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Introduction

The catalytic hydrogenation reaction is of fundamental interest in synthetic chemistry and is applied on a large scale for the production of fine chemicals, agrochemicals, and pharmaceuticals.¹ Among the various hydrogenation reactions, selective hydrogenation of heteroarenes is a significant scientific and technological challenge due to the high resonance stability and potential deactivation of the catalyst by covering of the catalyst surface with the substrate or its reduced products.² The hydrogenation of quinolines often takes place on their benzene ring to selectively give 5,6,7,8-tetrahydroquinoline, which is also known as a subunit in numerous medicinally interesting compounds.³ For the selective hydrogenation of heteroarenes, the most efficient and practical catalysts are mainly based on noble metals such as platinum, palladium,

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Unique nanocages of 12CaO·7Al₂O₃ boost heterolytic hydrogen activation and selective hydrogenation of heteroarenes over ruthenium catalyst[†]

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The chemoselective hydrogenation of heteroarenes is one of the most important synthetic reactions for the production of key intermediates in agrochemicals, pharmaceuticals and various fine chemicals. The development of new heterogeneous catalysts for the environmentally benign synthesis of heterocycle hydrogenated products is a fundamental objective for chemists. Here, we report that $12CaO\cdot7Al_2O_3$ with a unique sub-nanocage structure loaded with Ru nanoparticles exhibits higher activity, chemoselectivity and sustainability for the hydrogenation of heteroarenes in a solvent-free system than traditional oxide-supported metal catalysts. Conversion of >99% and a selectivity close to 99% were achieved for the hydrogenation of a variety of N- and O-heteroarenes with high yields. The superior catalytic performance can be attributed to a cooperative effect between the hydrogen-storage ability and large amount of strong basic sites on the surface of the support, which promotes heterolytic H₂ cleavage and prevents poisoning of the metal surface caused by the adsorption of heteroarenes.

rhodium, gold, ruthenium, and iridium.⁴ Among these precious metals, ruthenium is the cheapest with a price of \$42 per oz (BASF, Mar 2016), which is one tenth to one thirtieth the price of the other noble metals. A noble metal-free catalyst based on N-graphene-modified cobalt nanoparticles has very recently been reported for the chemoselective hydrogenation of heteroarenes, with excellent chemoselectivity for numerous structurally diverse substrates.5 However, this catalyst requires relatively long reaction time (more than 48 h) at 120 °C. Therefore, the relative low cost and high availability of ruthenium makes it promising for large-scale commercial processes. However, ruthenium catalysts also generally require severe conditions, organic solvents, and environmentally harmful processes.⁶ Thus, from both economic and environmental perspectives, it is imperative to design a new ruthenium-based catalyst that is efficient for the hydrogenation of heteroarenes under mild conditions, and even using a solventfree system.

Homogeneous catalysts are known to be catalytically active and selective; however, they typically involve the problem of separation. Moreover, several molecularly defined homogeneous catalysts generally require extra additives such as I_2 to achieve successful hydrogenation of heteroarenes.⁷ In contrast, heterogeneous catalysts appear to be much more versatile for heteroarene hydrogenation because they can be easily recycled. Supported-metal catalysts have been studied extensively for

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heterogeneous catalysis.⁸ The availability of efficient supported-metal catalysts has been the driving force of many publications devoted to the chemoselective hydrogenation of heteroarenes. It is well known that the catalytic properties of metal particles are significantly influenced by the support materials. Hence, the development of new effective support materials that can realize enhancement of the metal catalyst remains a significant challenge.

The nanoporous crystal 12CaO·7Al₂O₃ (C12A7:O²⁻) is a fast oxygen ion conductor that possesses extra framework oxygen ions in subnanometer-sized cages with an inner free space of ca. 0.4 nm in diameter.⁹ C12A7:O²⁻ has a positively charged lattice framework $[Ca_{24}Al_{28}O_{64}]^{4+}$, in which the positive charge of the cage wall is compensated by anions that are accommodated within the cages.¹⁰ The O²⁻ ions can be replaced by different anions such as hydroxide ions (OH⁻), hydride ions (H^{-}) , halogen anions (F^{-}, Cl^{-}) , sulfur ions (S^{2-}) and electrons (e⁻) via appropriate chemical/physical treatment.¹¹ Electronembedded C12A7:e⁻ is an electride in which electrons act as anions.¹² Our group has recently reported that the electronembedded C12A7:e⁻ electride in combination with Ru functions as a highly efficient catalyst for ammonia synthesis under mild conditions.¹³ In this reaction, H⁻ can be incorporated into the positively charged nanocages of C12A7:e⁻. For the hydrogenation of heteroarenes, the key point is to facilitate heterolytic H₂ activation at the metal-support interface.

We expect that nanoporous crystal C12A7:O²⁻ also has the potential to trap H⁻ ions and promote heterolytic H₂ cleavage. Therefore, we have examined nanometric Ru supported on C12A7:O²⁻ (Ru/HT-C12A7) with a high specific surface area, prepared through a hydrothermal approach, as a catalyst for the hydrogenation of various heteroarenes in a solvent-free system. For the chemoselective hydrogenation of the N-heteroarene quinoline, the catalyst shows a high conversion of >99% and a selectivity of close to 99% toward 1,2,3,4-tetra-hydroquinoline. Furthermore, a wide range of heteroarenes such as N-heteroarenes and O-heteroarenes can also be exclusively hydrogenated to the desired products under mild conditions in a solvent-free system. C12A7 is demonstrated to be a new and efficient Ru catalyst support material for the hydrogenation of heteroarenes.

Results and discussion

The preparation of Ru/HT-C12A7 involves a two-step method. Firstly, HT-C12A7 was prepared by simple hydrothermal processing of a ball-milled mixture of Ca(OH)₂ and Al(OH)₃. X-ray diffraction (XRD) analysis (Fig. S1†) indicated that as-prepared HT-C12A7 had a cubic mayenite structure. The deposition of Ru nanoparticles was then achieved by the thermal decomposition of Ru₃(CO)₁₂, in which the metal is in the zero oxidation state, as demonstrated by X-ray photoelectron spectroscopy (XPS) measurements (Fig. S2†).¹⁴ A representative scanning transmission electron microscopy (STEM) image of Ru/ HT-C12A7 is shown in Fig. 1a. The mean Ru particle size was





Fig. 1 HAADF STEM image of 2 wt% Ru/HT-C12A7. (a) Overview image of Ru/HT-C12A7 and (b) metal particle size distribution histogram.

estimated to be 1.9 nm on the basis of a count of more than 100 individual nanoparticles (Fig. 1b).

The hydrogenation of quinoline to 1,2,3,4-tetrahydroquinoline was selected as a probe reaction to investigate the catalytic performance of Ru/HT-C12A7 because 1,2,3,4-tetrahydroquinoline has been identified as a platform molecule with a variety of applications in biologically active natural products and pharmacologically relevant therapeutic agents. Control experiments showed that Ru/HT-C12A7 with 2 wt% Ru or more provides excellent conversion and selectivity to the hydrogenated product without a solvent when Ru nanoparticles are supported on HT-C12A7 pre-annealed at 600 °C (Table 1). The optimized reaction conditions were determined to be 80 °C under a H₂ pressure of 1.0 MPa. From the kinetic data shown in Fig. S3,† the starting material was almost fully consumed after 12 h. Moreover, no intermediates could be detected by gas chromatography (GC) analysis during the entire reaction process. Note that the Ru/HT-C12A7 catalyst exhibited significantly higher catalytic activity within a shorter time and under much milder reaction conditions than other supported metal catalysts reported to date in a solvent-free system (Table S1[†]). A tiny amount of decahydroquinoline was formed as a side product. In addition, Ru/HT-C12A7 has efficient activity for the hydrogenation of 6-chloroquinoline, comparable to that of Ru- or Au-loaded high surface area TiO₂ catalysts under extremely mild conditions (Table S1[†]).^{4b}

To further examine the important role of HT-C12A7 for the hydrogenation of quinoline, other oxide materials, such as Al₂O₃, CaO, Al₂O₃-SiO₂, MgO, ZrO₂ and TiO₂ were also employed as supports for the Ru catalyst (5 wt%) for quinoline hydrogenation (Fig. 2a). Ru-loading was conducted using the same thermal decomposition method as that for HT-C12A7. Table S2[†] shows that the Ru particle sizes are almost identical for each support, except for Ru/ZrO2. Therefore, the difference in the catalytic performance is not due to the Ru particle size but most likely due to the nature of the support material. For the acidic oxide support, Al₂O₃-SiO₂, the yield of 1,2,3,4-tetrahydroquinoline remained only 1.3% after 12 h reaction, which was 75 times lower than that for Ru/HT-C12A7. The Al₂O₃, TiO₂ and ZrO₂ supports with low acidic or basic properties also gave low yields. Notably, the strongly basic oxide CaO catalyst exhibits higher catalytic activity than the other oxide

Table 1 Ru/HT-C12A7 catalytic performance for chemoselective hydrogenation of quinoline^a

Entry	$Catalyst^b$	Ru [wt%]	H_2 [MPa]	Temp. [°C]	Time [h]	Conv. [%]	Sel. [%]
1	Ru/HT-C12A7-500	2	1.0	80	12	89.9	96.8
2	Ru/HT-C12A7-600	2	1.0	80	12	99.2	98.6
3	Ru/HT-C12A7-800	2	1.0	80	12	52.6	96.5
4	Ru/HT-C12A7-1000	2	1.0	80	12	33.3	95.6
5	Ru/HT-C12A7-600	0.5	1.0	80	12	50.7	91.7
6	Ru/HT-C12A7-600	5	1.0	80	12	99.6	98.7
7	Ru/HT-C12A7-600	2	0.5	80	12	52.5	92.3
8	Ru/HT-C12A7-600	2	1.0	60	12	51.5	92.4
9	Ru/HT-C12A7-600	2	1.0	80	6	72.5	98.2
10^{c}	Ru/HT-C12A7-600	2	1.0	80	24	—	—

^{*a*} Typical conditions: 5 mmol quinoline, catalyst 40 mg. ^{*b*} HT-C12A7-X (X: calcination temperature) was prepared by calcination of hydrothermally produced Ca–Al mixed hydroxide at various temperatures. ^{*c*} Hot filtration test was carried out from the mixture after 6 h of reaction (entry 9), proceeding the reaction without catalyst for 24 h under the same reaction condition as entry 9. Conversion (Conv.) and selectivity (Sel.) were determined by gas chromatography (GC) and GC-mass spectrometry (GCMS) analyses, respectively.



Fig. 2 (a) Catalytic activities for hydrogenation of quinoline over various Ru-based catalysts with different supports. (b) Recycle experiment for (b) hydrogenation of quinoline over Ru/HT-C12A7. Reaction conditions: 5 mmol substrate, 40 mg catalyst, H_2 (1.0 MPa), 80 °C, 12 h.

supports, and even higher than the basic oxide MgO catalyst. However, the activity of Ru/HT-C12A7 was higher than that of Ru/CaO by an order of magnitude. Comparison of the catalytic performance indicated that the HT-C12A7 support was beneficial for enhancement of both the catalytic activity of Ru and the chemoselectivity for the hydrogenation of quinoline. This can be attributed to the abundance of surface basic sites on HT-C12A7, which will be discussed later.

Recycling experiments were conducted to demonstrate the stability and reusability of Ru/HT-C12A7. Fig. 2b shows that both the catalytic activity and chemoselectivity were well retained in eight consecutive runs. TEM observation clearly demonstrated that the Ru nanoparticle size and morphology of the support remained unchanged after recycling (Fig. 1 and S4†), which indicates excellent stability and recyclability. To check whether the hydrogenation of quinoline over Ru/HT-C12A7 catalyst is a heterogeneous reaction or homogeneous one, the catalyst was removed from the reaction mixture by hot filtration after 6 h of reaction, and the filtrate was heated under the same reaction condition. No further conversion of quinoline was observed, even after reaction for 24 h under identical conditions (Table 1, entry 10), which led to the

conclusion that no leaching of the catalyst occurred and the process was truly heterogeneous. Therefore, the Ru/HT-C12A7 catalyst presents impressive catalytic activity and recyclability, and possesses a truly heterogeneous catalytic nature that has potential application in the chemical industry.

Encouraged by the excellent performance of Ru/HT-C12A7, the reaction protocol was further extended to different quinolines with various functional groups. Table 2 shows that quinolines with methyl substituents either on the benzene ring or the heteroarene ring could undergo hydrogenation of the heteroarene ring to the corresponding products with excellent yields above 85% (Table 2, entries 1-5). The electron-donating group (CH_3O) and electron-withdrawing functional groups (F, Cl) had no significant influence on the activity of this catalytic system (entries 6-8). Although we also tried the hydrogenation of the most challenging substrate bearing aldehyde, both quinoline ring and aldehyde group were hydrogenated (Scheme 1). In the case of methyl 6-quinolinecarboxylate, quinoline ring was selectively reduced to the corresponding product with excellent selectivity (entry 9) and it is hard to hydrogenate ester group due to the low electrophilicity of the carbonyl group.¹⁵ The main side products of part substrates with relative low selectivity (<90%) were provided in Table S3.† It is noteworthy that the Ru/HT-C12A7 catalyst can also hydrogenate pyridine and pyrrole to the corresponding piperidine and pyrrolidine, which are used as building blocks for the synthesis of chemical products and pharmaceuticals.¹⁶ In the literature work about the hydrogenation of pyridine and pyrrole, harsh reaction conditions (such as high temperature and/or high hydrogen pressure) are often required.¹⁷ Compared to these processes, the Ru/HT-C12A7 catalyst allows for the synthesis of piperidine and pyrrolidine with extremely high yields of 99.9% (entries 10, 11) under relatively mild conditions, which is advantageous in real application. These results confirm that the Ru/HT-C12A7 catalyst is remarkably selective for the hydrogenation of N-heteroarenes under mild experimental conditions in a solvent-free system.

The high activity of the Ru/HT-C12A7 catalyst toward a series of N-heteroarenes encouraged us to test the catalyst for

Table 2 Ru/HT-C12A7-catalyzed hydrogenation of various N-heteroarenes^a

Entry	Substrate	Product	Conv. [%]	Sel. [%]
1^b		N N N N N N N N N N N N N N N N N N N	94.6	93.4
2 ^{<i>c</i>}			99.9	88.9
3		L H	91.2	97.9
4		N H	99.9	88.3
5			99.9	85.7
6 ^{<i>d</i>}	CI	CI N H	99.9	95.5
7 ^{<i>d</i>}	F	F N H	99.9	93.2
8 ^{<i>c</i>}	H ₃ CO	H ₃ CO	99.7	85.6
9 ^e	H ₃ CO	H ₃ CO	99.9	95.1
10 ^{<i>f</i>}		NH NH	99.9	99.9
11^f		$\langle N \rangle$	99.9	99.9

^{*a*} Reaction condition: 5 mmol substrate, 40 mg catalyst (2 wt% Ru/HT-C12A7), 1.0 MPa H₂, 12 h, 80 °C. ^{*b*} 18 h. ^{*c*} 15 h. ^{*d*} 60 °C. ^{*e*} 100 °C. ^{*f*} 24 h. Conversion (Conv.) and selectivity (Sel.) were determined by gas chromatography (GC), GC-mass spectrometry (GCMS), and NMR analyses.



Scheme 1 Hydrogenation of 6-quinolinecarboxaldehyde over Ru/ HT-C12A7.

the chemoselective hydrogenation of other heteroarene compounds, such as O-heteroarenes. The hydrogenation of O-heteroarenes is also important in the biological and chemical industries. Hydrogenated O-heteroarenes derivatives can be used for pharmaceuticals, agrochemicals, and other chemical materials.¹⁸ The Ru/HT-C12A7 catalyst had good activity for the hydrogenated formation of 2,3-dihydrobenzofuran from benzofurans (Table 3, entry 1). Moreover, substituted derivatives such as 2-butylbenzofuran and 3-methylbenzofuran could be converted to the corresponding heterocycle hydrogenated products under optimized reaction conditions (entries 2 and 3). These results also highlight the superior activity of the Ru/HT-C12A7 catalyst for the selective hydrogenation of various heteroarenes. Interestingly, the reaction also proceeds with furan, even at room temperature. The expected products were obtained in more than 93% yield from furan and its derivatives 2-methyl-, 2-ethyl-, and 2,3-dimethyl-substituted furan (entries 4–7).

To elucidate the reaction mechanism for the chemoselective hydrogenation of heteroarenes over Ru/HT-C12A7, kinetic analyses were conducted on both Ru/HT-C12A7 and Ru/CaO by changing the substrate concentration and H_2 pressure. Fig. 3a shows the reactions are zero-order with respect to the initial reactant concentration, which indicates that the adsorption of quinoline on the catalyst surface becomes saturated during the reaction process, most likely due to the strong interaction between the substrate and catalyst surface. Fig. 3b shows the variation of the hydrogenation rates as a function of the H_2 pressure. The rates steadily increased with increasing pressure on both catalysts and the reaction order with the H_2 pressure over Ru/HT-C12A7 and Ru/ CaO were estimated to be +0.87 and +0.88, respectively. These

Table 3Ru/HT-C12A7-catalyzedhydrogenationofvariousO-heteroarenes^a

Entry	Substrate	Product	Conv. [%]	Sel. [%]
1			95.2	93.8
2 ^{<i>b</i>}			96.7	91.2
3 ^{<i>b</i>}			85.6	92.9
4 ^{<i>c</i>}	$\langle \rangle$	$\langle \rangle$	96.9	99.9
5 ^{<i>c</i>}		$\sqrt{\mathbf{r}}$	99.9	96.2
6 ^c			99.2	94.5
7 ^c			99.9	96.5

^{*a*} Reaction condition: 5 mmol substrate, 40 mg catalyst (2 wt% Ru/HT-C12A7), 1.0 MPa H₂, 12 h, 80 °C. ^{*b*} 24 h. ^{*c*} 24 h, 25 °C. Conversion (Conv.) and selectivity (Sel.) were determined by GC and GCMS analyses, respectively.

Fig. 3 Effect of (a) substrate concentration and (b) H_2 pressure on the rates of quinoline hydrogenation. Reaction conditions: (a) 5 mg catalyst, 5 mL tetrahydrofuran (THF), H_2 (1.0 MPa), 80 °C, 12 h, (b) 5 mmol substrate, 40 mg catalyst, 80 °C, 12 h.

results imply that a hydrogen species is involved in the ratedetermining step over these catalysts.

To further verify the difference in catalytic activity between Ru/HT-C12A7 and the other Ru-based catalysts, electron paramagnetic resonance (EPR) measurements were conducted on the Ru/HT-C12A7 catalysts before and after reaction. As shown in Fig. 4a, an EPR signal appeared at g = 2.004, which was superposed on the signals of the oxygen anions $(O^- \text{ or } O_2^-)$.¹⁹ This signal is ascribed to the adsorbed product, 1,2,3,4tetrahydroquinoline radicals. Subsequently, irradiation of the Ru/HT-C12A7 with ultraviolet (UV) light resulted in the appearance of a new signal with an almost isotropic shape at g =1.994, which is similar to an F⁺-like center where an electron is trapped at an oxygen ion vacancy and is coordinated by Ca²⁺ ions (Fig. S5[†]).²⁰ According to our previous studies, UV irradiation can induce electron emission from H- ions encaged in C12A7:H⁻ (H⁻ + $O^{2-} \rightarrow OH^- + 2e^-$) and a similar EPR signal appears at g = 1.994.²¹ Accordingly, it can be concluded that H⁻ ions are incorporated in the cages of HT-C12A7 during the hydrogenation reaction. A plausible explanation for this phenomenon of Ru/HT-C12A7 is that the surface framework cages of C12A7 are truncated and can capture hydrogen species as H⁻. The surface of C12A7:e⁻ contains low-coordinated cations associated with the truncated cages, while the near-surface regions retain the intact cage structure.²²



Fig. 4 (a) EPR spectra for Ru/HT-C12A7 catalyst before and after hydrogenation reaction, and Ru/HT-C12A7 after reaction under UV light irradiation (microwave frequency = 9.7 GHz, temperature = 25 °C). (b) Rate for HD formation at 50 °C over Ru/HT-C12A7 and Ru/CaO with and without pre-adsorbed quinoline.

These cages can accommodate anion species such as H⁻ or e⁻ ions. The soft chemical preparation process used for HT-C12A7 and the relatively low annealing temperature cause this material to possess abundant truncated surface framework cages compared with that synthesized by the solid-state method.²³ Therefore, H⁻ ions can enter into the truncated surface cages much more easily than the intact cages with higher crystallinity in C12A7.

It is widely accepted that the H^+/H^- pair derived from the heterolytic cleavage of H₂ preferentially reacts with polar bonds such as C=N and C=O in chemoselective hydrogenation.²⁴ For the hydrogenation of heteroarenes, this H⁺/H⁻ pair also prevents catalyst poisoning by the strong interaction between the heteroarene and metal catalyst through direct binding of the heteroatoms of heteroarenes to the metallic sites.^{4b,25} To confirm this, H₂-D₂ exchange reactions were conducted over the Ru/HT-C12A7 catalyst with and without preadsorbed quinoline. There was no noticeable change in the H₂-D₂ exchange rate between the Ru/HT-C12A7 catalyst with and without quinoline (Fig. 4b). In contrast, the HD formation rate over Ru/CaO catalyst was significantly reduced after quinoline molecules were adsorbed on the catalyst surface, which indicates that the H2 dissociation reaction on Ru/CaO is strongly suppressed through poisoning by quinoline adsorption. Furthermore, it can be considered that quinoline molecules play an important role in the heterolytic cleavage of H₂ to yield H^+/H^- ion pairs over Ru/HT-C12A7.

The incorporation of H⁻ ions into the cages of C12A7 in the presence of Ru often requires a relatively high temperature of approximately 360 °C.²⁶ In the present reaction system, the reaction temperature was as low as 80 °C, which is not adequate for the incorporation of H⁻ ions into the intact cages of bulk C12A7. However, H⁻ ions were formed in Ru/HT-C12A7 after the chemoselective reaction (Fig. 4a), and these species may be trapped in the truncated framework cages on the surface. HT-C12A7 contains a large amount of OH⁻ ions in the framework cages due to preparation from the Ca-Al mixed hydroxides. The OH⁻ ion concentration of the Ru/HT-C12A7 catalyst was therefore compared before and after the reaction. The amount of OH⁻ ions remained consistent, which demonstrates that H⁻ ions are only incorporated into the truncated surface cages, irrespective of the inner cages with OH⁻ ions (Fig. S6[†]).²⁷ For comparison, EPR measurements were also conducted on Ru/CaO without a nanocage structure as a reference sample. The EPR spectra showed no signal due to trapped electrons centered at g = 1.994 in Ru/CaO after the same reaction process as that for Ru/HT-C12A7 (Fig. S7[†]). Accordingly, the catalytic activity of Ru/CaO was also poor, as expected. Moreover, a clear distinction of the catalytic activity between the Ru/C12A7 and Ru/CaO·Al2O3 catalysts emphasizes that the truncated surface framework cages in C12A7 favor the chemoselective hydrogenation of heteroarenes (Fig. S8[†]).

The heterolytic cleavage of H_2 to yield H^+/H^- ion pairs plays a crucial role in determining the selectivity. The truncated surface cages could promote the heterolytic hydrogen splitting by incorporated H^- . On the other hand, when HT-C12A7 is

used as a support, the surface O atoms can function as strong basic sites to efficiently fix the H⁺ ions. Therefore, the basic properties of HT-C12A7 were investigated using temperature programmed desorption (TPD) with CO_2 as a probe molecule. The TPD profile for the Ru/HT-C12A7 catalyst shows three CO₂ desorption peaks at approximately 235 °C, 315 °C, and 390 °C (Fig. S9[†]). Recent density of states (DOS) calculations confirmed that three different oxygen sites are located at or near to the surfaces of truncated cages in C12A7, including (i) one site coordinated by one Ca and one Al neighbor, (ii) one site coordinated by two Al neighbors, and (iii) an initial extraframework ion that merged with the cage wall.²⁸ These three types of basic sites correspond well with the CO₂-TPD results, which indicates the existence of a variety of basic sites of different adsorption strengths on the surface of HT-C12A7. Moreover, the average coordination number of these oxygen sites is below four which is the same as the local environment in the bulk, due to the truncated cage structure. Therefore, the basicity of these sites is much stronger than that in conventional oxides. Various Ru based catalysts with different oxide supports were also measured and the order of the amount of basic sites was determined as Ru/SiO₂·Al₂O₃ < Ru/ZrO₂ < Ru/TiO₂ < Ru/Al₂O₃ < Ru/MgO < Ru/CaO < Ru/HT-C12A7, which corresponds well with the activity of these catalysts for the hydrogenation of quinoline (Fig. S9[†]). These results unambiguously demonstrate that the basic sites of HT-C12A7 presumably act to facilitate the formation of the heterolytic hydrogen species (H⁺).

Based on these results, we propose a possible mechanism for the chemoselective hydrogenation of heteroarenes over the Ru/HT-C12A7 catalyst, as follows. As shown in Scheme 2, the crucial factor in the hydrogenation of heteroarenes is the unique surface configuration of Ru/HT-C12A7 with truncated cages. These positively charged truncated cages can serve as anchors capable of trapping anions, such as H⁻. The heterogeneous dissociation of H₂ occurs preferentially at the interface between a catalyst metal and a basic oxide support (H₂ \rightarrow H⁻ + H⁺). Therefore, in the case of Ru/HT-C12A7, it can be expected that H⁻ species are formed on Ru metal sites and H⁺ is simultaneously formed on the framework basic sites at the surface of HT-C12A7. The H⁻ ions on Ru surfaces would



readily spill over onto HT-C12A7 and be incorporated into the truncated surface cages that have the capability to trap H⁻, thereby facilitating the heterolytic H₂ activation at the surface of the Ru/HT-C12A7 catalyst. However, due to the weak interaction between H⁻ ions and the truncated cages, the H⁻ ions may desorb from the truncated surface cages and then participate in the hydrogenation reaction. As a result, a large amount of H⁺ and H⁻ species are generated on the surface of Ru/ HT-C12A7, which promotes efficient and selective hydrogenation of the heteroarenes to form the corresponding heterocycle hydrogenated products. Additionally, Ru/HT-C12A7 catalyst preferentially hydrogenated aldehyde group in the presence of quinoline ring, also suggesting the heterolytic manner of H₂ splitting on the surface of Ru/HT-C12A7 (Scheme 1). Moreover, these surface hydrogen species also prevent catalyst poisoning caused by the strong interaction between heteroarenes and the metal catalyst through the direct binding of heteroatoms (N or O) to the metallic sites.

Conclusions

In summary, we have developed a highly active and chemoselective catalyst of Ru/HT-C12A7 for the hydrogenation of both N- and O-heteroarenes in a solvent-free system. The key to successful catalysis is the use of stable, durable and low-cost nanoporous HT-C12A7 as the support. The HT-C12A7 support can act as a special hydrogen storage material with abundant surface basic sites to enhance the catalytic activity and selectivity for the chemoselective hydrogenation of heteroarenes. Moreover, the heterolytic ionic hydrogenation approach prevents catalyst poisoning caused by the strong interaction between the substrate and metallic sites. This catalyst was also successfully recycled and reused without significant deactivation. The unique nanoporous structure of HT-C12A7 can be extended to guide the design and development of novel catalysts for a broad spectrum of green syntheses of many important chemicals.

Experimental

Preparation of HT-C12A7

HT-C12A7 was synthesized by the calcination of hydrothermally produced Ca–Al mixed hydroxide. Briefly, a stoichiometric mixture (Ca : Al = 12 : 14) of Ca(OH)₂ and Al(OH)₃ was dispersed in distilled water and ball-milled at a speed of 300 rpm for 4 h. Then, the mixture was hydrothermal treated in a Teflon-lined stainless autoclave at 150 °C for 6 h with stirring. The product was separated by centrifugation at 3000 rpm and dried in an oven at 70 °C overnight. The resultant powder was calcined at 600 °C for 5 h in air, which resulted in the formation of HT-C12A7 powder with a mayenite structure.

Preparation of Ru/HT-C12A7

Ru loading was conducted by chemical vapor deposition (CVD) process using the corresponding metal carbonyl Ru₃(CO)₁₂

precursors. In a typical catalyst synthesis, HT-C12A7 powders with $Ru_3(CO)_{12}$ was sealed in an evacuated silica tube and heated under a temperature program of 2 °C min⁻¹ up to 40 °C, held for one hour, 0.25 °C min⁻¹ up to 70 °C, held for one hour, 0.4 °C min⁻¹ up to 120 °C, held for one hour, 0.9 °C min⁻¹ up to 250 °C, hold for two hours and then cooled to ambient temperature. Other oxide materials, such as Al_2O_3 , CaO, Al_2O_3 -SiO₂, MgO, ZrO₂ and TiO₂ were commercial products and Ru-loading was conducted by the same thermal decomposition method as HT-C12A7.

Catalytic hydrogenation of heteroarenes

All reactions were carried out in a 25 mL stainless steel autoclave fitted with a glass mantel, 60-bar manometer, and a magnetic stirrer. In a typical reaction, 40 mg catalyst and 5 mmol substrates were sealed in the autoclave. Then autoclave was flushed three times with H_2 , pressurized with H_2 (1.0 MPa), and heated to 80 °C over 30 min with stirring (800 rpm). The reactor was held at this temperature for 12 h. The products were analyzed by gas chromatography (GC) and the identity of the products was further confirmed by GC-MS.

H₂-D₂ exchange reaction

Before the reaction, the catalyst was heated in Ar flow (10 mL min⁻¹) at 200 °C for 0.5 h, followed by cooling to the desired temperature under He flow. The H_2 - D_2 exchange reaction was conducted in a fixed bed quartz reactor that was supplied with an extra pure (99.99995%) mixture of $H_2:D_2:Ar$ (1:1:3) at 50 °C. Reaction products (H_2 , HD and D_2) were analyzed with an online mass spectrometer (ANELVA, Quadrupole Mass Spectrometer). Trace amounts of HD formed in the experimental setup without catalyst and the product concentrations were corrected for this. For the pre-adsorbed quinoline to the samples, the liquid quinoline (1 ml) was heated above its saturated vapor pressure and then injected into the sample chamber under a vacuum cycle system.

Characterization of catalysts

Samples for examination by scanning transmission electron microscopy (STEM) were prepared by dispersing the dry catalyst powder onto a holey carbon film supported by a 300 mesh copper TEM grid. STEM high angle annular dark field (HAADF) images of the supported metal nanoparticles were obtained using an aberration corrected JEM ARM-200F STEM operating at 200 kV. The mean Ru particle diameters were calculated by determining the size of more than 100 particles per sample using iTEM software (soft Imaging System GmbH). X-ray photoelectron spectroscopy (XPS, ESCA-3200, Shimadzu) measurements were carried out using Mg Ka radiation at $<10^{-6}$ Pa (applied bias voltage to X-ray source of 8 kV). The Brunauer-Emmett-Teller specific surface areas of the samples were determined by the measurement of nitrogen adsorptiondesorption isotherms at -196 °C using an automatic gasadsorption instrument (BELSORP-mini II, MiccrotracBEL) after evacuation of the samples at 150 °C. Ru content was determined by inductively coupled plasma atomic emission

spectroscopy (ICP-AES; ICPS-8100, Shimadzu). X-band electron paramagnetic resonance (EPR) of the sample Ru/HT-C12A7 was performed on a spectrometer (EMX8/2.7, Bruker, Germany). Data for UV-irradiated samples were collected at RT. The g-value at RT was calibrated using a solution of di (phenyl)-(2,4,6-trinitrophenyl)iminoazanium (DPPH) in benzene with a g-value of 2.0035. The spin density in the sample was calibrated using standard samples of CuSO₄·5H₂O. CO2-TPD measurement was measured in a BELCAT-A instrument (MiccrotracBEL, Japan). The samples (50 mg), placed in a U-shaped quartz reactor with an inner diameter of 0.5 cm, was exposed to a flow of CO₂ at 300 °C for 30 min and then cooled to room temperature. Subsequently, TPD was then started, with a heating rate of 10 °C min⁻¹ till 500 °C. The desorbed products were analyzed by a thermal conductivity detector (TCD) and mass spectrometer (Bell Mass, MiccrotracBEL, Japan). Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL ECP-300 instrument (JEOL, Tokyo, Japan) using tetramethylsilane as an internal standard (300 and 75 MHz for ¹H NMR and ¹³C NMR, respectively).

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