

## FULL PAPER

# Supported ruthenium hydride catalysts for direct conversion of alcohols to carboxylic acids using styrene oxide as oxidant

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In the present work, the ability of two ruthenium hydride catalysts supported on multiwall carbon nanotubes, [Ru-H@EDT-MWCNT], and gold nanoparticles cored triazine dendrimer, [Ru-H@AuNPs-TD], in the direct conversion of alcohols to carboxylic acids *via* transfer hydrogenation using styrene oxide as oxidant is reported. Different alcohols were successfully converted to their corresponding carboxylic acids. The results showed that these two heterogeneous catalysts are more efficient than the homogeneous counterpart. In addition, the catalysts were reused several times.

**KEYWORDS**

alcohols, carboxylic acids, nanoparticle, oxidation, ruthenium hydride catalyst

## 1 | INTRODUCTION

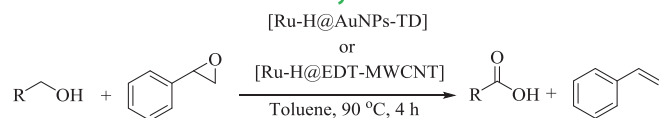
Carboxylic acids are a class of essential chemicals in daily life, academic laboratories, and industry. Therefore, direct oxidation of alcohols to carboxylic acids is one of the most important reactions in organic synthesis.<sup>[1]</sup> Traditionally, stoichiometric amount of an expensive and toxic oxidant used in this reaction.

Several catalysts and reagents such as RuCl<sub>3</sub>/NaIO<sub>4</sub>,<sup>[2]</sup> CrO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub>,<sup>[3]</sup> TEMPO/NaClO,<sup>[4]</sup> Na<sub>2</sub>WO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>,<sup>[5]</sup> CrO<sub>3</sub>/H<sub>5</sub>IO<sub>6</sub>,<sup>[6]</sup> TEMPO/NaClO<sub>2</sub>,<sup>[7]</sup> Na<sub>2</sub>WO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> in the presence of quaternary ammonium hydrogensulfate,<sup>[8]</sup> *o*-iodoxybenzoic acid (IBX)/Oxone,<sup>[9]</sup> PCC/H<sub>5</sub>IO<sub>6</sub>,<sup>[10]</sup> VO(acac)<sub>2</sub>/Cu(II) salt/O<sub>2</sub>,<sup>[11]</sup> Bi<sub>2</sub>O<sub>3</sub>/*t*-BuOOH,<sup>[12]</sup> and Pd/C/NaBH<sub>4</sub>/base<sup>[13]</sup> have been used for direct oxidation of alcohols to carboxylic acids. Recently, photooxidation of alcohols to carboxylic acids and ketones using 2-chloroanthraquinone as an organocatalyst under visible light irradiation under air atmosphere is was reported.<sup>[14]</sup> Jiang and coworkers reported the application of silver NHC catalyst for selective oxidation of alcohols to aldehydes or carboxylic acids in the presence of BnMe<sub>3</sub>NOH or KOH.<sup>[15]</sup> Prechtl group reported the application of ruthenium PNP pincer

complexes, [Ru(H<sub>2</sub>)H<sub>2</sub>(Me-PNP)] and [RuH<sub>2</sub>(CO)(Me-PNP)], in the oxidation of alcohols to carboxylic acids using water as oxygen source.<sup>[16]</sup> Chemoselective oxidation of 1,2-diols to  $\alpha$ -hydroxy acids using TEMPO/NaOCl/NaClO<sub>2</sub> catalytic system was reported by Shibuya group.<sup>[17]</sup> Madson and his coworkers introduced a method for synthesis of carboxylic acids from primary alcohols catalyzed by a Ru-NHC complex.<sup>[18]</sup> Ma group applied the Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O/TEMPO/MCl catalytic system in the presence of O<sub>2</sub> as oxidant for oxidation of alcohols to carboxylic acids.<sup>[19]</sup> The [RuH(CO)(py-NP)(PPh<sub>3</sub>)<sub>2</sub>]Cl catalyst was found as an efficient catalyst for conversion of primary alcohols to carboxylic acid salts.<sup>[20]</sup>

The ruthenium hydride catalysts have been reported as efficient catalysts for dehydrogenation of alcohols. For example, Hong and Muthaiah reported the ability of RuH<sub>2</sub>(CO)(PPh<sub>3</sub>)<sub>3</sub>, RuH<sub>2</sub>(PPh<sub>3</sub>)<sub>4</sub> and Shvo's complexes in the dehydrogenation of secondary alcohols.<sup>[21]</sup>

The RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> has found many applications in organic synthesis.<sup>[22-34]</sup> Recently, we reported the direct conversion of alcohols to carboxylic acids using styrene oxide or DMSO as oxidant *via* transfer hydrogenation.<sup>[35,36]</sup> But the main disadvantage of this expensive



**SCHEME 1** Oxidation of alcohols to carboxylic acids with styrene oxide catalyzed by supported ruthenium hydride catalysts

catalyst is that the catalyst is not recoverable and reusable. One way to solve this problem is to immobilized this homogeneous catalyst on solid supports such as carbon nanotubes and gold nanoparticles.<sup>[37,38]</sup>

In this paper, we wish to report the application of  $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$  complex supported on multiwall carbon nanotubes,  $[\text{Ru-H@EDT-MWCNT}]$ , and gold nanoparticles cored triazine dendrimer,  $[\text{Ru-H@AuNPs-TD}]$ , in the direct conversion of alcohols to carboxylic acids *via* transfer hydrogenation using styrene oxide as oxidant (Scheme 1).

## 2 | EXPERIMENTAL

Chemicals obtained from Merck and Fluka chemical companies. FT-IR spectra were recorded on a Jasco 6300 spectrophotometer.  $^1\text{H}$  and  $^{13}\text{C}$  NMR (400 and 100 MHz) spectra were recorded on a Bruker Avance 400 MHz spectrometer using  $\text{CDCl}_3$  as solvent. Elemental analysis was performed on a LECO, CHNS-932 analyzer. The scanning electron microscope measurements were carried out on a Hitachi S-4700 field emission-scanning electron

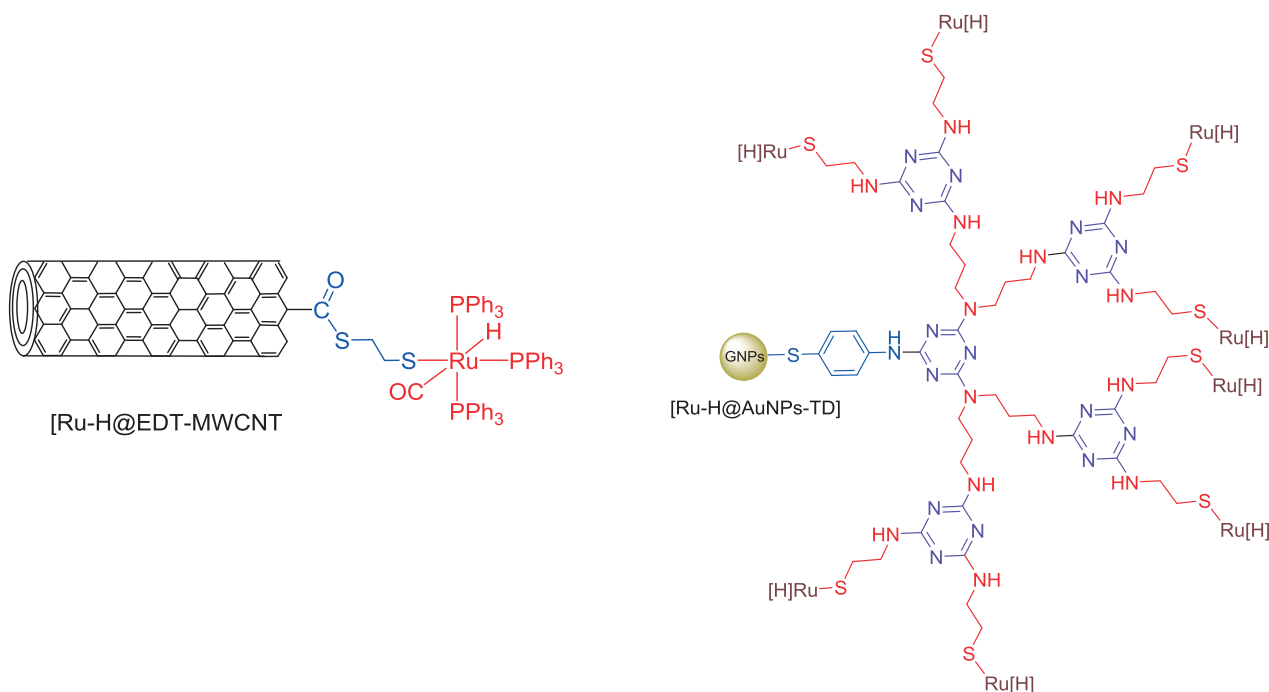
microscope (FE-SEM). The transmission electron microscopy (TEM) was carried out on a Philips CM10 Transmission Electron Microscope operating at 100 kV. The Ru content of the catalyst was determined by a Jarrell-Ash 1100 ICP analysis. The  $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$  complex was prepared and supported on MWCNT and gold nanoparticles according to the literature.<sup>[37-39]</sup> The procedure for catalysts preparations are supplied in supporting information.

### 2.1 | General procedure for oxidation of alcohols to carboxylic acids catalyzed by $[\text{Ru-H@EDT-MWCNT}]$ and $[\text{Ru-H@AuNPs-TD}]$ using styrene oxide as oxidant

In a screw capped test tube, a mixture of alcohol (1 mmol), styrene oxide (1.3 mmol),  $[\text{Ru-H@EDT-MWCNT}]$  (300 mg, 0.03 mmol) or  $[\text{Ru-H@AuNPs-TD}]$  (80 mg, 0.02 mmol) in toluene (5 ml) was prepared. The test tube was purged with argon and sealed, and the reaction mixture was stirred at 100 °C for 4 h. At the end of the reaction, the catalyst was filtered, washed with EtOH (5 ml). The pure product obtained by thin layer chromatography (EtOAc:petroleum ether, 6:1).

### 2.2 | Catalyst recovery

The recovery of both catalysts was checked in the oxidation of benzyl alcohol with styrene oxide. The reaction



**FIGURE 1** The structure of heterogeneous catalysts

procedure is as described above. At the end of each reaction, the filtered catalyst was dried and used in the next run using fresh benzyl alcohol and styrene oxide.

### 3 | RESULTS AND DISCUSSIONS

#### 3.1 | Oxidation of alcohols with styrene oxide catalyzed by supported ruthenium hydride catalysts

The structure of both catalysts is shown in Figure 1.

After successful application of these two catalysts in organic synthesis<sup>[37,38]</sup> we decided to investigate their catalytic activity in the direct synthesis of carboxylic acids from alcohols. In this manner, first the reaction parameters were optimized in the oxidation of benzyl alcohol with styrene oxide (Table 1). Among THF, acetonitrile, 1,2-dichloroethane and toluene; the highest yields obtained in toluene (entries 1–4). Different amounts of both catalysts were used and 0.03 mmole of [Ru-H@EDT-MWCNT] and 0.02 mmole of [Ru-H@AuNPs-TD] were the optimized amount (entries 4–8). While in the absence of both catalysts, no product was detected in the reaction mixture (entry 10). In the absence of styrene oxide, only benzaldehyde obtained as product. This is due to the ability of RuHCl(CO)(PPh<sub>3</sub>)<sub>3</sub> in the oxidation of alcohols to aldehydes.<sup>[34]</sup> Note that in all reactions trace amounts of the corresponding aldehyde was

also observed. The effect of temperature was also investigated in both catalytic systems and 100 °C was the best (entries 4, 9, 10).

Despite the ability of gold nanoparticles in the aerobic oxidation of alcohols to aldehydes,<sup>[40]</sup> when gold nanoparticles cored triazine dendrimer, AuNPs-TD, used as catalyst in the oxidation of benzyl alcohol, no benzaldehyde was produced (entry 12). This is due to the absence of oxygen in the reaction mixture.

After optimization of reaction conditions, different substituted benzyl alcohols were successfully oxidized and the corresponding carboxylic acids were produced in good to excellent yields (Table 2, entries 1–6). The *N*-(2-hydroxyethyl)benzamide and *N*-(2-hydroxyethyl)-4-methylbenzamide were also oxidized to corresponding carboxylic acids in good yields (entries 7 and 8).

As we mentioned previously,<sup>[35]</sup> the plausible mechanism is as following:

The Ru catalyst has a dual role in this mechanism. The first role is its ability to react with styrene oxide to produce the intermediate **I** (This step was confirmed by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy). The second role is its ability for conversion of alcohols to aldehydes and releasing H<sub>2</sub>.<sup>[34]</sup> This produced aldehyde then reacts with complex **I** via a nucleophilic reaction and gives the intermediate **II**. This intermediate converts to styrene and carboxylic acid and releases the Ru-hydride catalyst for the next catalytic cycle (Scheme 2).

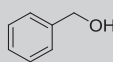
**TABLE 1** Optimization of conditions in the reaction benzyl alcohol with styrene oxide<sup>a</sup>

Entry	Catalyst amount, mg (mmol)		Solvent	T (°C)	Yield (%) <sup>b</sup>	
	(1)	(2)			(1)	(2)
1	300 (0.03)	80 (0.02)	CH <sub>3</sub> CN	100	41	35
2	300 (0.03)	80 (0.02)	THF	100	53	48
3	300 (0.03)	80 (0.02)	1,2-DCE	100	78	72
4	300 (0.03)	80 (0.02)	Toluene	100	94	92
5	100 (0.01)	40 (0.01)	Toluene	100	45	38
6	200 (0.02)	60 (0.015)	Toluene	100	73	65
7	400 (0.04)	100 (0.025)	Toluene	100	95	92
8	300 (0.03)	80 (0.02)	Toluene	90	85	84
9	300 (0.03)	80 (0.02)	Toluene	110	95	93
10	0	0	Toluene	100	0	0
11	300 (0.03)	80 (0.02)	Toluene	100	57 <sup>c</sup>	51 <sup>c</sup>
12	-	AuNPs-TD	Toluene	100	-	trace <sup>c</sup>

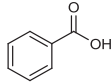
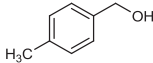
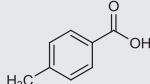
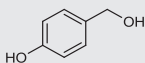
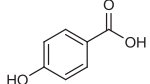
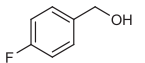
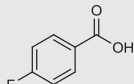
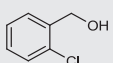
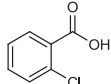
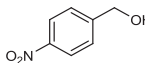
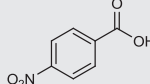
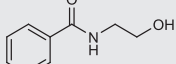
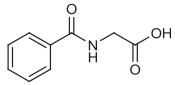
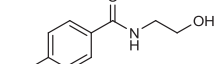
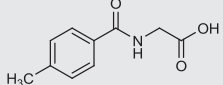
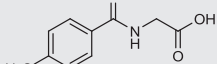
<sup>a</sup>All reactions were performed using benzyl alcohol (1 mmol), styrene oxide (1.3 mmol), supported catalyst and solvent (5 ml) in a screw test tube for 4 h.

<sup>b</sup>Isolated yield.

<sup>c</sup>The benzaldehyde was produced.

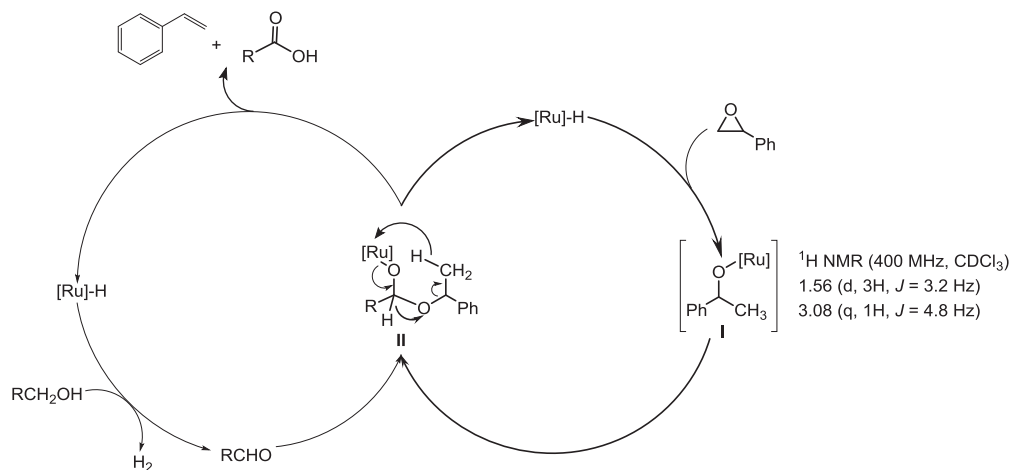


**TABLE 2** Oxidation of alcohols to carboxylic acids with styrene oxide catalyzed by supported ruthenium hydride catalysts<sup>a</sup>

Entry	Alcohol	Acid	Yield (%) <sup>b</sup>		TOF (h <sup>-1</sup> )	
			1	2	1	2
1			83	80	6.92	10.0
2			84	82	6.92	10.25
3			90	88	7.5	11.0
4			93	92	7.75	11.5
5			85	84	7.1	10.5
6			91	92	7.60	11.5
7			77	72	6.42	9.0
8			80	78	6.67	9.75

<sup>a</sup>Reaction conditions: Alcohol (1 mmol), styrene oxide (1.3 mmol), [Ru-H@EDT-MWCNT] (1) (0.03 mmol) or [Ru-H@AuNPs-TD] (2) (0.02 mmol), toluene (5 ml) in a screw test tube for 4 h.

<sup>b</sup>Isolated yield.

**SCHEME 2** The proposed mechanism for direct oxidation of alcohols to carboxylic acids

The liberated hydrogen converts the produced styrene to ethyl benzene. On the other hand, the styrene oxide acts as hydrogen acceptor and is converted to 1-phenyl ethanol.<sup>[35]</sup> Therefore, in all reactions, small amounts of ethyl benzene, 1-phenyl ethanol and the corresponding aldehyde were also detected.

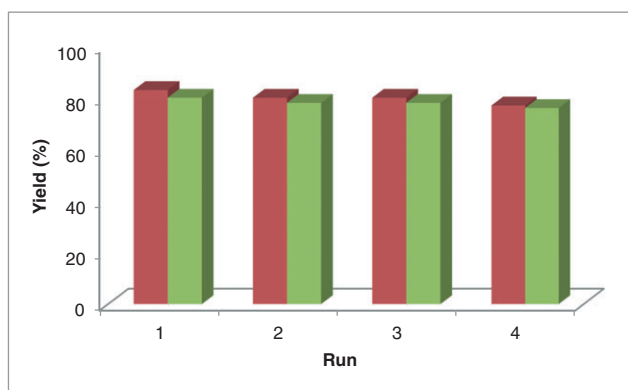
Comparison of the catalytic activity of these two catalysts shows that the [Ru-H@AuNPs-TD] is more reactive than [Ru-H@EDT-MWCNT] in the direct oxidation of alcohols to carboxylic acids with styrene oxide. This can be attributed to the smaller size of the gold nanoparticles compared to MWCNTs.<sup>[37,38]</sup>

On the other hand, these two catalysts are more efficient than homogeneous counterpart. The TOFs for homogeneous catalyst are about 1.33–1.55 h<sup>-1</sup>, while in the presence of both these catalysts the TOFs reached to 6.42–11.5 h<sup>-1</sup>. This may be due to the dispersion of catalytic active site on high surface area nanoparticles which increases the accessibility of active sites for the substrates.

### 3.2 | Catalysts recovery and reuse

In addition of higher catalytic activity of heterogeneous catalysts compared to homogeneous catalyst, the latter catalyst is not reusable and this limits the practical application of the homogeneous catalyst.

The reusability of heterogeneous catalysts was investigated in the oxidation of benzyl alcohol. At the end of the reaction, the catalyst was filtered and used in the next run with fresh benzyl alcohol and styrene oxide. The results showed that both catalysts reused four consecutive times without significant loss of their catalytic activities (Figure 2). The yields reached to 77 and 76% for catalysts **1** and **2**, respectively. Also, the filtrates were used for determination of Ru leached after each cycle. The ICP results showed that only in the first run about 5 and 4% of the initial Ru were leached.



**FIGURE 2** Catalyst recovery and reuse in the oxidation of benzyl alcohol. Green: [Ru-H@EDT-MWCNT] (**1**) and red: [Ru-H@AuNPs-TD] (**2**)

## 4 | CONCLUSION

In conclusion, two heterogeneous catalysts based on the supporting of ruthenium hydride catalyst supported on multi-walls carbon nanotubes and gold nanoparticles cored triazine dendrimer were applied for direct oxidation of alcohols to carboxylic acids with styrene oxide via transfer hydrogenation. The prepared catalysts were high stability and reusability in oxidation of alcohols.

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## SUPPORTING INFORMATION

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