catalysts under several sets of conditions, and the comparison of catalytic activity was performed with turnover number (TON) based on Ru. A typical reaction was performed in a 25 mL stainless-steel reactor in a basic aqueous solution containing 1.0 M of $NaHCO_3$ under a total pressure of 2.0 MPa ($H_2 : CO_2 = 1 : 1$) at 100°C for 24 h. Ru/LDH (Mg^{2+}/Al^{3+}=5) was proven to be an effective heterogeneous catalyst with > 99% selectivity without the formation of methanol, affording a substantial TON of 461 with a turnover frequency (TOF) of ca. 19 h^{-1} (entry 1). No reaction was observed in the case of the inherent LDH (entry 2). The use of a homogeneous $RuCl_3 \cdot nH_2O$ solution did not result in efficient catalysis (entry 3). There was no distinct relationship between the catalytic activity and S_{BET}; other heterogeneous Ru catalysts, such as Ru/MgO, Ru/$Mg(OH)_2$, Ru/Al_2O_3, and Ru/$Al(OH)_3$, were found to be less active (entries 4–7). Thus, the creation of a single-site Ru catalyst on the surface of LDH is indispensable in achieving high catalytic activity.

Table 1. Hydrogenation of CO_2 to produce formic acid under various catalytic conditions.

entry	catalyst	base	TON based on Ru	S_{BET} /$m^2 \cdot g^{-1}$
1	Ru/LDH (Mg^{2+}/Al^{3+}=5)	$NaHCO_3$	416	81.6
2	LDH (Mg^{2+}/Al^{3+}=5)	$NaHCO_3$	-	84.3
3	$RuCl_3$ solution	$NaHCO_3$	120	-
4	Ru/MgO	$NaHCO_3$	239	13.8
5	Ru/$Mg(OH)_2$	$NaHCO_3$	181	30.7
6	Ru/Al_2O_3	$NaHCO_3$	90	123.0
7	Ru/$Al(OH)_3$	$NaHCO_3$	29	40.8
8	RuCl/LDH(Mg^{2+}/Al^{3+}=5)	$NaHCO_3$	149	73.0
9	Rh/LDH (Mg^{2+}/Al^{3+}=5)	$NaHCO_3$	28	80.1
10	Ir/LDH (Mg^{2+}/Al^{3+}=5)	$NaHCO_3$	16	81.0
11	Ru/LDH (Mg^{2+}/Al^{3+}=5)	NaOH	698	-
12	Ru/LDH (Mg^{2+}/Al^{3+}=5)	KOH	489	-
13	Ru/LDH (Mg^{2+}/Al^{3+}=5)	-	43	-

In a separate experiment, a reaction with RuCl/LDH that had been prepared using the $RuCl_3 \cdot nH_2O$ precursor without the addition of $NaOH_{aq}$ showed moderate activity, indicating the importance of pretreatment (entry 8). The use of Rh/LDH and Ir/LDH, prepared by the same method as Ru/LDH, gave poor results (entries 9 and 10). Among the bases examined, NaOH and KOH were excellent, giving high TONs of 698 and 489 (entries 11 and 12), whose TOFs corresponds to 29 h^{-1} and 20 h^{-1}, respectively. Notably, the Ru/LDH catalyst under discussion enabled direct hydrogenation of CO_2 even under neutral conditions in the absence of additional bases (entry 13). The origin of the produced formic acid was proved by the catalytic reaction using isotopic $^{13}CO_2$ in D_2O solvent (0.5 M NaOH) and the products was identified by ^{13}C NMR. Deprotonated $H^{13}COOH$ can be observed at 170. 88 ppm as a sole product without the formation of byproducts (**Figure S7**).[33] The isotopic $^{13}CO_2$ reaction provides solid proof that the produced formic acid is originated from CO_2.

A characteristic feature of the Ru/LDH catalyst is its high activity even under low-pressure conditions. It is noteworthy that the TON and TOF values achieved by the Ru/LDH system were comparable or higher than those reported for other heterogeneous catalyst systems, including Au/Al_2O_3 (TON and TOF respectively 696 and 29 h^{-1} at 4 MPa in DMF/NEt_3),[24], Pd/mpg-C_3N_4 (85 and 3.5 h^{-1} at 4 MPa in H_2O/NEt_3),[25] and Au/TiO_2 (284 and 12 h^{-1} at 18 MPa in neat NEt_3).[22] Even under the direct hydrogenation to produce pure formic acid without bases, the achieved TOF (5.0 x 10^{-4} s^{-1}) is four times higher than that with carbon nanotube-graphene supported PdNi alloy (1.2 x 10^{-4} s^{-1} at 5 MPa).[34] Upon completion of the reaction, separation of the heterogeneous catalyst from the reaction system is straightforward. The recovered catalyst was recycled at least three times while keeping 90 % of its original catalytic activity. Ru K-edge XAFS analysis revealed no structural changes around the isolated single-atomic Ru catalyst in the recovered Ru/LDH (**Fig. S8**). TEM analysis also showed that the LDH surfaces remained virtually unchanged even after the reaction, without the formation of Ru nanocrystallites. Furthermore, ICP analysis of the filtrate confirmed that the Ru content was negligible, from which it may be deduced that the hydrogenation reaction occurs on a solid surface. Such prominent characteristics may be due to the presence of a structurally robust mononuclear Ru catalyst on the LDH surface. Because of this, the Ru/LDH catalyst is a pivotal contribution to the development of environmentally benign chemical processes.

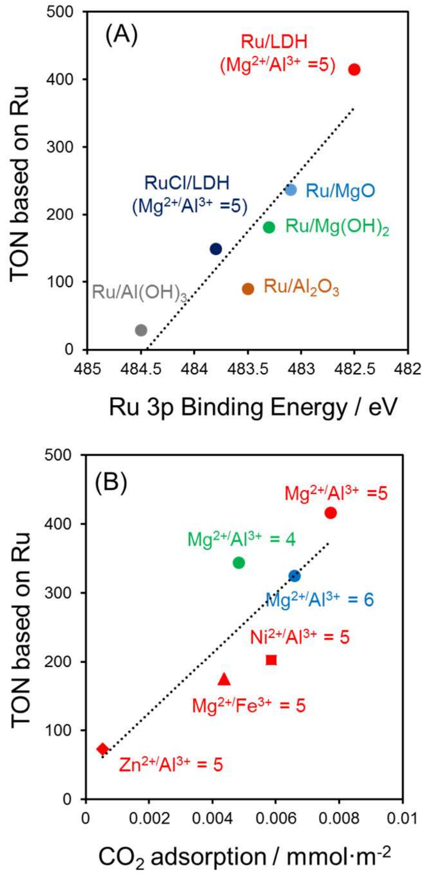
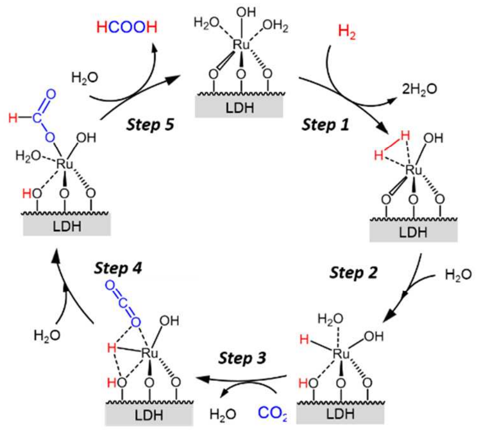


Figure 2. (A) Relationship between the TON for CO_2 hydrogenation based on Ru, and Ru 3p binding energy as determined by XPS spectroscopy. (B) Relationship between the TON for CO_2 hydrogenation based on Ru and CO_2 adsorption for various Ru-supported LDH samples.

It is well accepted that the strong electron-donating ability of PNP pincer-type ligands or N-heterocyclic carbenes in Ir(III) complexes facilitates hydrogenation of CO_2.[35-37] Moreover, a linear correlation between the hydrogenation rate and the electron-donating ability of bipyridine ligands with various substituents has been reported.[38] Upon consideration of these results, it may be concluded that one possible reason for the high catalytic activity of Ru/LDH is ascribed to an electron-rich single-site Ru catalyst with the assistance of a triad of basic hydroxyl ligands. XAFS analysis proved the formation of an isolated single-atomic Ru structure for all analogous supports investigated (**Fig. S9**), while different coordination environments changed the electronic state of Ru center via electronic metal-support interaction (EMSI),[39,40] as determined by XPS analysis (**Fig. S10**). It should be noted that the catalytic activity corresponded well with the Ru 3p binding energy; the TON based on Ru increased with decreasing binding energy (**Fig. 2A**), thus suggesting that special placement of hydroxyl groups with an ordered arrangement on the LDH surface is a promising platform for the electronically promoted Ru species.

A series of LDHs with different M^{2+}/M^{3+} components and ratios may be easily synthesized, and the catalytic activities of these materials in CO_2 hydrogenation were further investigated. The optimal ratio among Mg-Al-LDHs investigated was Mg^{2+}/Al^{3+} = 5 (**Fig. 2B**). Other combinations with an M^{2+}/M^{3+} ratio of 5 resulted in low catalytic activity. Interestingly, such catalytic activity is well correlated with differences in CO_2 adsorption originating from different levels of basicity in the LDHs. Based on metal atom ordering, two types of hydroxyl site exist on the surface; one is connected to three M^{2+} ions, while the other is bound to two M^{2+} cations and one M^{3+}.[41] Changes in the cation ratio and the combination used can change the basicity of the LDH, allowing adjustment.[28] It has been reported that basic sites tuned in this way show a diverse array of pK_a values in the range 9.0–16.5.[42] High CO_2 adsorption property on the hydroxyl site results in a concentration effect on the surface of LDH support, which boosts the interaction with active single-site Ru catalyst and ultimately influences on the catalytic activity.

Based on the consideration of experimental and theoretical studies on previously reported reaction mechanisms of metal complexes,[43,44] we propose a plausible catalytic cycle for CO_2 hydrogenation over Ru/LDH (**Scheme 1**). The reaction is initiated by H_2 activation (*step 1*), in which one basic oxygen ligand assists the heterolytic dissociation of the adsorbed H_2 in the periphery of the Ru center (*step 2*). Next, insertion of CO_2 into the Ru-hydride species (*step 3*), followed by the isomerization via the attack of hydride H species onto C atoms, affording a Ru η^1-formate intermediate (*step 4*), which regenerates the initial active species, accompanied by the formation of formic acid (*step 5*).



Scheme 1. Possible reaction pathway for CO_2 hydrogenation to produce formic acid with a Ru/LDH catalyst.

The activation energy (E_a) for CO_2 hydrogenation using Ru/LDH, determined from Arrhenius plots, was 54.3 kJ mol^{-1}, as shown in **Fig. S11**. This value is similar to that of $[Cp^*Ir(bpy)(OH_2)]SO_4$ (51.4 kJ mol^{-1}), but is different from that of Au/Al_2O_3 (74.0 kJ mol^{-1}), which may be indicative of the involvement of a single-site reaction pathway. The reaction rate (R) of CO_2 hydrogenation can be expressed by $R = k{\cdot}P_{H2}{}^{\alpha}{\cdot}P_{CO2}{}^{\beta}$, where k is the rate constant, P_{H2} and P_{CO2} represent the partial pressure of H_2 and CO_2, and α and β represent the reaction order of H_2 and CO_2, respectively. Kinetic investigation determined that α and β were 1.95 and 1.71 at 100 °C, respectively (**Fig. S12**). Based on these facts, it was concluded that the initial Ru-hydride formation is the rate-determining step, rather than CO_2 insertion. This behavior contrasts with that observed in Au/Al_2O_3 catalytic systems, presumably because of the concentration effect of the adsorbed CO_2 in the vicinity of the neighboring Ru center, which allows the formation of a Ru η^1-formate intermediate. The use of a donating OH ligand is advantageous for this catalytic reaction because the electron-rich Ru species boost not only the insertion of CO_2 into the Ru-hydride species, but also the consecutive isomerization step.[44] Such cooperative actions explain the high activity of Ru/LDH for CO_2 hydrogenation.

In summary, the anchoring of a Ru precursor onto the surface of LDH in a basic medium successfully generated an isolated single-atomic Ru catalyst surrounded by OH ligands with strong basicity. The electronegativity was enhanced by the special location of the hydroxyl groups, which have an ordered arrangement on the LDH surface. The CO_2 adsorption capacity in the vicinity of the Ru center can be tuned by varying the M^{2+}/M^{3+} components and ratio in the LDH, for which the maximum was $Mg^{2+}/Al^{3+} = 5$. Even under low-pressure conditions, the Ru/LDH catalyst displayed significant catalytic activity for selective CO_2 hydrogenation to produce formic acid due to EMSI and CO_2 concentration effects. Further improvement of the catalytic performance under mild reaction conditions is expected to result in the realization of an environmentally friendly CO_2-mediated reversible hydrogen storage system as a practical application.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental details, Figures S1-S12 and Table S1 (PDF)

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ACKNOWLEDGMENT

The present work was supported by JST-PRESTO. The part of this work was supported by Grants-in-Aid for Scientific Research (Nos. 26220911, 25289289, and 26630409, 26620194) from the Japan Society for the Promotion of Science (JSPS) and MEXT.

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