Ruthenium(0) nanoclusters supported on hydroxyapatite: highly active, reusable and green catalyst in the hydrogenation of aromatics under mild conditions with an unprecedented catalytic lifetime†

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The preparation of ruthenium(0) nanoclusters supported on hydroxyapatite and their characterization by a combination of complementary techniques are described. The resultant ruthenium(0) nanoclusters provide high activity and reusability in the complete hydrogenation of aromatics under mild conditions (at 25 °C and with 42 psi initial H_2 pressure).

The complete hydrogenation of aromatics is one of the ubiquitous and challenging transformations used in both laboratory and industrial synthetic chemistry[1] and traditionally has been carried out at high temperature (≥ 100 °C) and/or high pressure (≥ 50 atm H_2).[2,3] Although a range of heterogeneous catalysts can achieve the hydrogenation of aromatics under mild conditions (≤ 25 °C and ≤ 3 atm H_2),[4–6] most of them suffer from difficult synthetic procedures, low activity or low stability. Therefore, the development of an easily prepared, highly active, long-lived and reusable catalyst that operates under mild conditions is still a paramount challenge.

Recently, hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAp)[7] has generated great interest in view of its potential usefulness as biomaterials,[8] adsorbents,[9] ion-exchangers,[10] and catalyst supports.[11] Of particular importance are the results of recent studies showing that hydroxyapatite supported Pd(0),[12] Ru(0),[13] Ag(0)[14] and Au(0)[15] nanoparticles exhibit outstanding catalytic activities in the aerobic oxidation of alcohols, oxidative cleavage of alkenes, oxidation of phenylsilanes, and epoxidation of styrene, respectively. These results encouraged us to focus on the use of HAp matrix in the stabilization of transition metal nanoclusters catalysts in the hydrogenation of aromatics. The choice of HAp as support[16] is also motivated by the following advantages: (i) HAp has nonporous structure and doesn't cause significant mass transfer limitation, (ii) it has high ion-exchange ability and adsorption capacity, and (iii) its low surface acidity prevents side reactions arising from the support itself.[11] Since we have achieved unprecedented catalytic activities in the hydrogenation of benzene by using ruthenium(0) nanoclusters previously,[6,17] the same metal was selected as catalyst supported on the HAp.

In this communication, we report the preparation and characterization of ruthenium(0) nanoclusters, supported on hydroxyapatite, Ru(0)/HAp, and their superb catalytic performance in terms of activity, selectivity, reusability and lifetime in the hydrogenation of aromatics under mild conditions (at 25 °C, with 42 ± 1 psig initial H_2 pressure). Ru(0)/HAp were easily and reproducibly prepared by a method[18] that differs from the one previously reported for the preparation of Ru(0)/HAp.[19] Our methodology in the preparation of Ru(0)/HAp comprises the ion-exchange[20] of Ru^{3+} ions with Ca^{2+} ions in the lattice of HAp, followed by the reduction of the Ru^{3+}-exchanged HAp with sodium borohydride in aqueous solution at room temperature. After centrifugation, copious washing with water, and drying under vacuum (10^{-3} Torr) at 80 °C, Ru(0)/HAp were obtained as dark grey powders and characterized by ICP-OES, XRD, TEM, XPS and the N_2 adsorption–desorption technique.

The XRD patterns of Ru(0)/HAp containing 0.42% wt Ru as determined by ICP-OES are identical with that of HAp (Fig. ESI-1†); any impurities or other phases were not observed, indicating that the host material remains intact at the end of the procedure without observable alteration in the framework lattice and loss in the crystallinity.

The size and the morphology of the Ru(0)/HAp were analyzed by using transmission electron microscopy. Fig. 1 shows the TEM image of the Ru(0)/HAp sample with a ruthenium loading of 0.42% wt. This reveals the presence of randomly distributed ruthenium(0) nanoclusters on the HAp surface in the range of 0.9–4.0 nm with a mean diameter of 2.6 ± 0.6 nm which corresponds to $Ru(0)_{\sim 670}$ nanoclusters.[21] It should be noted that the TEM observation of the same sample from different areas confirms the stability of ruthenium(0) nanoclusters against agglomeration.

The oxidation state of ruthenium and the surface composition of Ru(0)/HAp were investigated by X-ray photoelectron spectroscopy. The survey scan XPS spectrum of Ru(0)/HAp indicates that ruthenium is the only element detected in addition to the HAp framework elements (Fig. ESI-2a†). The high resolution Ru 3d and 3p XPS spectra of Ru(0)/HAp show two prominent bands at 281.5 and 462.3 eV, which are readily assigned to Ru(0) $3d_{5/2}$ (Fig. ESI-2b†) and Ru(0) $3p_{3/2}$ (Fig. ESI-2c†), respectively.[22] The N_2 adsorption–desorption isotherms of both HAp and Ru(0)/HAp

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† Electronic supplementary information (ESI) available: Experimental section; Table S-1: The eight catalyst systems achieving the complete hydrogenation of neat benzene arranged chronologically, Fig. ESI-1: XRD patterns of HAp, fresh Ru(0)/HAp and Ru(0)/HAp recovered at the end of the third reuse from the hydrogenation of benzene, Fig. ESI-2: Survey, Ru 3d and 3p XPS spectrum of Ru(0)/HAp, Fig. ESI-3: N_2 adsorption–desorption isotherms of HAp, Ru(0)/HAp, Fig. ESI-4: Graphs of [aromatic] consumption *versus* time for Ru(0)/HAp catalyzed hydrogenation. Fig. ESI-5: TEM micrograph of recovered Ru(0)/HAp. See DOI: 10.1039/c0cc00494d

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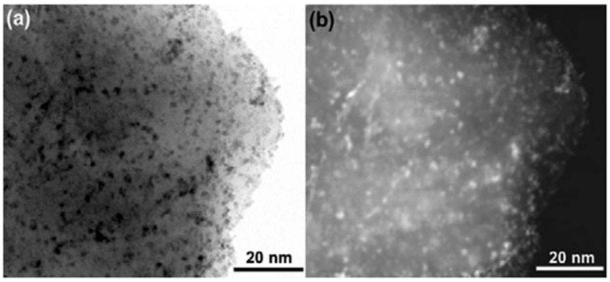


Fig. 1 (a) TEM, (b) ZC-TEM image of ruthenium(0) nanoclusters supported on hydroxyapatite.

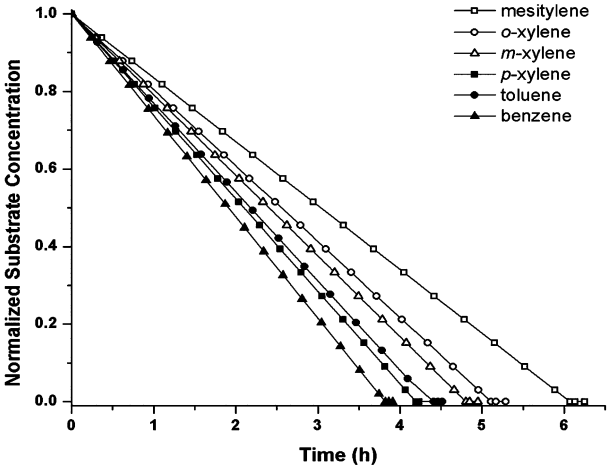


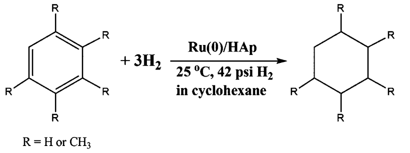
Fig. 2 Normalized substrate concentration *versus* time for the Ru(0)/HAp catalyzed hydrogenation of aromatics under mild conditions at 25 ± 0.1 °C and 42 ± 1 psig initial H_2 pressure.

(Fig. ESI-3a and b†, respectively) show type III isotherms, reflecting the absence of micropores (<2 nm).[23] The Brunauer–Emmett–Teller surface area of Ru(0)/HAp was found to be 82.5 m^2 g^{-1}, which is larger than that of the parent HAp (69.3 m^2 g^{-1}). This result accounts for the physical adsorption of ruthenium(0) nanoclusters on the HAp surface.

The catalytic activity of Ru(0)/HAp was tested in the hydrogenation of aromatics. The catalytic hydrogenation of aromatics was started by agitation of a Ru(0)/HAp sample in the aromatic substrate at 25 ± 0.1 °C and 42 ± 1 psig initial H_2 pressure. The progress of the reaction could be followed by monitoring the hydrogen uptake which was converted to the concentration loss of aromatic substrate by using the stoichiometry (Scheme 1).

The complete hydrogenation of aromatics was also checked by taking the ^{1}H NMR spectra of the solution at the end of the reaction. Fig. 2 shows the normalized substrate concentration *vs.* time for the hydrogenation of benzene, toluene, *p*-xylene, *m*-xylene, *o*-xylene and mesitylene catalyzed by Ru(0)/HAp at 25 ± 0.1 °C and 42 ± 1 psig H_2. For all of the substrates the hydrogenation starts immediately without induction period as a preformed catalyst is used. The linear hydrogenation of benzene, toluene, *p*-xylene, *m*-xylene, *o*-xylene and mesitylene continues until the consumption of substrate with a TOF value of 705, 519, 477, 423, 384 and 300 h^{-1}, respectively (see Fig. ESI-4†).[24] The observed trend in TOF values of different substrates is attributed to an electronic effect[25] of the methyl substituents on the aromatic ring. Besides, the steric hindrance also appears to be responsible for the slow rate of *o*-xylene hydrogenation compared to *p*- and *m*-xylenes.[26]

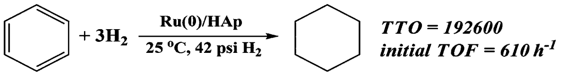
Ru(0)/HAp catalyzing the hydrogenation of neat benzene is an important achievement as performing the reactions in a solventless system is one of the requirements for "Green Chemistry".[27] There exist only seven catalyst systems reported for the complete hydrogenation of neat benzene at ≤25 °C (see Table 1 in ESI†).[5,6] The new Ru(0)/HAp catalyst (150 mg, with a Ru content of 0.42% wt corresponding to 6.23 μmol Ru) provides 192 600 turnovers in benzene hydrogenation over 400 h before deactivation (Scheme 2). The average TOF value during this lifetime experiment is 480 h^{-1} which is smaller than the initial TOF value (610 h^{-1}), indicating that the nanoclusters are deactivating as the catalytic reaction proceeds. Nevertheless, this is the longest catalytic lifetime reported to date since the highest TTO known for neat benzene hydrogenation is 7250.[6]



Scheme 1 Ru(0)/HAp catalyzed hydrogenation of aromatics in cyclohexane under mild conditions.

The isolability and reusability of Ru(0)/HAp, two crucial measures in heterogeneous catalysis, were also tested in the hydrogenation of benzene. After the complete hydrogenation of benzene, Ru(0)/HAp was isolated as dark-grey powders by suction filtration and dried under vacuum at room temperature. The Ru(0)/HAp sample can be bottled and stored under ambient conditions. Furthermore, when reused Ru(0)/HAp are still active catalysts in the hydrogenation of benzene, they retain 96% of their initial catalytic activity with the complete conversion of benzene to cyclohexane even at the third run. The slight decrease in the catalytic activity of Ru(0)/HAp in the third run may be attributed to the decrease in the number of active surface atoms by the increase of the size of ruthenium(0) nanoclusters. Formation of clumps is also evidenced by the TEM image of the Ru(0)/HAp recovered at the end of the third run of benzene hydrogenation (Fig. ESI-5†), which shows an increase of the average size to 3.1 ± 0.8 nm ($Ru(0)_{\sim1100}$ nanoclusters). It is also noteworthy that XRD analysis of the same sample (Fig. ESI-1†) reveals no loss in the crystallinity of the host material.

Taking all the results together one can conclude that Ru(0)/HAp are isolable, bottleable and repeatedly usable as active catalysts in the hydrogenation of aromatics. That no Ru was detected in the filtrate by ICP (with a detection limit



Scheme 2 Ru(0)/HAp catalyzed hydrogenation of neat benzene under mild conditions.

of 24 ppb for Ru) confirms the retention of ruthenium within the HAp matrix (no Ru passes into the solution during the suction filtration). A control experiment was also performed to show that the hydrogenation of benzene is completely stopped by the removal of Ru(0)/HAp from the reaction solution.

In summary, Ru(0)/HAp could be reproducibly prepared from readily available reagents following the procedure reported herein. They exhibit exceptional catalytic activity in the hydrogenation of aromatics under mild conditions and provide a record catalytic lifetime (TTO = 192 600) in the hydrogenation of neat benzene at 25 ± 0.1 °C and 42 ± 1 psig initial H_2 pressure. Moreover, Ru(0)/HAp catalyzed hydrogenation of neat benzene at room temperature is "relatively green" in terms of its environmental impact as it fulfils 7 of the 12 requirements of green chemistry[27] including that (i) it is 100% selective and minimizes by-products or waste, (ii) it maximizes the incorporation of all reactants into the products, (iii) it is solventless (*i.e.*, uses neat aromatics as the substrate/solvent), (iv) it requires relatively low energy as it occurs under mild conditions of 25.0 ± 0.1 °C and ≤ 3 atm pressure, (v) it is catalytic not stoichiometric, (vi) it does not use any blocking, protecting/deprotecting group, (vii) real-time monitoring is easy by measuring the H_2 uptake, ^{1}H NMR or GC-analysis, for example. The high catalytic activity, easy preparation, isolability, bottleability, and reusability of Ru(0)/HAp raise the prospect of using this type of simply prepared material for the hydrogenation of aromatics in industrial applications as well as in small scale organic synthesis.

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