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Article

Ruthenium nanoparticles supported on mesoporous MCM-41 as an efficient and reusable catalyst for selective oxidation of arenes under ultrasound irradiation

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ARTICLE INFO

Article history:

Received 9 October 2015

Accepted 24 October 2015

Published 5 January 2016

Keywords:

Nanoparticle

Ultrasound

Ruthenium

Arene oxidation

MCM-41

ABSTRACT

Mesoporous MCM-41 was used as a support for the uniform dispersion of ruthenium nanoparticles having an average particle size of ~5 nm. The obtained nanocomposite, MCM-41-Ru, was characterized using inductively coupled plasma, transmission electron microscopy, energy dispersive X-ray analysis, X-ray diffraction, and BET surface area measurements. The material was employed as an efficient and recyclable catalyst in the ultrasound-assisted oxidation of arenes. It was observed that ultrasound irradiation in combination with KBrO_3 as the oxidant, in the presence of MCM-41-Ru nanoparticles, accelerates the oxidation reaction to afford the desired products in good yields. The recovered catalyst retained activity for successive runs, with a continuous change in the nature of its active sites.

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1. Introduction

Applying nanoparticles in the manufacture of fine chemicals is currently an area of intense interest because of their unique features. Such features include electrical and magnetic properties, selectivity and, above all, reusability, which is a valuable property in applications such as drug delivery, green chemistry, and sensors [1–8]. Oxidation products of arenes have also attracted attention because of their notoriety as carcinogens and their usefulness as chelating ligands and as intermediates in the preparation of fused-ring molecules [9–13]. Many investigations have reported the development of simple and efficient methods for direct oxidation of arenes [14–16]. Typically, oxidation of arenes in the presence of a metal oxidant, such as chromium(VI) oxide, requires a large excess of the oxidant. Metal residues, however, are environmentally undesirable and often cause difficulties during reaction and work-up. Bio-

transformation of arenes has also been reported. One study by Obbard's group [17] reported that the white rot fungus oxidation of polycyclic aromatic hydrocarbons had a limited applicability to higher arenes. Hence, developing new methods for selective oxidation of arenes, which utilizes a metal catalyst in combination with an appropriate stoichiometric oxidant, is in demand. Direct oxidation to diones has been reported in low yields by using osmium tetroxide, which is highly toxic [18]. RuO_4 species generated in situ, together with sodium periodate (NaIO_4) as a cheap and readily available oxidant, provides a promising alternative for such oxidations [19–23]. Harris' group [24] reported a one-step synthesis of pyrene-4,5-diones and pyrene-4,5,9,10-tetraones by using RuCl_3 as the catalyst and NaIO_4 as the oxidant. We studied their protocols for generating various arenes and heteroaromatic compounds, which used ultrasound irradiation to overcome the prolonged reaction time, and although the results were promising [25], the

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This work was supported by the Research Council of University of Guilan.

DOI: 10.1016/S1872-2067(15)61001-4 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 37, No. 1, January 2016

catalyst was not recoverable. Furthermore, previous studies on ruthenium-catalyzed oxidation of arenes yielded either dicarboxylic acids, tetracarboxylic acids, or diols [26–28]. Herein, we report an improvement to the limitations of our previous report by using ruthenium nanoparticles dispersed on mesoporous MCM-41 to circumvent the difficulty in catalyst recovery. The catalyst was found to be efficient and recyclable in the ultrasound-assisted oxidation of aromatic compounds.

2. Experimental

2.1. Materials

All materials were purchased from Merck and used without further purification. Pure-silica MCM-41 was synthesized according to the literature [29].

2.2. Preparation of MCM-41-Ru nanoparticles

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (51.8 mg) was added to a suspension of MCM-41 (1.0 g) in 10 mL of absolute ethanol under N_2 atmosphere in a two-necked round bottom flask. Thereafter, a NaBH_4 solution (0.2 mol/L in ethanol, excess) was added drop-wise under vigorous stirring using a magnetic stirrer for a period of 2 h. The entire reaction mixture was stirred overnight to stabilize the Ru nanoparticles according to the MCM-41 framework. The obtained dark-gray product (MCM-41-Ru) was filtered and washed with ethanol followed by drying at 150 °C overnight.

2.3. Characterization of catalyst

IR spectra were recorded on a Shimadzu FTIR-8400S spectrometer. ^1H NMR spectra and ^{13}C NMR spectra were obtained on a Bruker DRX-500 (or 125) Advance Spectrometer. Chemical shifts were expressed in ppm downfield from tetramethylsilane as the internal standard. Melting points were measured on a Büchi®B-540 melting point tube and were uncorrected. Elemental analyses were conducted using a Carlo-Erba EA1110 CNNO-S analyzer, and the results agreed with the calculated values. X-ray powder diffraction (XRD) measurements were performed using a Philips diffractometer with monochromatic $\text{Cu K}\alpha$ radiation. Ultrasonication was performed in a Techno-Gaz Tecna 3 ultrasonic cleaner, which subjected samples to a frequency of 50–60 kHz under a typical power of 250 W. The reaction flask was positioned within the water bath of the ultrasonic cleaner at a temperature, controlled by the device. Analytical gas chromatography (GC) evaluation of product mixtures was performed on a gas chromatograph (split/splitless injector, CP Sil 8CB column, FID assembly; Teif Gostar Faraz Co., Iran). Transmission electron micrographs were obtained using a Philips MC-10 transmission electron microscope (TEM) employing an acceleration voltage of 80 kV. BET measurements were acquired using a Sibata surface area apparatus 1100. Inductively coupled plasma analysis was conducted on a Labtam 8440 Plasma Lab.

2.4. Ultrasound assisted MCM-41-Ru catalyzed oxidation of

arenes

A 20-mL flask was charged with CH_2Cl_2 (5 mL), H_2O (5 mL), CH_3CN (5 mL), chrysene (228.3 mg, 1 mmol), and KBrO_3 (0.5 g, 2.99 mmol). MCM-41-Ru (75 mg) was added into the flask, and the dark suspension was irradiated at room temperature for 1 h. The catalyst was separated from the reaction medium by filtration and washed with water and acetone, and then dried at 150 °C overnight. The reaction mixture was poured into 50 mL of water, and the organic phase was separated. The aqueous phase was extracted with CH_2Cl_2 (3×10 mL). The CH_2Cl_2 extracts were combined with the organic phase, washed with brine (3×10 mL), and dried over anhydrous sodium sulfate to yield a dark orange solution. The solution was concentrated under reduced pressure, and the mixture was purified by preparative thin-layer chromatography (n -hexane/ethyl acetate = 10/3), providing chrysene-5,6-dione as the major product and 2-(2-formylphenyl)-1-naphthaldehyde as the side product. The same procedure was also used for the reactions of other arene substrates.

2.5. Characterization data for selected products

Chrysene-5,6-dione (**4a**): Orange crystals, m.p. = 189–191 °C; IR (KBr): ν (cm^{-1}) = 660, 713, 756, 835, 957, 1040, 1086, 1250, 1298, 1364, 1447, 1483, 1595, 1662, 1693, 1767, 2927, 3066; ^1H NMR (500 MHz, CDCl_3 , 25 °C): δ = 7.52 (t, J = 7.5 Hz, 1H), 7.60 (t, J = 7.7 Hz, 1H), 7.74 (t, J = 8.5 Hz, 1H), 7.77 (t, J = 8.1 Hz, 1H), 7.87 (d, J = 7.9 Hz, 1H), 8.12 (d, J = 8.6 Hz, 2H), 8.18 (d, J = 7.4 Hz, 1H), 8.20 (d, J = 8.6 Hz, 1H), 9.43 (d, J = 8.8 Hz, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3 , 25 °C): δ = 121.54, 125.64, 126.34, 127.62, 128.09, 129.09, 130.32, 130.45, 131.09, 131.28, 132.67, 134.23, 136.49, 137.06, 137.78, 138.29, 182.45, 184.63 ppm; Anal. calcd. for $\text{C}_{18}\text{H}_{10}\text{O}_2$ (%): C 83.71, H 3.90, O 12.39; found: C 83.75, H 3.88.

2-(2-Formylphenyl)-1-naphthaldehyde (**4b**): Yellow crystals, m.p. = 214–216 °C; IR (KBr): ν (cm^{-1}) = 648, 709, 764, 831, 954, 1057, 1196, 1354, 1429, 1504, 1591, 1686, 2754, 2852, 2926, 3057; ^1H NMR (500 MHz, CDCl_3 , 25 °C): δ = 7.46 (d, J = 8.2 Hz, 2H), 7.67–7.81 (m, 3H), 7.79 (t, J = 8.0 Hz, 1H), 8.01 (d, J = 8.05 Hz, 1H), 8.15 (d, J = 8.3 Hz, 2H), 9.32 (d, J = 8.6 Hz, 1H), 9.92 (s, 1H), 10.23 (s, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3 , 25 °C): δ = 126.26, 127.81, 128.95, 128.97, 129.15, 129.43, 130.18, 130.28, 130.86, 132.55, 133.77, 133.91, 134.40, 134.97, 142.49, 144.65, 191.27, 193.61 ppm; Anal. calcd. for $\text{C}_{18}\text{H}_{12}\text{O}_2$ (%): C 83.06, H 4.65, O 12.29; found: C 82.09, H 4.66.

Pyrene-4,5-dione (**5a**): Orange crystals, m.p. = 299–302 °C; IR (KBr): ν (cm^{-1}) = 703, 837, 1267, 1350, 1429, 1517, 1610, 1663, 2850, 2923, 3068; ^1H NMR (500 MHz, CDCl_3 , 25 °C): δ = 7.52 (t, J = 7.6 Hz, 2H), 7.61 (s, 2H), 7.95 (d, J = 7.4 Hz, 2H), 8.18 (d, J = 6.8 Hz, 2H) ppm; ^{13}C NMR (125 MHz, CDCl_3 , 25 °C): δ = 127.52, 128.21, 128.44, 130.11, 130.21, 132.22, 136.04, 180.50 ppm; Anal. calcd. for $\text{C}_{16}\text{H}_8\text{O}_2$ (%): C 82.75, H 3.47, O 13.78; found: C 82.72, H 3.45.

Pyrene-4,5,9,10-tetraone (**6a**): Orange crystals, m.p. >350 °C; IR (KBr): ν (cm^{-1}) = 711, 808, 908, 1054, 1276, 1336, 1421, 1446, 1562, 1676, 2923; ^1H NMR (500 MHz, $\text{DMSO}-d_6$, 25 °C): δ

Fig. 1. XRD pattern of MCM-41-Ru nanoparticle composite.

= 7.62 (t, $J = 7.7$ Hz, 2H), 8.38 (d, $J = 7.7$ Hz, 4H) ppm; ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$, 25 °C): $\delta = 131.29, 131.44, 134.80, 136.82, 178.13$ ppm; Anal. calcd. for $\text{C}_{16}\text{H}_6\text{O}_4$ (%): C 73.29, H 2.31, O 24.41; found: C 73.23, H 2.30.

3. Results and discussion

Deposition of Ru nanoparticles over the surface of mesoporous MCM-41 was performed via a facile procedure, and the MCM-41-Ru composite was first characterized by XRD analysis. The MCM-41-Ru diffractogram (Fig. 1) displays peaks attributed to both the mesoporous structure and Ru nanoparticles. Peak reflections related to the siliceous mesoporous structure, at $2\theta = 1.5^\circ\text{--}10^\circ$ and indexed as the (100), (110), and (200) crystallographic planes, are characteristic of MCM-41 [29]. The Ru nanoparticles possess peak reflections at $2\theta = 38.4^\circ, 42.2^\circ, 44.0^\circ, 58.2^\circ, 69.6^\circ$, and 78.4° corresponding to the diffractions (100), (002), (101), (102), (110), and (103) planes, respectively, which are identical to the hexagonally close-packed (hcp) Ru metal (ICDD-JCPDS card No. 06-0663).

TEM revealed an abundance of ultrafine spherical particles (Fig. 2), which were homogeneously dispersed over the surface of the mesoporous structure and possessed a narrow particle size distribution averaging ~ 5 nm according to the corresponding particle size analysis chart. EDS analysis further confirmed the presence of Ru in the composite (Fig. 2). The Ru content of 1.983%, however, was determined using inductively

Fig. 3. N_2 adsorption-desorption isotherms of MCM-41 and MCM-41-Ru.

coupled plasma.

Deposition of the Ru nanoparticles, however, did not significantly affect the textural properties of the support. The N_2 adsorption-desorption isotherm of the calcined MCM-41 displays typical type-IV behavior with an observed H1-type hysteresis loop. The inflection point as given by the sharp inflection point over a narrow relative pressure indicates a highly ordered mesoporous material (Fig. 3). Conversely, the MCM-41-Ru sample showed a similar pattern (Fig. 3); however, a slight decrease in the uptake of adsorbed N_2 is observed, which can be attributed to the reduced surface area ($897 \text{ m}^2/\text{g}$ vs. $930 \text{ m}^2/\text{g}$). The small hysteresis loop is present at the same relative pressures, p/p_0 , between 0.25 and 0.35, indicating that no considerable pore-filling effect occurred after deposition of the Ru nanoparticles over the surface of MCM-41.

The characterized composite was then employed as a catalyst with naphthalene selected as the substrate. A set of optimization experiments were conducted to determine the optimum reaction conditions with respect to the catalyst loading, solvent, temperature, and oxidant. These results are summarized in Table 1.

The presence of MCM-41-Ru is necessary for the selective transformation of naphthalene to phthalaldehyde. In the absence of the catalyst, even after 12 h, only trace concentrations of naphthalene-1,4-dione and dihydronaphthalene-1,2-diol

Fig. 2. TEM image of the MCM-41-supported Ru nanoparticles (a), corresponding particle size distribution (b), and EDS spectrum (c).

Table 1

Experimental parameter effect on the oxidation reaction of naphthalene to phthalaldehyde.

Entry	Catalyst loading (mg/mmol)	Oxidant	Temperature (°C)	GC yield ^a (%)
1	0	NaIO ₄	25	0
2	25	NaIO ₄	25	11
3	50	NaIO ₄	25	24
4	75	NaIO ₄	25	41
5	100	NaIO ₄	25	43
6	150	NaIO ₄	25	39
7	75	H ₂ O ₂ (30%)	25	5
8	75	KBrO ₃	25	45
9	75	KBrO ₃	50	37
10	75	KBrO ₃	75	32

were detected by GC. In the presence of the catalyst, however, good selectivity toward phthalaldehyde resulted, with the optimum result utilizing KBrO₃ as the oxidant (entry 8). Elevating the temperature has an unfavorable impact on the yield, likely as a result of forming higher oxidation products, such as carboxylic acids, which were not characterized. All experiments required vigorous stirring of the reaction mixture because of the multiphase nature of the reactants.

Successful application of ultrasound irradiation in promoting such reactions [25] prompted the evaluation of applying sonic waves in the present method. Employing this technique increased the yield of the desired product to 68% (Table 2). Reaction yield was studied as a function of ultrasound frequency and irradiation intensity and compared with tunable sonotrode ultrasound intensity levels at 24 kHz. As shown in Table 2, at the same irradiation power, frequency does not have a noticeable impact on the reaction yield. The ultrasonic cleaner, however, has a much lower noise.

With the optimized conditions set, a series of arenes were subjected to the oxidation reaction in a multiphase system consisting of substrate, CH₂Cl₂, H₂O, CH₃CN, KBrO₃, and MCM-41-Ru. Typical results are shown in Table 3. Treatment of naphthalene (1 mmol) and KBrO₃ (0.5 g, 2.99 mmol) in a mixture of solvents (H₂O, CH₂Cl₂, CH₃CN, 5 mL) was performed in the presence of MCM-41-Ru composite as the catalyst. Employing sonication in an open vessel at room temperature until the

Table 2

Effect of ultrasound frequency and intensity on the reaction yield.

Frequency (kHz)	Max power density (W/cm ²)	GC yield (%)
24	110	30
24	180	44
24	250	69
50–60	250	68

starting naphthalene concentration was undetectable (1 h, checked by thin-layer chromatography) gave phthalaldehyde as the major product with a yield of 68%. Previously reported methods, however, formed 1,4-naphthoquinone or naphthols as the predominant products [30,31]. It is clear that preventing further oxidation improved the product yield as a result of decreasing the reaction time, compared with our previous report [25].

Anthracene and phenanthrene under the same conditions gave corresponding quinones in good yields (Table 3, entries 2 and 3). Oxidation of chrysene resulted in chrysene-5,6-dione as the main product and, interestingly, also resulted in 2-(2-formylphenyl)-1-naphthaldehyde as a by-product (**4a**:**4b** = 94:6). The enhanced ratio of 96:4 in this case may be attributable to a decrease in the reaction time. Perylene, when subjected to this reaction, was resistant, and after 6 h of irradiation at 50 °C, it resulted in no remarkable products. Increasing the oxidant (KBrO₃) equivalent three-fold resulted in pyrene-4,5-dione being obtained at room temperature with an improved yield of 58%. Further increasing the oxidant to six equivalents under the same conditions afforded pyrene-4,5,9,10-tetraone in 46% yield (Table 3, entries 5 and 6). Formation of benzoic acid as the main product of biphenyl oxidation was also noteworthy (Table 3, entry 7). Encouraged by these results, we further examined the cleavage of C=C double bonds. While *trans*-stilbene completely converted to benzoic acid and benzil (42:58 ratio), the isomeric 1,1-diphenyl-ethylene produced benzophenone as the main product in 98% yield.

To clarify the effect of ultrasound irradiation on the oxidation reaction, all reactions were conducted in the absence of ultrasound irradiation. In this case, vigorous mechanical stirring of the reaction mixture for 12 h yielded similar products (Table 3). Although these results revealed that the MCM-41-Ru catalyst has the advantage of selectivity in the oxidation of

Table 3

Ultrasound assisted MCM-41-Ru nanoparticles catalyzed oxidation of arenes.

Entry	Substrate	Product	Isolated yield (%)	
			Sonicated ^a	Non-sonicated ^b
1	Naphthalene	Phthalaldehyde (1a)	68	45
2	Anthracene	Anthraquinone (2a)	92	77
3	Phenanthrene	9,10-Phenanthrenequinone (3a)	95	79
4	Chrysene	Chrysene-5,6-dione (4a)	63	43
		2-(2-Formylphenyl)-1-naphthaldehyde (4b)	4 ^c	0
5	Pyrene	Pyrene-4,5-dione (5a)	58	40 [24]
6	Pyrene	Pyrene-4,5,9,10-tetraone (6a)	46 ^d	33 [24]
7	Biphenyl	Benzoic acid (7a)	90 ^e	69
8	<i>Trans</i> -stilbene	Benzoic acid (8a)	42	70
		Benzil (8b)	58	0
9	1,1-Diphenyl-ethylene	Benzophenone (9a)	98	80

^a Reaction time 1 h (^d, ^e 1.5 h). ^b Reaction time 12 h. ^c GC yield. ^d Irradiation at 50 °C.

Fig. 4. XRD patterns of the recycled catalyst after the 2nd run (1) and 5th run (2).

arenes, the application of ultrasound irradiation in promoting the catalyzed oxidation reaction is, however, unavoidable.

To evaluate reusability of the catalyst, oxidation of naphthalene was performed in the presence of the recycled catalyst in successive runs. For reaction runs 1 to 5, the yields were 68%, 68%, 59%, 53%, and 45%, respectively. After five runs, a 23% decrease in the efficiency of catalyst was observed. The catalyst itself, however, underwent structural changes during reaction cycles as evident from the XRD patterns of the recycled catalyst of the 2nd and the 5th run. As shown in Fig. 4, characteristic peaks of hexagonal Ru diminish in favor of newly formed tetragonal RuO_2 , with the crystallographic planes indexed as (110), (101), (200), (211), (220), (002), (310), (112), and (202) (JCPDS 21-1172).

To evaluate the potential of Ru leaching during the course of the reaction, the MCM-41-Ru composite was removed halfway through the oxidation reaction of biphenyl, and the reaction allowed to continue until the desired reaction time was complete (up to 1.5 h). Product yields of 48% and 49% were obtained at half and full reaction time, respectively, indicating that no considerable leaching of Ru into the solution occurred. To obtain further insight into the reaction mechanism and understanding better the key role in product selectivity, commercial micro-sized Ru(0) and Ru(IV) oxide was used as the catalyst in the oxidation of chrysene under optimized conditions. Although Ru(0) was unable to catalyze the oxidation reaction, Ru(IV) oxide resulted in chrysene-5,6-dione (**4a**) being yield of 11% with no detectable trace concentrations of **4b** observed by GC analysis. Even though good selectivity resulted, the lower yield may be attributable to the bulk size of RuO_2 crystals. Compared with our previous report based on homogeneous RuO_4 species, RuO_2 nanoparticles showed milder oxidation activity, and complete C=C bond cleavage was prevented. Based on these results and that obtained from the XRD analysis of the recycled catalyst, we can deduce that the key reaction mechanism feature is the conversion of surface Ru nanoparticles to the RuO_2 species. It has previously been reported that RuO_2 can populate species such as molecular oxygen on the (110) surface [32]. In analogy with other reports [33] based on tetrahedral RuO_2 species, the proposed mechanism (Scheme 1) may pro-

Scheme 1. Reaction mechanism in the selective oxidation of arenes by the conversion of Ru nanoparticles to RuO_2 species.

vide a pathway in the selective oxidation of arenes, which should be confirmed by future studies.

4. Conclusions

MCM-41-Ru was found to be an effective catalyst for the selective oxidation of aromatic compounds in the presence of ultrasound irradiation. The present method improved reaction time at room temperature, however, developing catalysts with improved selectivity for the oxidation of arenes remains a great challenge.

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Graphical Abstract

Chin. J. Catal., 2016, 37: 153–158 doi: 10.1016/S1872-2067(15)61001-4

Ruthenium nanoparticles supported on mesoporous MCM-41 as an efficient and reusable catalyst for selective oxidation of arenes under ultrasound irradiation

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MCM-41 crystallites loaded with Ru nanoparticles were used as heterogeneous catalysts in selective oxidation of arenes under sonic waves. The catalyst active site was found to be RuO₂ species formed during the course of reaction.

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中孔MCM-41负载Ru纳米粒子催化剂用于超声辐射下芳烃选择氧化反应

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摘要: 以中孔MCM-41为载体制得均一分散的粒径约5 nm的Ru纳米粒子催化剂MCM-41-Ru, 采用电感耦合等离子体、透射电镜、能量散射谱、X射线衍射和N₂吸附-脱附法对其进行了表征, 并将其作为可重复使用高效催化剂用于超声辅助芳烃选择氧化反应。结果表明, 在超声辐射和KBrO₃为氧化剂条件下, MCM-41-Ru催化剂加速了氧化反应, 并以较高产率得到目的产物。回收的催化剂用于下次反应时活性保持不变, 但其活性中心性质发生变化。

关键词: 纳米粒子; 超声; 钌; 芳烃氧化; MCM-41

收稿日期: 2015-10-09. 接受日期: 2015-10-24. 出版日期: 2016-01-05.

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