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Titanium dioxide supported ruthenium nanoparticles for carbon sequestration reaction

Praveenkumar Ramprakash Upadhyay, Vivek Srivastava*
NIIT University, NH-8 Jaipur/Delhi Highway, Neemrana (Rajasthan), 301705, India
*vivek.shrivastava@niituniversity.in

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Ru metal doped TiO_2 nanoparticles were synthesized using a sol gel method with and without ionic liquid. Ru metal is well dispersed while utilizing ionic liquid as reaction medium for catalyst synthesis with respect to Ru–TiO_2 catalyst. A TEM image for Ru–TiO_2–IL catalyst reveals, stable, well dispersed and agglomeration free Ru metal doped TiO_2 nanoparticles. CO_2 Hydrogenation reaction on task specific ionic liquid medium, offered the formic acid in high TON/TOF value with added advantage of 5 times catalyst recycling.

Keywords: ruthenium metal, titanium dioxide, nanoparticles, hydrogenation, carbon sequestration, formic acid.

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1. Introduction

Various physiochemical methods have been reported for the fixation of CO_2 gas, such as carbonates, geological or ocean storage or afforestation [1–4]. However, these approaches have severe drawbacks in terms of economic factors, safety, efficiency, and reliability of their immediate application. It is also known that functionalized ionic liquid mediated Ru (II) compounds can promote the partial hydrogenation of CO_2 to formic acid where the ionic liquid not only captures the formed formic acid but also shifts the equilibrium of the hydrogenation reaction. The pre-organized structure of imidazolium based ionic liquids (ILs) provides structural directionality though their hydrogen bonding, as opposed to classical salts in which the aggregates display charge-ordering structures [4]. The structural organization of ILs provides a special "entropic drivers" for natural, precise, and prolonged assembling of nanoscale assemblies [5, 6]. We successfully applied imidazolium ionic liquids as a template, additive, and solvent for the synthesis of an excess of transition-metal nanoparticles [7]. The catalytic properties (activity and selectivity) of these soluble metal nanoparticles direct that they possess a pronounced surface like (multi-site) rather than single-site-like catalytic properties [8–10]. The main goal of this proposed work is to develop supported functionalized ionic liquid ruthenium nanoparticles [11] in TiO_2 (nanoparticles and nanotubes) for the hydrogenation of CO_2.

2. Experimental

Reagent Plus® grade ruthenium (III) chloride hydrate and titanium tetraisopropoxide were purchased from Aldrich. Other ReagentPlus® and extra pure grade chemicals were purchased from Spectrochem. Nuclear Magnetic Resonance (NMR) spectra were recorded on a standard Bruker 300WB spectrometer with an Avance console at 400 and 100 MHz for ^{1}H NMR. All the hydrogenation reactions were carried out in a 100 mL stainless steel autoclave (Amar Equipment, India). The catalyst material was characterized by TEM (Hitachi S-3700N) and Energy-dispersive X-ray spectroscopy (EDX) (Perkin Elmer, PHI 1600 spectrometer). FTIR data for all the samples were studied with Bruker Tensor-27. 1-Butyl-3-methylimidazolium Chloride, 1,3-*di*(*NN*-dimethylaminoethyl)-2-methylimidazolium trifluoromethanesulfonate ([DAMI][TfO]), 1,3-*di*(*NN*-dimethylaminoethyl)-2-methylimidazolium *bis* (trifluoromethylsulfonyl) imide ([DAMI][NTf_2]) and 1-butyl-3-methylimidazolium chloride ionic liquids were synthesized as per reported procedures [12, 13]. FTIR data for all the samples were studied with Bruker Tensor-27. The morphology of catalysts was investigated by transmission electron microscopy (TEM) using a Philips CM12 instrument. XRD was performed on Philips X-Pert diffractometer. The normalized X-ray absorption near stretcher (XANES) spectra was recorded on BL01C1.

3. Result and discussion

We synthesized two different ruthenium metaldoped TiO_2 nanoparticles with and without ionic liquids, Ru–TiO_2–IL and Ru–TiO_2 respectively, using the sol-gel method and followed by calcination at 250 °C for 5 hours. The XRD pattern of TiO_2 was compared with that of Ru–TiO_2–IL and Ru–TiO_2 (Fig. 1) [14] from the wide angle XRD pattern The titania samples were found only in anatase phase with characteristic diffraction peaks of 2 degree values near 42 – 44 °, being assigned to metallic ruthenium (PDF No. 06-0633) observed for the Ru–TiO_2

catalyst. However, there were no characteristic peaks of Ru° observed for the Ru–TiO_2-IL catalyst, indicating a high dispersion of Ru on the TiO_2 support.

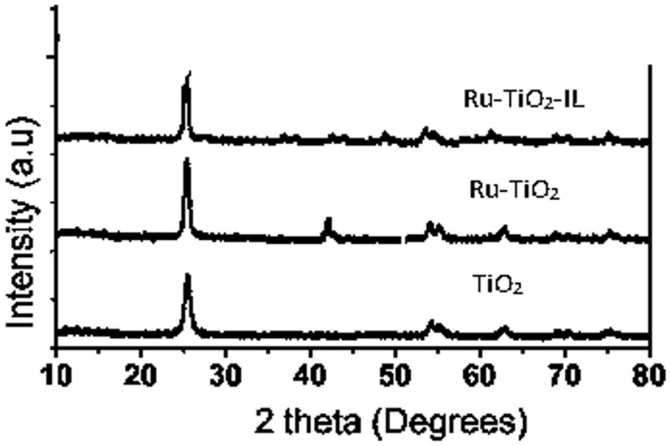

FIG. 1. XRD data for ruthenium metal doped titanium dioxide nanoparticles

The FTIR analysis of TiO_2 with respect to Ru–TiO_2–IL and Ru–TiO_2 catalysts was carried out from 400 – 4000 cm^{-1} (Fig. 2). In Ru loaded TiO_2, clear bands for the O–Ti–O bonding were found near 445 and 708 cm^{-1}. The representing band for δ-H_2O bending appeared near to 1605 cm^{-1}. A broad absorption band showing the-O and O–Ti–O flexion vibration band found between 400 cm^{-1} and 800 cm^{-1}.

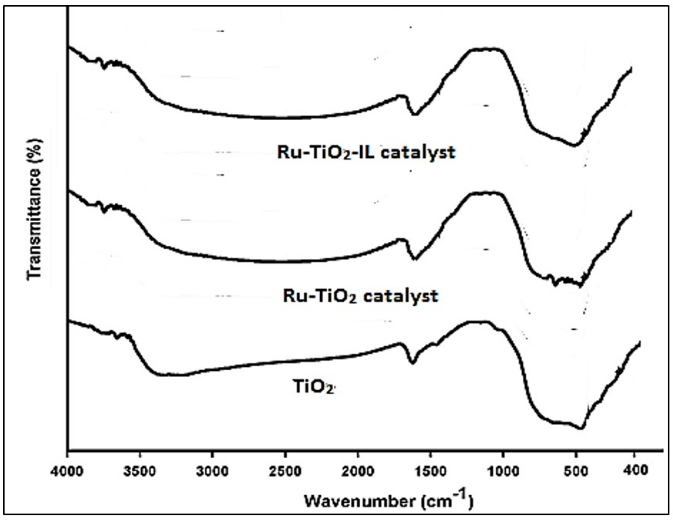

FIG. 2. Infrared data for Ru-TiO_2 nanoparticles

TEM micrographs of TiO_2, Ru–TiO_2–IL and Ru–TiO_2 are shown in Fig. 3. Electron microscopy reveals the morphology of the TiO_2, Ru–TiO_2–IL and Ru–TiO_2. It was clearly observed that for Ru–TiO_2 catalyst, many severely strained ruthenium nanoparticles larger than 25 ± 5 nm were found on the surface of TiO_2 while in Ru–TiO_2–IL catalysts, ultrafine Ru nanoparticles with uniform particle size were dispersed on the surface of TiO_2. It is worth noting here that no particles larger than 20 nm, were observed despite our careful attention. More intuitively, the average particle size for the Ru–TiO_2 catalyst was found to be 25 ± 5 nm. However, it was only 15 ± 5 nm with narrower particle size spreading for the Ru–TiO_2–IL catalyst. These observations indicated that the reaction medium type could remarkably affect the dispersion of Ru on the TiO_2 surface and the ionic liquid was a more efficient reaction medium than conventional solvents to stabilize the smaller nano-sized particles of Ru.

Theoretical (cation exchange capacity) and an experimental (ICP-AES) method was used to calculate the amount of Ru species in TiO_2. Both theoretical and experimental values were found to be in good agreement, and 2.5 wt% Ru was found in the Ru–TiO_2–IL catalyst while in Ru–TiO_2 catalyst, there was 2.1 wt% Ru metal.

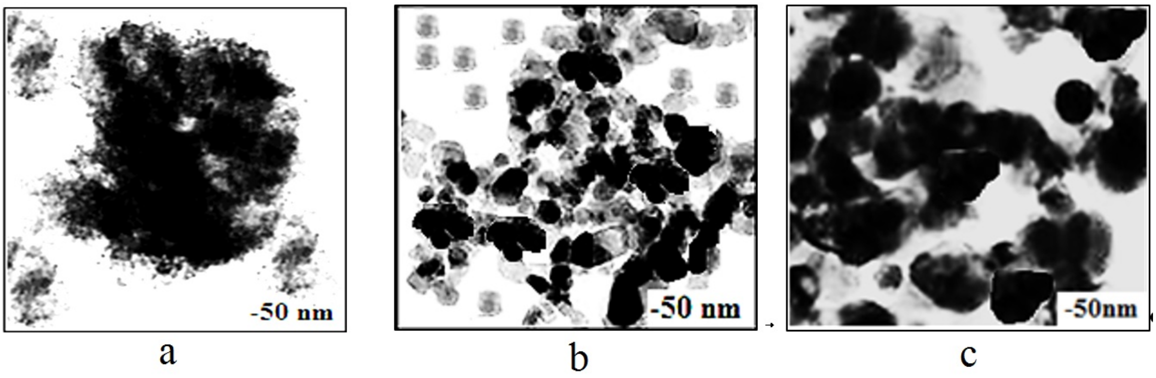

FIG. 3. TEM data for Ruthenium Metal Doped Titanium Dioxide Nanoparticles. (a) Ru-TiO_2 catalyst,(b) Ru-TiO_2-IL catalyst (Before catalysis), (c) Ru-TiO_2-IL catalyst (After catalysis)

This protocol also minimizes the loss of Ru nanoparticles during the process. Hydrogenation of CO_2 was carried out using H_2 gas in the presence of both the catalysts (without any pretreatment) with functionalized ionic liquids separately at 80 °C under high pressure. After the reaction, formic acid was isolated from the reaction mass followed by the nitrogen flow at 125 – 130 °C. The results obtained while optimizing the reaction conditions with respect to TON/TOF values for formic acid were summarized in Table 1, entry 1 – 17. Acid-base titration using phenolphthalein indicator and ^{1}H NMR analysis was used to calculate the quantity of formic acid formed [12, 13].

Initially, both catalysts were tested under the same reaction conditions for CO_2 hydrogenation and high TON/TOF values were obtained with [DAMI][NTf_2] immobilized Ru–TiO_2–IL (Table1, Entry 1 & 2). All the other important reaction parameters and technical variables were investigated using [DAMI][NTf_2] immobilized Ru–TiO_2–IL (Table 1, Entry 3 – 17). We obtained good TON/TOF value at 100 °C when, the total H_2/CO_2 gas pressure was 40 MPa (Table 1, Entry 3). The effect of water was also studied on the reaction kinetics of CO_2 hydrogenation reaction only, with 2 ml of water with a high TON/TOF value (Table 1, entry 12). CO_2 may react with water and an amine group of ionic liquid to give off bicarbonates which may act as a perfect substrate for the hydrogenation reaction. $RuCl_3$ was also evaluated for the hydrogenation reaction, but formic acid was obtained with a low TON/TOF value compared to [DAMI] [NTf_2] immobilized Ru–TiO_2–IL (Table 1), Entry 17). After the reaction, formic acid was isolated with the aid of N_2 gas and the [DAMI] [NTf_2] ionic liquid immobilized Ru–TiO_2–IL went for a recycling test after washing with diethyl ether. [DAMI] [NTf_2] ionic liquid immobilized Ru–TiO_2–IL were recycled up to 5 times with slight loss of their catalytic action mainly because of agglomeration of Ru NPs which was also confirmed by TEM analysis of the Ru NPs (Fig. 4).

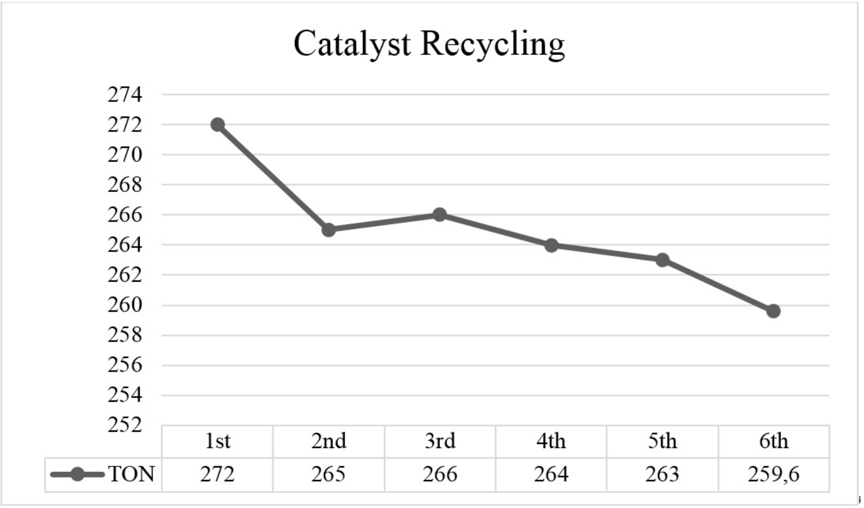

FIG. 4. Catalyst recycling experiment

TABLE 1. Hydrogenation of CO_2 to Formic acid using ionic liquid immobilized TiO_2 dropped Ru metal[1]

Entry	Catalytic system	$P(H_2)$ P_{total} (MPa)[2]	Temperature(°C)	Time (h)	TON[3]
1.	Ru–TiO_2–IL /[DAMI][TfO]	20 (40)	80	1	252
2.	Ru–TiO_2/[DAMI][TfO]	20 (40)	80	1	222
3.	Ru–TiO_2–IL /[DAMI] [NTf_2]	20 (40)	80	1	246
4.	Ru–TiO_2–IL /[DAMI][TfO]	20 (40)	100	1	253
5.	Ru–TiO_2–IL /[DAMI][TfO]	20 (40)	120	1	253
6.	Ru–TiO_2–IL /[DAMI][TfO]	20 (40)	50	1	195
7.	Ru–TiO_2–IL /[DAMI][TfO]	20 (40)	100	1.5	152
8.	Ru–TiO_2–IL /[DAMI][TfO]	20 (40)	100	0.3	85
9.	Ru–TiO_2–IL /[DAMI][TfO]	10 (20)	100	1	195
10.	Ru–TiO_2–IL /[DAMI][TfO]	30 (60)	100	1	252
11.	Ru–TiO_2–IL /[DAMI][TfO]+ H_2O (1 mL)	20 (40)	100	1	258
12.	Ru–TiO_2–IL /[DAMI][TfO]+H_2O (2 mL)	20 (40)	100	1	270
13.	Ru–TiO_2–IL /[DAMI][TfO]+H_2O (3 mL)	20 (40)	100	1	272
14.	Ru–TiO_2–IL / [DAMI] [TfO] (0.100g)+ H_2O (2 mL)	20 (40)	100	1	272
15.	Ru–TiO_2–IL / [DAMI] [TfO] (0.500g)+ H_2O (2 mL)	20 (40)	100	1	272
16.	Ru–TiO_2–IL / [DAMI][NTf_2]+ H_2O (2 mL)	20 (40)	100	1	260
17.	$RuCl_3$ (0.07g)[4]+ [DAMI][NTf_2](0.250g)	20 (40)	100	1	224

1. Reaction conditions: 0.250 g catalytic system; 2. The total pressure of the system is indicated in parentheses; 3. Turn over number $= n$ (formic acid) n (Ru) $^{-1}$ in one reaction cycle; 4. Turnover frequency $= n$ (formic acid) n (Ru) $^{-1}h^{-1}$; 5. $RuCl_3 \cdot xH_2O$ (50 % Ru metal).

4. Conclusion

Here, we reported the synthesis of air/moisturestable, TiO_2 supported Ru nanoparticles with a narrow particle size distribution. The [DAMI] [NTf_2] ionic liquid immobilized Ru–TiO_2–IL catalyst was found to be highly active in terms of TON/TOF value for the production of formic acid over conventional and Ru–TiO_2 catalyst. Effect of water was also studied during the CO_2 hydrogenation reaction. The presence of functionalized ionic liquid as well as water was promising. Five times catalyst recycling, low catalyst loading and selectivity were the major advantages for this proposed protocol.

Acknowledgement

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