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Low-temperature hydrogen production from methanol over ruthenium catalyst in water

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11 Abstract

12 Traditionally, methanol-reforming at a very high temperature > 200 °C has been explored for 13 hydrogen production. Here, we show that *in situ* generated ruthenium nanoparticles (ca. 1.5 nm) 14 from an organometallic precursor promote hydrogen production from methanol in water at low temperature (90 $^{\circ}C - 130 ^{\circ}C$), which leads to a practical and efficient approach for low-temperature 15 16 hydrogen production from methanol in water. The reactivity of ruthenium nanoparticles is tuned 17 to achieve a high rate of hydrogen gas production from methanol. Notable, use of pyridine-2-ol 18 ligand significantly accelerated the hydrogen production rate by 80% to 49 mol H_2 per mol Ru per 19 hour at 130 °C. Moreover, the studied ruthenium catalyst exhibits appreciably long-term stability 20 to achieve a turn over number of 762 mol H₂ per mol Ru generating 186 L of H₂ per gram of Ru.

21 Keywords

22 Hydrogen, Methanol, Ruthenium, Water, nanoparticles

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2 Hydrogen is a potential clean energy carrier, and when used in fuel cell it produces only water as a byproduct. Unfortunately, the presence of hydrogen gas in the earth's atmosphere is extremely 3 low (≈ 1 ppm by volume). Therefore, one of the major hurdles in exploring hydrogen economy 4 5 with full potential is the safe production and storage of hydrogen gas. Notably, carrying big and heavy hydrogen cylinders with high pressure has critical safety and economical challenges. On the 6 7 other hand, using liquid hydrogen storage materials (such as HCHO, CH₃OH, HCOOH) in the fuel 8 tank of existing vehicles (using petroleum products) and generate hydrogen on-board to supply to Fuel Cell is not only a viable concept but is also very economical.¹⁻¹² In this context, methanol, 9 10 which contains an appreciably high gravimetric content of hydrogen 12.5 wt% is a promising candidate for on-board and off-board (stationary) large-scale production of hydrogen gas.¹³⁻²⁰ 11 Notably, methanol offers several advantages, such as it is an inexpensive liquid, low carbon 12 13 content (C1 alcohol), easy to store, and is being produced on large scale from biomass resources and hydrogen and carbon monoxide, or as industrial byproducts.¹³⁻²⁰ Traditionally, hydrogen gas 14 is being produced from methanol steam reforming process at a high-temperature range (200 $^{\circ}$ C – 15 16 350 °C), while catalyst assisted hydrogen production from methanol in water is more energy 17 efficient as it operates at low temperature (< 190 °C).

In principle, hydrogen production from methanol is mildly endothermic, therefore a suitable catalyst may activate methanol to produce hydrogen gas.¹⁴⁻²⁴ Experimental evidences revealed that in the presence of a catalyst the dehydrogenation of methanol may follow the three consecutive pathways: initially, the dehydrogenation of methanol to formaldehyde and hydrogen (eq. 1), followed by the dehydrogenation of formaldehyde in the presence of water (gem-diol) to 3

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hydrogen and formic acid (eq. 2), and finally dehydrogenation of formic acid to hydrogen and CO₂
(eq. 3).

$$CH_3OH \rightarrow H_2CO + H_2 (\Delta H = 129.8 \text{ kJ mol}^{-1})$$
(1)

$$H_2CO + H_2O \rightarrow HCOOH + H_2 (\Delta H = -30.7 \text{ kJ mol}^{-1})$$
(2)

$$HCOOH \rightarrow CO_2 + H_2 (\Delta H = 31.6 \text{ kJ mol}^{-1})$$
(3)

6 A wide range of catalysts has been explored to utilize methanol, as a potential liquid hydrogen storage material, for the production of hydrogen gas at low-temperature with regulated 7 emission of unwanted CO and methane.^{21,25} Recently, homogeneous catalysts based on Ru, Ir, Fe, 8 9 and Mn have been explored to dehydrogenate methanol in presence of water and produce H₂ without or very low ppm of CO at the temperature below 100 °C.^{14,21,25-30} In particular, ruthenium-10 11 pincer based molecular catalysts exhibited higher activity to produce hydrogen from methanol in basic condition.²⁵⁻²⁶ In contrary to the above, heterogeneously catalyzed reforming of methanol to 12 13 produce hydrogen and carbon dioxide has been continuously studied and developed, using different metal-based catalysts such as CuO/ZnO/Al₂O₃,³¹ Pd/CeO₂-ZrO₂,³² Pt₃Ni,³³ and Ni-Fe-14 Mg³⁴ alloys, but most of these catalysts require higher temperature over 200 °C and pressure. On 15 16 the other hand, industrially viable heterogeneous catalysts for low-temperature hydrogen 17 production are rarely explored, until recently when Pt/MoC catalyst was explored for hydrogen 18 production from methanol, but this catalyst worked effectively only at higher temperature (150-190 °C) and using an expensive Pt catalyst.³⁵ 19

Notable, the development of catalysts for the selective transformation of methanol to hydrogen gas (eq. 1) with the generation of formic acid is of critical importance, as it eliminates the energy-intensive process of CO₂ scrubbing from H₂ and CO₂ mixture obtained from complete

9

transformation of methanol (eq. 1 and 2). Furthermore, the byproduct formic acid is also a worthful 1 product and a potential hydrogen storage material.⁹ Herein, we synthesized ruthenium 2 nanoparticles *in-situ* from an organometallic ruthenium complex and a ligand and utilized it to 3 achieve efficient catalytic activity to produce hydrogen gas and formate/formic acid from methanol 4 5 in the water at the lower temperature (90-130 °C). The structure of the ruthenium catalyst was 6 established by TEM, XPS, P-XRD, ICP, TGA and several reaction parameters were evaluated to 7 achieve high catalytic activity for the low-temperature conversion of methanol to hydrogen gas 8 and formate over the ruthenium catalyst in water.

Results and Discussion

At an outset, we employed $[\{(\eta^6\text{-benzene})\text{RuCl}_2\}_2]([\text{Ru}]-1)$ as a pre-catalyst for hydrogen 10 11 production from methanol (2:1 molar ratio of CH₃OH:H₂O) at 110 °C in the presence of 1.2 equiv. KOH, where we observed the release of 73 mol H₂ per mol of Ru (initial TOF 9 h^{-1}) (Table 1, entry 12 1). The evolved gas was identified as hydrogen by GC-TCD. Notably, the initial dark brown color 13 14 of the reaction solution turned to a black suspension, which was identified as Ru nanoparticles (ca. 15 18.7 nm) by TEM (Fig. S1). Further, recent studies revealed that pyridine-based ligands can act as an internal base and play a crucial role in C-H activation reaction.³⁶⁻³⁷ We, therefore, investigated 16 17 the role of 2-hydroxy pyridine (L1) as a promoter in the ruthenium-catalyzed hydrogen production 18 from methanol. For Ru/L1 catalyst (pre-catalyst [Ru]-1 in the presence of L1), we observed a 19 significant enhancement of ca. 82% in the initial TOF with the release of 0.66 mol of H₂ per mol 20 of methanol (TON of 106 mol H₂ per mol of Ru) (Table 1, entry 2 and Fig. 1a). When the reaction 21 was performed using CH₃OH:H₂O molar ratio of 1:1, the intrinsic activity increased further to yield a TON of 134 mol of H₂ per mol of Ru (0.83 mol of H₂ per mol of methanol) with an 22 23 improved initial TOF of 20 h⁻¹ (Table 1, entry 5 and Fig. 1b). Notably, further increasing the water

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1 content (1:2 molar ratio of CH₃OH:H₂O) resulted in lower catalytic activity for H₂ production from 2 methanol over **Ru/L1** catalyst (Table 1, entry 6, and Fig. 1b), as compared to the reaction 3 performed with high methanol content (CH₃OH:H₂O molar ratio of 1:1, 2:1 or 4:1) (Table 1 and Fig. 1a). Literature reports on aqueous methanol dehydrogenation outlined the beneficial role of 4 water in methanol dehydrogenation reaction.^{11,14} For instance, Grützmacher et al. achieved 5 6 dehydrogenation of methanol using CH₃OH/H₂O 1:1 molar ratio, and mentioned that in the 7 presence of water high gravimetric content of hydrogen can be achieved form methanol.¹¹ Beller 8 and other researchers also highlighted the role of water-promoted dehydrogenation of formaldehyde to formic acid and H₂ during methanol dehydrogenation reaction.^{25,38} Notably, Lin 9 *et al.* also reported efficient hydrogen production from methanol over Pt/ α -MoC using higher water 10 content (CH₃OH/H₂O molar of 1:3 and 1:1).³⁵ 11

Entry	Cat.	$n(alc.)/n(H_2O)$	T (°C)	KOH (equiv.)	$n({\rm H_2})/n({\rm alc.})$	$n({\rm H_2})/n({\rm cat.})$	$\mathrm{TOF}^{h}(\mathrm{h}^{-1})$
1^b	Ru	2:1	110	1.2	0.45	73	9
2	Ru/L1	2:1	110	1.2	0.66	106	18
3	Ru/L1	4:1	110	1.2	0.68	109	13
4	Ru/L1	neat	110	1.2	0.63	102	14
5	Ru/L1	1:1	110	1.2	0.83	134	20
6	Ru/L1	1:2	110	1.2	0.25	40	14
7^c	Ru/L1	1:1	110	-	0.67	107	19
8	Ru/L1	1:1	130	1.2	1.42	229	49

12 Table 1. Screening of catalyst to producing hydrogen from methanol^{*a*}

9	Ru/L1	1:1	90	1.2	0.24	38	5
10^d	Ru/L1	1:1	110	1.2	0.50	81	11
11 ^e	RuNP/L1	1:1	110	1.2	0.13	21	12
12 ^f	Ru/L1	1:1	110	1.2	0.61	98	20
13 ^g	Ru/L1	1:1	110	1.2	0.69	111	16

^{*a*}Reaction condition: alcohol (16.08 mmol), Ru catalyst (0.625 mol%, n([Ru]-1)/n(L1) 1:2), KOH (1.2 equiv.), 10 h, argon, ^{*b*} in the absence of ligand L1, ^{*c*} reaction with NaOMe in place of CH₃OH, ^{*d*} with [Ru]-2 and L1 (n([Ru]-2)/n(L1) 1:2), ^{*e*} with pre-synthesised Ru nanoparticles and L1 (1 equiv.), ^{*f*} using ethanol as reactant, ^{*g*} using *n*-propanol as reactant and ^{*h*} average turnover frequency (TOF) at 1 h.

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1 Notably, we found that base played a crucial role in generating the active Ru nanoparticles 2 in the initial hour of the reaction. Moreover, lower activity was observed while using less content 3 of KOH (0.42 equiv.) (Table S1). Results inferred that compared to KOH, reaction with other bases 4 such as NaOH, K^tOBu, and K_2CO_3 exhibited either lower activity or no reaction (Table S2). It is 5 worth noting that almost a similar amount of H₂ was released when NaOMe was used as a substrate 6 instead of methanol, in absence of base, suggesting that presumably content of base is crucial for 7 the deprotonation of methanol (Table1, entry 7, and Fig. S2). Moreover, kinetic isotope effect 8 (KIE) studies indicated that CD_3OD is more influential than D_2O in tuning the reaction rate for the 9 **Ru/L1** catalyzed hydrogen production from methanol (Fig. S3 and Table S3). These results 10 inferred that the activation of methanol C-H bond is presumably the rate-determining step and not the proton assisted release of hydrogen gas from methanol. Further, ¹³C NMR of the reaction 11 12 aliquot after the completion of the catalytic reaction inferred the presence of formate with traces 13 of carbonate (Fig. S4a), suggesting that decomposition of formate does not take place. Notably, 14 performing the reaction with the spent **Ru/L1** catalyst resulted in no formate decomposition and

no traces of carbonate was detected in ¹³C NMR (Fig. S4b and S5, and Table S4). Furthermore, 1 2 the amount of formate formed as a co-product was also quantified to nearly half of the mol of H₂ gas generated during the reaction (Fig. S5). GC-TCD analysis of the evolved gas is in good 3 agreement with the observation of only purified hydrogen gas (Fig. S6). When reaction 4 temperature was increased to 130 °C, initial TOF increased by over ten-folds to 49 mol H₂ per mol 5 6 Ru per hour as compared to the reaction performed at 90 °C (TOF of 5 mol H₂ per mol of Ru per 7 hour) (Table 1, entries 5, 8, 9, and Fig. S7). Notably, the Ru/L1 catalyst exhibited the generation 8 of 1.42 mol H₂ per mol of methanol (\sim 71% conv.) (at 130 °C), which is several-folds higher than that reported for 0.2%Pt/α-MoC catalyst (0.037 mol H₂ per mol of methanol at 190 °C).³⁵ The 9 10 apparent activation energy for the conversion of methanol to H_2 over **Ru/L1** catalyst was estimated 11 as 18.3 kcal/mol (Fig. S7). Therefore, it is evident from these results that **Ru/L1** is active even at 12 lower reaction temperature of 90 °C - 130 °C.

13 Further to detect various species that might form during the dehydrogenation of methanol, the reaction mixture at various time intervals (0, 15 and 60 min) was analyzed by ¹H and ¹³C NMR, 14 where no traces of formaldehyde, methanediol, paraformaldehyde and trioxane were detected (Fig. 15 16 S5). Consistent with the literature reports, this can be attributed to the faster transformation of 17 formaldehyde to formic acid and hydrogen in water as compared to methanol dehydrogenation to formaldehyde (Fig. S5).^{11,18,38} Furthermore, we performed the catalytic dehydrogenation of 18 19 aqueous formaldehyde (37 wt.%) under analogous reaction condition to methanol dehydrogenation and analyzed the evolved gas by GC-TCD and the reaction aliquots by NMR. 20 21 Results inferred that indeed in the presence of base only pure hydrogen and formate was produced from formaldehyde dehydrogenation as confirmed by GC-TCD and NMR, respectively. Therefore, 22 23 these results evidenced that during methanol dehydrogenation under the optimized reaction

1 condition, the possible intermediates such as formaldehyde or methanediol formed during the 2 reaction may also undergo faster transformation to formic acid and H₂ gas, and therefore 3 formaldehyde was not detected in the reaction solution. However, we have detected and isolated 4 the formic acid generated during the methanol dehydrogenation reaction under the studied reaction 5 condition (Fig. S5). (a) 300 - [Ru]-1 + L1 - [Ru]-1 + L1 - [Ru]-1 - [



Fig. 1 Effect of (a) ligand L1 and (b) methanol to water molar ratio on the Ru/L1 catalyzed
hydrogen production from methanol at 110 °C. (c) Comparative catalytic activity of various
ruthenium catalysts with/without ligands to produce hydrogen from methanol at 110 °C.
(Reaction condition: methanol (16.08 mmol), Ru catalyst (0.625 mol%, n([Ru]-1)/n(L1) 1:2),
KOH (1.2 equiv.) and methanol to water molar ratio (1:1), argon, ^amethanol to water molar
ratio is 2:1, and ^b[Ru]-2 precursor is used).

6

1	Further, to obtain insights into the role of pyridine ligand, catalytic conversion of methanol
2	to H_2 was also examined using 2-methoxy pyridine (L2) where a significant decline in the initial
3	TOF (15 mol H_2 per mol Ru per hour) was observed with Ru/L2 catalyst as compared to the TOF
4	of 20 mol H_2 per mol Ru per hour obtained with Ru/L1 catalyst (Table S5 and Fig. S8). Further,
5	the reaction performed using Ru/pyridine (L3) and Ru/phenol (L4) showed even lower activity
6	(Fig. 1c, Table S5 and Fig. S8). These observations suggested the possible involvement of the 2-
7	hydroxy pyridine ligand (L1) in promoting the facile activation of methanol over Ru nanoparticles
8	to produce hydrogen gas with higher activity. Notably, performing the catalytic reaction with the
9	larger content of the ligand L1 (Ru/L1 1:4) resulted in lower activity yielding only 46 mol H ₂ per
10	mol Ru in 8 h as compared to 62 mol H ₂ per mol of Ru for Ru/L1 ratio of 1:2, presumably because
11	excess ligands may poison the catalyst (Fig. S9). Moreover, using [{ $(\eta^6-p-\text{cymene})\text{RuCl}_2$ }] ([Ru]-
12	2) precursor instead of [Ru]-1 could not improve the catalytic activity (Table 1, entry 10, Fig. 1c
13	and Fig. S10). Further, performing the catalytic reaction in the presence of pre-synthesized Ru
14	nanoparticles with L1 resulted in only lower activity, suggesting that in-situ generated Ru
15	nanoparticles in the presence of L1 in the more suitable condition to generate active Ru
16	nanoparticle catalysts (Table 1, entry 11, and Fig. 1c). Moreover, to know the nature of real catalyst
17	for methanol dehydrogenation, we performed a series of poisoning experiments using Whitesides'
18	mercury test. ²⁵ Results inferred that the catalytic reaction quenched in the presence of $Hg(0)$ (>300
19	equiv.) due to the poisoning of the Ru/L1 catalyst by amalgam formation. In contrary to the control
20	reaction, the addition of $Hg(0)$ (>300 equiv.) at the beginning of the reaction resulted in complete
21	quenching of the catalytic methanol dehydrogenation, suggesting the heterogeneous nature of the
22	Ru/L1 catalyst (Fig. S11a). Further, in another experiment, the spent Ru/L1 catalyst was also
23	stirred with an excess of added Hg(0) (>300 equiv.), before employing it as a catalyst for methanol

dehydrogenation reaction under the optimized reaction condition, but no gas release was observed 1 2 (Fig. S11b). It is worth noting here, that the spent **Ru/L1** catalyst was found to be highly active (in 3 the absence of Hg(0), supports the heterogeneous nature of the studied catalysts (Fig. S11b). Moreover, the Ru/L1 catalyst also exhibited appreciable long-term stability, where a total turnover 4 5 number (TON) of 762 mol of H_2 per mol of Ru was achieved in a 7-cycle recyclability experiment 6 generating 186 L of H_2 gas per gram of Ru (Fig. 2). On the other hand, continuing the reaction 7 with the reaction solution (supernatant), obtained after the removal of **Ru/L1** catalyst, resulted in 8 no release of gas even after extending the catalytic reaction for a longer duration (10 h) (Fig. S12). 9 The literature revealed that reaction performed under reducing condition may result in the transformation of organometallic Ru precursor to Ru(0) nanoparticles.³⁹⁻⁴³ Chaudret et al. 10 11 established the mechanism and the process for the transformation of organometallic ruthenium complexes to Ru nanoparticles.⁴²⁻⁴³ Similarly some other groups have also established the 12 transformation of organometallic ruthenium complexes to Ru nanoparticles.⁴⁰ Therefore, in 13 14 absence of induction period during the *in-situ* transformation of **[Ru]-1** to Ru nanoparticles can be 15 attributed to the highly reducing reaction condition due to the presence of KOH, H₂ gas and 110-16 130 °C. Further, ICP-OES analysis of the recovered nanoparticles inferred the presence of ~54 17 wt.% of Ru, whereas no traces of metal were detected (detection limit of 0.01 ppm) in the 18 supernatant, evidence the absence of ruthenium species in the reaction mixture also supports the 19 complete transformation of **[Ru]-1** precursor to Ru nanoparticles. Moreover, the liquid portion 20 (supernatant) was also analyzed by ESI-MS, where any isotopic patterns corresponding to 21 ruthenium was not observed, further suggesting that the ruthenium complex is converted to 22 ruthenium nanoparticles during the reaction and no residual ruthenium species is present in the 23 solution (Fig. S13). Therefore, the above findings evidenced the heterogeneous nature of the

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Ru/L1 catalyst for methanol dehydrogenation. Furthermore, the ethanol and *n*-propanol were also 1 2 investigated under catalytic reaction conditions and the results showed that the studied **Ru/L1** 3 catalysts can also efficiently generate hydrogen gas along with value-added products such as acetic acid (Table 1, entries 12, 13, and Fig. S14). The activity of the catalyst slightly decreased with 4 5 subsequent catalytic runs, attributed to the surface oxide coating of the Ru catalyst, as also 6 confirmed by XPS analysis (Fig. S15). Though the turnover number was relatively low for the 7 studied **Ru/L1** catalyst, it is evident that **Ru/L1** catalysts exhibited the generation of higher 8 equivalents of hydrogen gas per moles of methanol $(n(H_2)/n(MeOH) 1.42)$ as compared to the 9 earlier reported catalysts, (Table S6). Moreover, in the studied catalytic system, formate/formic acid is obtained as a worthful byproduct. Advantageously, this resulted in the generation of 10 11 hydrogen gas in high purity from methanol. Therefore, the studied **Ru/L1** catalytic system could 12 be a promising candidate for low-temperature bulk hydrogen production from methanol.



Fig. 2 Long term stability and recyclability experiment for Ru/L1 catalyzed production of H2
from methanol at 130 °C.

1 To obtain insights into the structural and chemical nature of the *in-situ* generated **Ru/L1** 2 catalyst, we employed several characterization methods. Powder X-ray diffraction of Ru 3 nanoparticles obtained after the catalytic reaction showed a broad peak at 25-45°, suggesting highly dispersed small Ru nanoparticles over the carbon support (Fig. S16).⁴⁴ Transition electron 4 5 microscopy (TEM) images confirm the existence of a homogenous dispersion of Ru nanoparticles 6 of particle size ca. 1.5 nm on the carbon support (Fig. 3a and Fig. S17). Furthermore, the dispersion 7 of *in-situ* generated ruthenium nanoparticles in the presence of L1 ligand was also estimated as 8 86%, as calculated from the generalized equations using mean particle size (d_{TEM}) as obtained from the TEM by considering ~110 particles (Table S7).⁴⁵⁻⁴⁶ In sharp contrast, without ligand, the Ru 9 10 nanoparticles have an average particle size of ca. 18.7 nm with poor dispersion (Fig. S1). High 11 angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) images 12 and energy-dispersive X-ray spectroscopic (EDS) analysis inferred the presence of Ru element 13 (Fig. 3b-d). Moreover, the EDS line scan also confirmed the even distribution of Ru nanoparticles 14 over the carbon support (Fig. 3d).

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Fig. 3 (a) TEM image (inset particle size distribution), (b) EDS point analysis, and (c) HAADF image and the corresponding (d) EDS line scan analyses for Ru/L1 catalyst.

4 Thermogravimetric analysis of the *in-situ* generated **Ru/L1** catalyst inferred the presence 5 of large organic content (~30% more) as compared to the Ru nanoparticles obtained in the absence 6 of the ligand L1 (Fig. S18). Further, the presence of 0.74% nitrogen content observed for Ru/L1 7 in the elemental analysis, further suggesting the presence of the ligand L1 in the catalyst. Such 8 behavior is consistent with the stabilization of smaller Ru nanoparticles with 2-hydroxypyridine 9 ligand (L1). This phenomenon was also revealed earlier where Ru nanoparticles were stabilized by small ligands.⁴⁷⁻⁴⁸ In addition, the binding energy of Ru/L1 as obtained from X-ray 10 photoelectron spectroscopy (XPS) experiment for both Ru(3d) and Ru(3p) core levels are assigned 11 to the oxidation state of Ru in the catalyst using CuO as a standard ($Cu^{2+}3p_{3/2}$ 933.5 eV in CuO). 12 13 In the XPS spectra of Ru/L1 catalyst, peak maxima observed at the binding energy values of 461.7



Fig. 4 XPS spectra corresponding to the (a) Ru 3p_{3/2} (b) Ru 3d_{5/2} and (c) N 1s core levels of
Ru/L1 catalyst.

8 Notably, XPS of the Ru nanoparticles obtained in the absence of ligand L1 inferred the 9 higher content of ruthenium oxide (Fig. S15), further suggesting that the presence of ligand L1 10 over the Ru nanoparticles prevented the facile oxidation of the surface in **Ru/L1** catalyst. Hence, 11 the observed enhanced catalytic performance of the **Ru/L1** catalyst can be attributed to the smaller 12 particle size ruthenium nanoparticles and the ligand L1.

13 Experimental

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14 **Catalytic hydrogen production from methanol.** Typically, an appropriate amount of $[\{(\eta^{6} - 15 \text{ benzene})\text{RuCl}_2\}_2]$ **[Ru]-1** (0.05 mmol) (or other precursors) and ligand (0.1 mmol - 0.2 mmol) in 16 methanol-water solution $(n(\text{CH}_3\text{OH})/n(\text{H}_2\text{O}) = 1:0 \text{ to } 1:2)$ was taken in a 5 mL test tube reaction 17 vessel and was added an appropriate base (1.1 equiv. with respect to methanol). Then the reaction 18 vessel, equipped with a condenser (-10 °C) and water displacement setup, was de-aerated and 19 flushed with Ar. Further, the reaction mixture was stirred at a suitable temperature on an oil bath

1 (Fig. S19). The amount of gas generated per unit time was quantified by the water displacement 2 method, and the composition of the released gas was confirmed by GC-TCD. The turnover number 3 (TON) was calculated by the formula $[n(H_2)/n(catalyst)]$. The turnover frequency (TOF) was 4 calculated as TON/time. After the catalytic reaction, the supported ruthenium nanoparticles were 5 collected by centrifugation and dried in a vacuum oven and weight to ~14 mg of catalysts (as 6 obtained from 25 mg of **[Ru]-1** used in the catalytic reaction) which can be used for the further 7 catalytic cycles.

8 Catalytic hydrogen production from ethanol/*n*-propanol. Catalytic hydrogen production from 9 ethanol/n-propanol was performed following the procedure used for methanol, by using ethanol/n-10 propanol (16.08 mmol), **Ru/L1** catalyst (0.625 mol%, n([Ru]-1)/n(L1) = 1:2) and potassium 11 hydroxide (1.2 equiv.) in water (1 equiv.). Then the 5 mL test tube reaction vessel, connected equipped with a condenser (-10 $^{\circ}$ C) and water displacement setup, was de-aerated and flushed with 12 13 Ar. Further, the reaction mixture was stirred at 110 °C on an oil bath. The amount of gas generated 14 per unit time was quantified by the water displacement method, and the composition of the released 15 gas was confirmed by GC-TCD. The turnover number (TON) was calculated by the formula 16 $[n(H_2)/n(\text{catalyst})]$. The turnover frequency (TOF) was calculated as TON/time.

17 **Synthesis of ruthenium nanoparticles.** Ru nanoparticles were synthesized by adding the 18 dropwise of an aqueous solution of NaBH₄ (0.025 g, in 5 mL of water) in an aqueous solution of 19 RuCl₃.3H₂O (0.026 g, 0.1 mmol, in 5 mL of water) and PVP (0.05 g). The content of the flask was 20 sonicated for 10 min to obtain a black suspension of Ru nanoparticles, which were collected by 21 centrifugation and was washed with distilled water (10 mL x 02).

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Long term stability and recyclability experiments. Initially, the Ru/L1 catalyst (0.625 mol%, 1 2 n([Ru]-1)/n(L1) = 1:2) in methanol (16.08 mmol) and water (1 equiv.) was taken in a 5 mL test 3 tube reaction vessel, and was added KOH (1.2 equiv.). Then the reaction vessel, connected equipped with a condenser (-10 °C) and water displacement setup, was de-aerated and flushed 4 5 with Ar. Further, the reaction mixture was stirred at 130 °C on an oil bath. The amount of gas 6 generated per unit time was quantified by the water displacement method. For the subsequent 7 catalytic run, the reaction mixture was centrifuged to separate the catalyst. Further, the catalyst 8 was transferred to the reaction vessel, and methanol (16.08 mmol), water (1 equiv.) and KOH (1.2 9 equiv.) were added to the reaction vessel, and the reaction mixture was stirred at 130 °C on an oil 10 bath under Argon atmosphere. The release of gas was monitored by water displacement process, 11 and the composition of the released gas was confirmed by GC-TCD.

13 Conclusion

14 We developed an efficient new Ru/L1 catalyst comprises of ligand capped ruthenium 15 nanoparticles homogeneously dispersed over the carbon support, in-situ generated from the 16 ruthenium arene precursor and 2-hydroxypyridine (L1) ligand. The Ru/L1 catalytic system 17 displayed excellent catalytic activity for CO₂ free hydrogen production from methanol (1.43 mol 18 of H₂ per mol of methanol) at low temperature (110 - 130 °C). This process also generated formic 19 acid as a byproduct. The studied catalyst exhibited outstanding long-term stability to generate 186 20 L of H₂ gas per gram of Ru. This catalytic system may encourage the search of an efficient 21 industrially viable process for the low-temperature transformation of methanol to hydrogen gas 22 and formic acid.

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Graphical Abstract

Efficient conversion of methanol to hydrogen gas and formate with appreciably high TOF and TON achieved over *in situ* generated ruthenium catalyst in water at low temperature.

