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Recent advances in heterogeneous catalytic hydrogenation and dehydrogenation of *N*-heterocycles

Zhongzhe Wei, Fangjun Shao, Jianguo Wang *

Institute of Industrial Catalysis, College of Chemical Engineering, State Key Laboratory Breeding Base of Green-Chemical Synthesis Technology, Zhejiang University of Technology, Hangzhou 310032, Zhejiang, China

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ABSTRACT

The selective hydrogenation of quinolines to 1,2,3,4-tetrahydroquinolines (py-THQ) and its derivatives has attracted a considerable amount of attention as they show great versatility in many pharmaceuticals, agrochemicals, and fine chemicals. Over the past few decades, great breakthroughs have been achieved in the controlled synthesis of efficient heterogeneous catalysts used for the selective hydrogenation of functionalized quinoline compounds, which allow one to correlate the structure-property relationships. In this review, we will summarize the recent significant progress achieved in this field covering the synthetic strategies, microstructural and chemical features, catalytic performance, and internal relationships. State-of-the-art noble metal-based single (Pd, Pt, Ru, Rh, Ir and Au) and bi/multi-metallic catalysts (RuCu, AuPd, and PdNi) are first introduced, followed by a summary of earth-abundant metal-based catalysts (Co, Fe, Ni, and Cu). Finally, the dehydrogenation of *N*-heterocycles is introduced to form a reversible hydrogenation/dehydrogenation system for H₂ storage, which can be employed in a liquid organic hydrogen system. Furthermore, the reaction mechanism and future research direction in these areas are also discussed. This review will deepen our understanding of the catalytic transformation of *N*-heterocycles and provide guidance for researchers on the rational design of catalysts.

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1. Introduction

The synthesis of functionalized 1,2,3,4-tetrahydroquinolines (py-THQ) has attracted more and more attention due to their immense utility as biologically active building blocks and key intermediates in the manufacture of pharmaceuticals, alkaloids, agrochemicals, and other fine chemicals [1]. For example, well-known prescription and potential drugs, such as oxamniquine, nicainoprol, viratmycin, and diclofensine, all contain py-THQ units [2,3]. Currently, conventional synthesis methods used to prepare py-THQ derivatives involve catalytic

cyclization [4,5], Beckman rearrangement [6], and chemoselective hydrogenation of *N*-heterocycles (Scheme 1(a)). Among these processes, the direct hydrogenation of readily available quinolines offers a straightforward and promising approach to access py-THQ in terms of its simplicity and high atom efficiency.

The chemoselective hydrogenation of quinoline compounds has the following drawbacks and challenges: (1) The hydrogenation of quinoline shows high reaction energy barriers, which makes the reaction process inherently sluggish and requires the use of harsh reaction conditions, (2) the hydrogenation

* Corresponding author. Tel/Fax: +86-571-88871037; E-mail: jgw@zjut.edu.cn

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Scheme 1. The synthetic routes used to prepare py-THQ (a); the possible catalytic hydrogenation pathways for the hydrogenation of quinoline (b).

tion process normally involves multiple intermediates and by-products may form during the reaction (Scheme 1(b)), (3) easily reducible groups in functionalized quinolines, such as alkenes, ketones, nitriles, aldehydes, amines and halogens, may also be hydrogenated causing unsatisfactory selectivity, and (4) leaching or poisoning of catalytic active sites may lead to poor reusability of the catalyst due to the strong coordination effect between the metal and N atoms in *N*-heterocycles. Therefore, the development of a novel high-performance heterogeneous catalysts is highly urgent yet a huge challenge.

Despite facing the above difficulties, the selective hydrogenation of functionalized quinolines has still been explored. The selective hydrogenation of *N*-heterocycles can be traced back to 1982, reported by Fish and co-workers [7] using a Ru-based homogeneous catalyst. Thereafter, a great deal of homogeneous catalysts based on Ru [8,9], Ir [10–12], Rh [13], Au [14], and Co [15] have been established to achieve this selective transformation. Despite their high catalytic activity and selectivity, homogeneous catalysts suffer from inherent difficulties in their separation and recovery. Moreover, extra additives such as I₂ are essential during the hydrogenation process to achieve the efficient hydrogenation of heteroarenes using Ir-based homogeneous catalysts, which limits their application on an industrial scale [16]. In contrast, heterogeneous catalysts play important roles in the chemical industry due to their low cost and ease of separation and recycling. It has been reported that over 90% of all chemical processes involve the use of catalysts. Among the most industrially important processes, heterogeneous catalysts are the most widely used and account for 80% of these reactions [17,18]. In terms of the selective hydrogenation of quinoline bearing methyl or methoxy substituents, precious metal-based heterogeneous catalysts such as Pd [19–25], Pt [26,27], Ru [28–32], Ir [33], and Rh [34] have received a large amount of interest due to their excellent activity and selectivity. However, the selectivity is not satisfactory for functionalized quinoline compounds bearing easily reducible groups, such as alkenes, ketones, nitriles, aldehydes, amines, and halogens [35,36]. By careful selection of the support, modifying the properties of the support or the fabrication unique catalyst structures, Pd [24,37], Pt [38], Ru [39,40], Ir [41], and Rh-based [42] catalysts have been transformed into chemoselective catalysts. For instance, the Li group modified the surface of mesoporous silica hollow nanospheres using amine groups to achieve significantly improved catalytic performance in the

hydrogenation of *N*-heterocycles [22]. Cao and co-workers [43] reported a breakthrough in regard functional group tolerance by employing Au nanoparticles (NPs) dispersed on high surface area TiO₂ as an efficient catalyst, even at temperatures under 25 °C. However, the risk in the supply and volatile price of noble metals severely hamper their industrial applications. As a response, earth-abundant metal (e.g., Co, Fe, Ni, and Cu)-based catalysts have been gradually used by researchers due to their low cost and distinctive electronic structures [44]. By supporting cobalt-based NPs on N-doped carbon and Al₂O₃, Beller and co-workers [45] observed encouraging catalytic performance for the hydrogenation of quinolines. Although the catalytic activity of non-noble metal catalysts is inferior to precious metal catalysts, the selectivity is high and easy to control.

The catalytic dehydrogenation of *N*-heterocycles, which is more feasible when compared to that of cycloalkanes, continues to be of great interest in organic synthesis [46]. Moreover, from the viewpoint of H₂ storage, the switchable transformation between quinolines and py-THQs can be used to construct a useful liquid organic H₂ storage system. The development of a single catalyst that can achieve reversible dehydrogenation/hydrogenation of *N*-heterocycles has recently attracted an increasing amount of attention.

Herein, we have attempted to summarize the recent progress on the selective hydrogenation of *N*-heterocycles in regard the catalyst synthesis, structural design and structure-activity relationships. To better understand these developments, this review is divided into chapters according to noble metal (Pd, Pt, Ru, Rh, Ir, Au, RuCu, AuPd, and PdNi) and earth-abundant metal (Co, Fe, Ni and Cu) catalysts. Finally, the dehydrogenation of *N*-heterocycles is discussed in regard the formation of a reversible hydrogenation/dehydrogenation system used for H₂ storage. We hope that this review can give guidance on the rational design of high-performance heterogeneous catalysts for the switchable transformation between quinolines and py-THQs.

2. Selective hydrogenation of *N*-heterocycles

2.1. Selective hydrogenation of *N*-heterocycles using H₂

The direct hydrogenation of quinolines using H₂ as the reducing agent is atom-efficient and green method. The reported works covers the state-of-the-art noble metal catalysts and

earth-abundant metal catalysts. To achieve high catalytic performance during the selective hydrogenation process, the authors have designed catalysts considering the following aspects: Reaction medium, properties of the support, metal-support interactions, bimetallic or multi-metallic effects, core-shell structure and particle size of NPs.

2.1.1. Selective hydrogenation of *N*-heterocycles using noble metal-based catalysts

The surfaces of noble metals with incomplete filled *d*-electron orbitals easily adsorb reactants and the strength of this interaction is moderate, which is favorable for the formation of intermediate “active compounds” [47]. In addition, noble metals have encouraging properties, such as resistance to high-temperature, anti-oxidation, and corrosion resistance, and thus they have received wide spread attention in catalysis [48]. Throughout the application of noble metals in the hydrogenation of quinolines, almost all the noble metals can be applied to this model reaction. Pd, Pt, Rh, Ir, Ru, etc. are commonly used, among which Pd and Ru are shown to be the most extensively researched (Table 2) [21,26,39,42,43]. Generally, noble metal-based catalysts are synthesized via an impregnation method to load the active component and co-catalyst onto the support. The performance of the target catalysts can be tuned via changing the synthetic technique, including the type of support, components, and dosage of the active phases.

Although noble metal-based catalysts have made considerable progress, their commercial applications are severely limited because of the low reserves and high cost of precious metals [49,50]. In addition, the hydrogenation of quinoline normally involves multiple intermediates and high reaction energy barriers, which make the kinetics of the reaction process sluggish. Moreover, the catalysts also suffer from leaching and poisoning of the catalytic active sites. Therefore, it is of great challenge to develop highly active precious metal catalysts with low metal loading [29,37].

2.1.1.1. Pd-based heterogeneous catalysts

Among the noble metal-based catalysts reported in the literature, Pd-based catalysts with encouraging performance in catalytic transformations are one of the most explored catalysts. Pd has a strong ability to absorb and dissociate H₂ [51,52]. Benefiting from its special properties, Pd-based catalysts exhibit great potential in hydrogenation and dehydrogenation reactions [53–55]. In terms of the selective hydrogenation of quinoline, a series of Pd-based catalysts have been designed. Summarizing the reported literature, the carriers mainly include metal oxides [19,20,22,25], organic polymers [23,24,56–59], polymeric graphitic carbon nitride (g-C₃N₄) [21], and nanoporous carbon materials [37,60,61].

It is generally accepted that the strong adsorption of quinoline and/or its hydrogenation products on the active metal sites causes catalyst poisoning. To overcome this obstacle, the heterolytic H₂ splitting and ionic hydrogenation mechanism (Noyori's mechanism in homogeneous catalysis) on a solid catalyst is regarded as a prevailing strategy [29]. This type of mechanism inhibits the direct binding of quinoline and/or the

target products to the metallic sites, thus opening the possibility to minimize catalyst poisoning. To achieve an ionic hydrogenation pathway, ultra-fine Pd NPs supported on MgO (Pd/MgO) were synthesized via NaBH₄ reduction [20]. Pd/MgO delivered satisfactory activity and selectivity in the hydrogenation of quinoline to py-THQ. The researchers suggested that the excellent selectivity stems from the ionic mechanism. Unfortunately, the reusability of the catalyst was unsatisfactory with a 30% loss of activity observed after the third reuse cycle. To improve the catalytic stability, modulation of the surface of the support to enhance the interactions between the active metal and support is an impressive strategy. As shown in Fig. 1(a), Li and co-workers [22] fabricated amine-rich mesoporous silica hollow nanospheres (HS-NH₂) using a one-pot condensation reaction (Fig. 1). Then, ultra-small Pd NPs supported on HS-NH₂ (Pd/HS-NH₂) were prepared using a conventional impregnation–reduction method. Pd/HS-NH₂ displays superb activity and selectivity for the hydrogenation of quinoline to give py-THQ. Notably, the TOF value was calculated to be as high as 5052 h^{−1}, which was much higher than that of Pd on silica hollow nanospheres without amine (Pd/HS) and Pd/C. Besides, CO stripping voltammetry (Fig. 1(b)) and XPS characterization (Fig. 1(c)–(d)) showed that Pd has enhanced electron-rich character on HS-NH₂ than that on SiO₂ and C. The extraordinary character of Pd/HS-NH₂ was primarily ascribed to the electron-donating properties of the amine groups on HS. Pd NPs with an electron-rich surface prefer the adsorption of quinoline over py-THQ, which may promote the catalytic activity and selectivity. The author noted that the hydrogenation of quinoline is a size-sensitive reaction and Pd NPs with a mean particle size in the range of 3.4–4.0 nm exhibit the highest activity. As the particle size of the metal decreases, the number of surface atoms increases rapidly. Incomplete coordination of the surface atoms and the large number of unsaturated bonds generated increases the surface activity [62]. A similar phenomenon was also observed in Pd NPs on hydroxyapatite (HAP) [25]. By simply adjusting the reduction temperature of the Pd^{II} species with H₂, Pd NPs with average particle size between 1 and 1.5 nm were finely controlled. The supported Pd NPs with an average particle size of 1.5 nm showed the highest catalytic activity in the regioselective hydrogenation of quinoline to access py-THQ. In different catalytic systems, Pd NPs with different average particle sizes showed optimal catalytic performance in the selective hydrogenation of quinolines. This phenomenon was also present in the selective hydrogenation of halogenated nitrobenzene using Pd-based catalysts, which is also a size-sensitive reaction. For Pd/C, Pd NPs with a mean size of 28 nm showed the highest selectivity with no sign of dichlorination [63]. In contrast, for Pd/−Fe₂O₃-PR, a 99.2% selectivity towards halogenated aniline was obtained using Pd NPs with an average particle size of 12 nm [64]. The satisfactory catalytic performance with different particle sizes was mainly attributed to the different catalytic active sites in the different catalysts. The strong metal-support interactions in Pd/C were not obvious due to the inert properties of carbon. As a result, the particle size effect was emphasized and the percentage of edge sites increased upon decreasing the particle

Fig. 1. (a) A schematic illustration of the synthetic procedures used to prepare HS-NH₂ and Pd/HS-NH₂; (b) CO stripping voltammetry of 5% Pd/HS-NH₂, 5% Pd/HS, and 5% Pd/C; the XPS spectra of Pd 3d in 5% Pd/HS-NH₂ (c), 5% Pd/HS (d), and 5% Pd/C (e). Reproduced with permission from Ref. [22]. Copyright 2017, The Royal Society of Chemistry.

size. Nevertheless, the strong interactions between the metal and support play a dominant role in the catalytic processes when Pd NPs are loaded onto reducible metal oxide supports, such as TiO₂ and CeO₂. On these strong metal-support interaction catalysts, the reactions mainly proceed on the interface between Pd and the metal oxide support and do not only consider the size effect. One must therefore take into account both the size-dependent geometric effect and the electronic effect when correlating the catalytic performance.

Polymers are often formed by the repeated connection of specific structural units via covalent bonds. Although the relative molecular mass of polymers is large, their compositions are not complicated. The abundant groups on the surface of polymers may influence the valence states and electronic properties of the metal NPs. Recently, g-C₃N₄, presumably one of the oldest polymers reported in scientific literature, has received tremendous attention in catalysis because of its interesting chemical and physical properties [65,66]. One study has shown this quite illustratively: Uniform Pd NPs supported on ordered mesoporous carbon nitride (Pd@ompg-C₃N₄) have been prepared using SBA-15 as a hard template (Fig. 2) [21]. All of the Pd NPs were ~4 nm in size and stable throughout the recycling reactions. The hybrid material exhibits a mesoporous structure with a BET surface area of 212 m²/g and mean pore size of 7.42 nm. Metallic Pd species (Pd⁰) account for 70% of the supported Pd species, which were generally regarded as the active sites for H₂ activation [67]. Pd@ompg/C₃N₄ was subsequently used as a catalyst for the selective hydrogenation of quinoline using H₂ under mild reaction conditions.

Pd@ompg-C₃N₄ gave a >99% yield toward py-THQ under 1 bar of H₂ at low temperature, which was much higher than

Pd/C and Pd@mpg-C₃N₄ (Fig. 2(d)). The higher catalytic activity was attributed to the uniform cylindrical pores promoting the free diffusion of molecules and shortened diffusion distances in the channels [68]. The good selectivity towards py-THQ was deduced from the prior adsorption of the N-containing aromatic ring on C₃N₄ due to the formation of N-H-N hydrogen bonds between the N-heterocycle and amine groups on the surface of carbon nitride, which was also confirmed by benzene and pyridine TPD (Fig. 2(e)). Pleasingly, Pd@ompg-C₃N₄ was reused six times without any deactivation and delivered a broad scope of substituted quinoline compounds.

Water is considered as an eco-friendly alternative to organic solvents because of advantages such as its non-toxic and non-flammable properties, low-cost, sustainability, and high heat capacity. Some works have illustrated that catalysts perform better in water than in conventional organic solvents in certain catalytic reactions [54,69]. The above-mentioned catalysts all work well in organic solvents, such as cyclohexane, toluene and THF. However, they display poor catalytic activity or inactivity in water. This is attributed to the formation of hydrogen bonds between the hydroxyl groups of water and the N-heterocycle of quinoline, which suppresses the absorption of quinoline onto the surface of the catalyst, causing low activity [28]. Pd NPs supported on organic polymers can achieve the efficient hydrogenation of quinoline in water [24,56]. A polymer-supported Pd catalyst (prepared via the co-polymerization of Pd(AAEMA)₂, ethyl methacrylate, and ethylene glycol dimethacrylate) gave a 99% yield of py-THQ at 80 °C and 10 bar H₂ in an aqueous medium [23].

Apart from organic polymers obtained using artificial syn-

Fig. 2. The representative TEM image (a), N_2 adsorption-desorption isotherms (b), and Pd 3d XPS spectra (c) of Pd@mmpg- C_3N_4 ; (d) the yield of py-THQ as a function of time using different catalysts; (e) the TPD profiles of benzene and pyridine; the reusability of Pd@mmpg- C_3N_4 (f) and the proposed reaction mechanism (g) for the hydrogenation of quinoline on Pd@mmpg- C_3N_4 . Reproduced with permission from Ref. [21]. Copyright 2014, Elsevier.

thesis working well in water, biphasic catalytic systems do not only interact with organic substrates, but are also effectively dispersed in water, which may afford satisfactory catalytic behavior in water for the hydrogenation of quinoline. Plant tannins constitute among the largest fractions of terrestrial biomass that can be readily produced from plants via simple extraction. The abundant phenolic hydroxyl groups in their molecular backbone make tannins water-soluble and amphiphilic, providing the possibility for the hydrogenation of quinoline in water [58]. Similarly, Pd tightly loaded on black wattle tannin (BWT) was successfully applied in an aqueous-organic biphasic system used for quinoline hydrogenation [59]. The network of BWT can effectively inhibit the aggregation and leaching of Pd NPs due to the strong chelating ability of BWT towards Pd NPs, thus making Pd/BWT a reusable catalyst.

N-doped porous carbon materials hold great promise as supports due to their high specific surface area, well-developed porous structures, rich defects, high resistance to acid and alkali conditions, and strong coordination interactions with metal NPs [70–73]. As a result, they are widely used in heterogeneous catalytic systems [74,75]. To fabricate carbon materials with micro-, meso-, and macroporous structures, activation agents or soft/hard templates are necessary [76–78]. 3D Hierarchi-

cally porous N-doped carbon materials are created via the self-assembly of chitosan, ionic liquids, and KZ molten salt [37]. The Pd NPs were then anchored onto the porous carbon materials using an ultrasound-assisted deposition method. Pd@CIL-900 catalyzed the selective hydrogenation of quinoline with encouraging yield towards py-THQ under an atmospheric pressure of H_2 . For example, the catalytic hydrogenation of quinoline using 0.6 mol% Pd@CIL-900 at 80 °C proceeded with 98% conversion in 4 h and more than 99% selectivity for py-THQ. The observed reaction rates were much higher than those afforded using a commercial Pd/C catalyst. The apparent activation energy was calculated to be 41.1 kJ/mol, which was much lower than Pd/C and Ru/AC [79]. The large surface area, hierarchically porous structure, high dispersity of Pd NPs, and surface amine groups were regarded as the factors contributing to the high activity of Pd@CIL-900.

Unsupported nanoporous metal materials acting as heterogeneous catalysts have attracted an increased level of interest due to their satisfactory properties, such as non-toxicity, high recyclability, and ease of separation [80–82]. Bao and co-workers [83] successfully applied unsupported nanoporous Pd (PdNPore) in the hydrogenation of quinolines. Good to excellent yields of py-THQ were achieved under relatively mild

reaction conditions (2–5 atm H_2 , room temperature to 50 °C). The catalyst can be reused six times with no leaching of Pd observed, proving the robustness and recyclability of the catalyst. Notably, the authors skillfully verified the heterolytic cleavage of H_2 to yield $[H\text{-base}]^+$ and $Pd\text{-H}^-$ during the selective hydrogenation reaction using deuterium-labeling experiments. In previous works, the phenomenon of heterolytic cleavage of H_2 was mostly a simple inference without any direct evidence. Only a few works have reported the observation of metal hydride species using IR spectroscopy. However, some metal hydrides were sensitive and not stable, and are hard to detect using IR spectroscopy [23,43]. The deuterium-labeling method mentioned in this work was practical and easy to perform, providing a useful method to investigate the high catalytic selectivity and reaction mechanism.

2.1.1.2. Pt-based heterogeneous catalysts

Pt-based catalysts are promising candidates for catalysis and have been intensively employed in refining petroleum, hydrogenation of unsaturated compounds, removal of CO and NO_x in gases, oxygen reduction reaction, and so on [84,85]. With the development of new Pt catalysts, the chemical reaction processes were simplified, along with boosting the economic benefits. Therefore, Pt-based catalysts still have long-term development prospects. As described above, the selective hydrogenation of quinoline may suffer from deactivation via poisoning by the substrate or products. The design of efficient and durable catalysts remains a huge challenge, especially under mild reaction conditions (room temperature and low pressure H_2). A series of excellent and attractive works based on Pt catalysts have been dedicated to meeting the requirement of high performance in the catalytic hydrogenation

of quinoline under mild conditions [26,27,38,86]. In a word, two strategies, including the size effect and electronic metal-support interaction (EMSI), are elaborately involved in the design of these catalysts. Experiments have shown that the proposed catalysts produced using the above strategies achieve impressive catalytic activity and selectivity.

Pt-based catalysts are similar to Pd-based catalysts, exhibiting a size effect during the regioselective hydrogenation of quinoline. In response to this issue, Gao *et al.* [26] conducted a detailed investigation on the size effect (Fig. 3). The researchers designed a series of Pt catalysts with a mean particle size of 0.7, 1.2, 2.4, and 5.6 nm, respectively. A strong size effect of Pt NPs on their catalytic ability in the hydrogenation of quinoline was observed. From an electronic structure point of view, the size effect has been ascribed to the shift of the d-band center with reference to the valence band (Fig. 3(a) and (b)), which is directly related to the strength of the interactions between the Pt NPs and H_2 /quinoline. A volcano-shape relationship was observed between the activity and mean particle size of the Pt NPs. Specifically, Pt-1.2 outperformed all the prepared catalysts, affording a >99% yield of py-THQ under mild conditions and five reuse cycles without any loss of activity (Fig. 3(c)). Furthermore, the authors revealed a size-dependent interaction between the Pt NPs and the reactants (H_2 /quinoline) (Fig. 3(d)). Pt-1.2 shows the greatest ability in H_2 dissociation and showed a relative strong interaction with quinoline, which together promotes the catalytic hydrogenation reaction. The ionic reaction mechanism was proposed based on the primary isotope effect. The authors confirmed that hydrogen transfer from the Pt-H- and $[O\text{-H}]^+$ species to the quinoline molecules was the rate-determining step, further emphasizing the importance in the size-dependence between the Pt NPs and quinoline (Fig.

Fig. 3. (a) Core-level Pt 4f XPS, (b) FT-EXAFS spectra using Pt foil as a reference, (c) plots of the conversion of quinoline and selectivity toward py-THQ against reaction time at room temperature and ambient H_2 pressure, and (d) plot of TOF (per surface Pt atom) against the diameter of the Pt NPs. The TOF for activation of H_2 and D_2 to form HD is listed for comparison for Pt- x ($x = 0.7, 1.2, 2.4$, and 5.3). (e) The primary isotope effect observed using Pt-1.2 in the hydrogenation of quinoline. (f) The FTIR spectrum of the Pt-1.2 after exposure to D_2 . Reproduced with permission from Ref. [26]. Copyright 2016, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

3(e) and (f)).

Apart from tailoring the particle size of the NPs to alter the electronic structure, EMSI, describes the electronic perturbations between the metal and support, being successfully introduced to regulate the catalytic performance in heterogeneous catalysis [87]. Notably, the Qu's group did a good job of employing Pt NPs supported on CeO₂ nanorods (Pt/NR-CeO₂) as a highly efficient and selective catalyst in the hydrogenation of various functionalized quinolines at room temperature [38]. The excellent performance of Pt/NR-CeO₂ was mainly attributed to the enhanced electron density of Pt caused by the electron transfer between the Pt NPs and CeO₂ nanorods. By combining control experiments with density functional theory (DFT) calculations, the authors revealed that Pt with high electron density improved the H₂ dissociation ability and further benefited the desorption of py-THQ. Due to the weak interaction between the Pt NPs and py-THQ, the poisoning of the active sites is largely inhibited. Meanwhile, the active sites on the Pt surface are readily regenerated, thus ensuring high catalytic activity, selectivity, and stability. A similar observation in which Pt NPs with enhanced electron density display high catalytic behavior has also been reported by the Han's group [27]. The authors also put forward a new method to support Pt sub-nanoparticles on TiO₂ using N,N'-(ethane-1,2-diyl)diformamide (ED) as both the reducing agent and stabilizing agent. When Pt⁴⁺ was reduced *in situ*, ethylenediamine was formed and an interfacial electronic effect was induced by the interactions between the Pt NPs and ethylenediamine. Ethylenediamine surrounding the Pt surface and interfacial electronic effect can effectively stabilize the ultra-fine Pt NPs and inhibit the growth of the Pt NPs. What should be mentioned is that the dispersion of Pt achieved was as high as 92.5%, which shows it was an efficient method for obtaining catalysts with highly dispersed of NPs.

2.1.1.3. Ru-based heterogeneous catalysts

The Ru-based catalysts possess encouraging catalytic performance in many fields, such as hydrogenation, oxidation, hydrogenolysis, ammonia synthesis and hydroformylation [88,89]. When compared with Pd, Pt, Ir, and Rh, Ru is the cheapest at a cost of \$42 per oz (BASF, Mar 2016) [40]. DFT calculations verified that Ru displays a Pt-like metal-hydrogen bond strength, which means that using Ru as a catalyst will help to reduce the synthetic cost, while the catalytic activity remains almost constant [90,91].

When compared with Pd- and Pt-based catalysts, the catalytic activity of Ru-based catalysts is relatively poor. To drive

the reaction, high reaction temperatures and high H₂ pressure are always needed. To optimize the catalytic activity and selectivity, the primary strategies include: (1) Modification of the surface properties of the support (acid, base, etc.) to enhance the interactions between the metal and support, (2) regulation of the environment surrounding the metal centers to alter the electronic structure or control the morphology of the metals to expose a specific metal plane, and (3) reduction of the metal dimensions to isolate single atomic site catalysts, obtaining maximum atom efficiency and exposing the most active sites.

As noted previously, heterolytic H₂ activation and ionic hydrogenation routes benefit the catalytic hydrogenation of quinoline. To achieve this, the fabrication of a catalyst composed of active metal NPs and a basic support are highly desirable. Some works have reported that Ru NPs on basic supports (MgO and CaO) deliver much higher catalytic activity than those on acidic supports in the hydrogenation of quinoline [28–30]. It has also been demonstrated that the catalytic activity of Ru NPs supported on different metal oxides ranked in the order of: Ru/SiO₂-Al₂O₃ < Ru/ZrO₂ < Ru/TiO₂ < Ru/Al₂O₃ < Ru/MgO < Ru/CaO, which match well with the order of the number of basic sites [40]. For example, Sanchez-Delgado *et al.* [29,30,92] reported that Ru metals on basic supports (P4VPy or MgO) smoothly catalyzed the hydrogenation of *N*-heterocycles with high activity and selectivity (92%–93%). Ru/MgO displayed higher activity than Ru/P4VPy due to the strong basic functional groups on the surface of MgO, which form appropriate sites for the heterolytic splitting of H₂ with the aid of the Ru atoms located at the interface between the Ru NPs and MgO (site A, Fig. 4). Although the main reaction pathways involve an ionic mechanism with the main product being py-THQ, by-products such as bz-THQ and DHQ were also generated in about 7% yield. The formation of by-products suggests that the aromatic ring was adsorbed on the Ru surface, accompanying with homolytic splitting of H₂. This was attributed to the bulk Ru atoms on the Ru NPs located away from the surface basic sites enabling the homolytic splitting of H₂ (site B, Fig. 4). That is, there are two different types of active sites in Ru/MgO responsible for the heterolytic splitting of H₂, respectively. Recently, Ru NPs supported on another basic support, 12CaO·7Al₂O₃ (Ru/HT-C₁₂A₇), with a unique sub-nanocage structure have been reported by Hosono and co-workers. The catalyst achieved the efficient hydrogenation of quinoline in a selective and recyclable manner [40]. Similarly, the heterolytic splitting of H₂ was confirmed, promoted by the positively charged truncated cages on C₁₂A₇, which have the ability to trap

Fig. 4. (a) The proposed dual-site structure of Ru/MgO; (b) the proposed dual-site mechanism for the hydrogenation of quinoline on Ru/MgO. Reproduced with permission from Ref. [29]. Copyright 2014, Elsevier.

H-. The general scope of the active catalyst was investigated, including more than 10 functionalized N-heteroarenes, even those substituted with easily reducible groups. The reducible functional groups were almost unaffected with good to excellent selectivity (85%–100%). Even after being reused eight times, the activity of Ru/HT-C₁₂A₇ remains unchanged. Unfortunately, some by-products were inevitably generated during the hydrogenation process, which inferred that homolytic splitting of H₂ on the Ru surface still occurs, although in a very small amount. Inspired by the observation that basic supports significantly improve the catalytic performance of Ru-based catalysts, other basic supports such as ordered mesoporous N-doped carbon [32,93], cetyltrimethylammonium bromide intercalated montmorillonite (CTAB-MMT) [94], and imidazolium based ionic liquids (ILs) [31,95] have shown good catalytic performance in the selective hydrogenation of quinolines.

To further improve the catalytic selectivity during the hydrogenation of quinoline towards py-THQ with no DHQ formation in water, modulation of the hydrophobic/hydrophilic properties of the metals surface has been used as an appealing approach. In a subsequent work, a core-shell Ru-SiO₂@mSiO₂ catalyst designed by the Li's group appeared to mirror just that [39]. Ru-SiO₂@mSiO₂ with almost all of the Ru NPs surrounded by hydroxyl groups possessed higher activity (100%), selectivity (100%), and excellent reusability in water for the hydrogenation of quinoline, than Ru/SiO₂ and Ru/SiO₂-spheres with no core-shell structure. The unprecedented high performance of Ru-SiO₂@mSiO₂ was mainly attributed to the hydrophilic surface induced by the abundant hydroxyl groups. The water film formed on the hydrophilic surface of Ru-SiO₂@mSiO₂ promotes the selective adsorption of N-heterocycles on the metal surface via a hydrogen bond formed between the nitrogen atom of the quinoline and hydroxyl groups, which suppresses the adsorption of the phenyl ring. The hydrogen bond not only improves the catalytic selectivity, but also enhances the reusability through weakening the interaction between the N atom and catalytic active species.

As an alternative to modifying the surface properties of the support to enhance the interactions between the metal and support, the development of single atomic catalysts was found to be an efficient approach. The metal atoms are distributed in a uniform and discrete form, which realizes the maximum utilization of the atoms and increases highly active low coordinated atoms [97]. Single-atom catalysts have both the "isolated active site" of homogeneous catalysts and the characteristic of ease of recycling of heterogeneous catalysts, which are considered to be a bridge connecting heterogeneous catalysis with homogeneous catalysis [98,99]. More importantly, the uniform active-center structure of monoatomic catalysts provides a good platform for researchers to study the complex heterogeneous catalytic process on an atomic level. Recently, Li and co-workers have proposed a facile synthesis of isolated single Ru atoms supported on N-doped porous carbon (Ru SAs/N-C) using the strong coordination between Ru³⁺ and the free amine groups (-NH₂) present on the skeleton of UiO-66-NH₂ (Fig. 5) [96]. The fabrication mechanisms shown in Fig. 5(a) clearly emphasize the important role of -NH₂ in the controlled synthe-

sis of the single atomic Ru catalyst. Without the decoration of -NH₂, Ru clusters supported on the carbon architecture (Ru NCs/C) were produced as a control catalyst. The magnified HAADF-STEM images demonstrate that the Ru species in Ru SAs/N-C exhibit atomic dispersion (Fig. 5(b)–(g)). Confirmed using EXAFS spectra, no metallic Ru-Ru peak was observed in Ru SAs/N-C. The coordination number of the first shell of the Ru atoms in Ru SAs/N-C was three with a mean bond length of 2.08 Å (Fig. 5(h)–(k)), which again highlights that nearly all of the Ru atoms in Ru SAs/N-C are atomically dispersed. As expected, the single atomic Ru structure ensures that Ru SAs/N-C possesses both high activity, selectivity, and encouraging stability in the hydrogenation of quinoline. Almost complete conversions of a variety of quinoline compounds with satisfactory selectivity (>99%) towards py-THQ were achieved, which was much higher than Ru NCs/C (Fig. 5(l)–(n)). This work not only opens up an avenue for the synthesis of single atomic catalysts using strong metal-N coordination, but also affords high activity and selectivity toward py-THQ.

Apart from generating py-THQ as the main product on Ru-based catalysts, DHQ can also be formed using strongly acidic media, longer reaction times, and harsh reaction conditions (>200 °C, >100 bar H₂) [100,101]. In fact, the above-mentioned catalysts cannot achieve the catalytic formation of DHQ. The preferential formation of py-THQ or bz-THQ, which are inevitably adsorbed on the surface of the catalyst, thus inhibit further hydrogenation toward DHQ [102]. As a response to this, Ru NPs supported on hydroxyapatite (Ru/HAP) [103] and Ru NPs intercalated in hectorite (Ru@hectorite) [104] were sequentially reported and their catalytic selectivity was found to be sensitive to the solvent used. A high selectivity towards DHQ was only obtained in aprotic solvents, such as cyclohexane. However, the yield of DHQ was rather low when the reaction was carried out in water. This was mainly attributed to the inhibition of coordination between the active metal and the aromatic ring because a hydrogen bond is formed between the benzene ring of quinoline and water. In order to improve the selectivity towards DHQ in water, the interaction between the aromatic ring of quinoline or py-THQ and the support should be enhanced to escape the pull of the hydrogen bond. Inspired by this, Ru NPs supported on glucose-derived carbon spheres (Ru/CSP) were produced and successfully applied in the hydrogenation of quinoline in water [105]. As expected, a high conversion (98%) of quinoline and high selectivity (95%) toward DHQ were obtained under the optimized reaction conditions (120 °C, 20 bar H₂). This was attributed to the aromatic structures in the CSP backbone promoting the adsorption of the aromatic ring in quinoline or py-THQ onto CSP through π - π interactions. This catalytic system was green and sustainable in regard the synthetic procedure and catalytic performance.

2.1.1.4. Other precious metal (Rh, Ir, Au)-based heterogeneous catalysts

Apart from Pd-, Pt-, and Ru-based catalysts, the works on Rh, Ir and Au-based catalysts in the selective hydrogenation of quinolines are relatively less reported. When it comes to

Fig. 5. (a) The proposed fabrication mechanisms for Ru SAs/N-C (top) and Ru NCs/C (bottom). (b–d) Magnified HAADF-STEM images of Ru SAs/N-C. (e–g) Magnified HAADF-STEM images of Ru NCs/C. (h) XANES spectra of Ru SAs/N-C and Ru NCs/C for Ru K-edge. (i) Fourier transformed (FT) k^2 -weighted $\chi(k)$ -function of the EXAFS spectra recorded for the Ru K-edge. (j) WT of the Ru K-edge and (k) fitting results of the EXAFS spectra of Ru SAs/N-C. (l) The catalytic results obtained for the regioselective hydrogenation of quinoline. The catalytic activity and reusability of Ru SAs/N-C (m) and Ru NCs/C (n) in the hydrogenation of quinoline. Reproduced with permission from Ref. [96]. Copyright 2017, American Chemical Society.

Rh-based catalysts, metal oxides [34,101,106], functionalized ILs [42,107], polymers [108], and reduced graphene oxide [36] are generally used as supports in the catalytic hydrogenation process. As stated above, MgO is a versatile support due to its basic character; Pd/MgO [20] and Ru/MgO [29] both exhibit excellent performance in the selective hydrogenation of quinoline. Likewise, Rh/MgO also presents high reactivity and selectivity, affording 100% yield of py-THQ though the mean particle size of Rh was as high as 46 nm [106]. It was deduced that the activity may be improved substantially by lowering the particle size of the Rh NPs. Very recently, sub-nanometric Rh clusters supported on superparamagnetic iron oxide NPs (Rh/Fe₃O₄) were synthesized via an *in situ* reduction using aqueous ammonia [34]. A series of N-heterocyclic compounds such as quinoline, pyridine, pyrazine, and indole were selectively hydrogenated using tetrahydroxydiboron (THDB) as the reducing agent under mild reaction conditions. The activity was comparable to that using H₂ as the H-resource and the catalyst displayed high reusability over 16 successive runs. Also noteworthy was that the method of reduction of the Rh precursor was efficient and novel, achieving a very uniform dispersion of Rh NPs, which can be extended to other catalytic systems. Very recently, evenly distributed Rh NPs supported on reduced gra-

phene oxide induced by the microwave thermal decomposition of Rh₆(CO)₁₆ in an ionic liquid ([bmim][BF₄]) were prepared [36]. The catalysts achieved significantly improved catalytic activity in the hydrogenation of quinoline when compared to those prepared using conventional thermal methods. This microwave induced thermal decomposition of the metal precursor to synthesize NPs was efficient and easy to operate, and can be employed using other metals.

To further extend the catalytic system, functionalized ILs have been employed as the support to promote the catalytic efficiency of Rh. ILs are frequently used as supports to anchor transition-metal NPs. Unfortunately, the NPs were not stable and prone to agglomerate so that the modification of ILs with specific groups was imperative. Phosphine-functionalized IL was found to be effective in the stabilization of Rh NPs and the resulting Rh-PIL catalyst was successful in the selective hydrogenation of quinoline [107]. In follow-up work, Paul J. Dyson and co-workers designed a Lewis acidic IL system containing Rh NPs and chlorozincate-[bmim][BF₄] (bmim = 1-butyl-3-methylimidazolium cation) (Rh-LAIL) [42]. The acidity of the catalyst was easily adjusted and the catalyst with the maximum acidity produced the most effective system. The hydrogenation process was universally valid and N-heteroarenes

bearing easily reducible substituents, such as hydroxy, amine, aldehyde and halogen groups, all proceeded smoothly in the reaction to give their corresponding py-THQs. The high catalytic activity and selectivity was ascribed to the Lewis acidic system, which can coordinate with the N atoms (Lewis bases) in the heteroarenes, promoting the activation of quinoline and the subsequent hydrogenation process. In these ILs system, the ILs play a dual role, not only acting as supports and stabilizers for the NPs, but also functionalized with various groups that actively participate in the reaction and affect the activation energy of the hydrogenation process.

From observing the current published works, noble metal oxides catalysts have been rarely reported in the hydrogenation of quinolines. However, “naked” IrO₂ NPs prepared using a ball-milling method furnished high catalytic activity and chemoselectivity for a variety of diverse quinoline compounds to access their corresponding THQs under mild reaction conditions (25 °C, 1 bar H₂) [41]. More excitingly, the IrO₂ NPs are unprecedentedly stable and can be used for 30 runs without any deactivation. Furthermore, the activation of H₂ and the hydrogenation process observed on IrO₂ NPs is unclear and should be explored in detail.

Gold has rich coordination properties, but was believed to be catalytically inactive for a long time. From 1973, Au catalysis has become a highly dynamic hot topic in homogeneous and heterogeneous catalysis due to Au-based catalysts displaying significantly higher activity and selectivity to other metal catalysts, including platinum-group metals, under mild reaction conditions in specific reactions [109–111]. Generally speaking, hydrogenation reactions catalyzed by Au typically occur under demanding conditions due to the limited capability of Au toward H₂ activation and dissociation. Typically, the Cao group employed Au NPs (with a mean particle size of 2 nm) dispersed on high surface area (HSA) has (Au/HSA-TiO₂) as an efficient catalyst for the selective hydrogenation of a wide range of substituted quinolines, even at temperatures under 25 °C [43]. Table 1 shows that Au/HSA-TiO₂ delivers noticeably better catalytic activity and selectivity than Pd-, Pt-, and Ru-based catalysts. Most remarkably, this work demonstrated that quinolines play a distinctive role in the hydrogenation process cat-

Table 1

The conversion and selectivity obtained for the hydrogenation of 6-chloroquinoline under various reaction conditions, adapted from Ref. [43].

Entry	Catalyst	T (°C)	t (h)	Conv. ^a (%)	Sel. ^g (%)		
					2	3	4
1 ^b	Au/TiO ₂ -WGC	80	4	43	100	0	0
2 ^c	Au/TiO ₂ -M	80	4	100	100	0	0
3 ^d	Pd/C	80	4	74	61	28	11
4 ^d	Pt/C	80	4	81	53	31	16
5 ^d	Ru/Al ₂ O ₃	80	4	37	46	30	24
6	Au/HSA-TiO ₂	80	1.5	100	100	0	0
7	Au/HSA-TiO ₂	60	3	100	100	0	0
8 ^e	Au/HSA-TiO ₂	25	16	92	100	0	0
9	Pd/HSA-TiO ₂	60	3	92	86	12	2
10	Pt/HSA-TiO ₂	60	3	97	92	7	1
11	Ru/HSA-TiO ₂	60	3	93	88	11	1
12 ^f	Au/HSA-TiO ₂	60	3	98	100	0	0

^a 6-chloroquinoline (0.5 mmol), toluene (3 mL), catalyst (metal: 1 mol%), 2 MPa H₂. ^b Au/TiO₂-WGC sample was provided by the World Gold Council. ^c Au/TiO₂-M was supplied by Mintek. ^d Pd/C, Pt/C, and Ru/Al₂O₃ were provided by Alfa Aesar. ^e 6-chloroquinoline (0.5 mmol), toluene (3 mL), catalyst (metal: 5 mol%), 2 MPa H₂. ^f Fifth run. ^g Conversion (Conv.) and selectivity (Sel.) were based on 6-chloroquinoline consumption (GC analysis).

alyzed by Au/HSA-TiO₂, in which quinoline promoted the activation and dissociation of H₂. In stark contrast, quinoline and its hydrogenation products are usually thought to poison Pd-, Pt-, and Ru-based catalysts via the strong coordination observed between them (Fig. 6). Another advantage was that Au/HSA-TiO₂ displays impressive chemoselectivity in the hydrogenation of the most-challenging substrates bearing easily reducible groups, such as halogens, ketones, and olefins. This catalyst can be thought of as complementary to other catalytic systems with limited substrate scope.

2.1.1.5. Noble metal-based bimetallic heterogeneous catalysts

In order to further improve the catalytic activity and selec-

Fig. 6. (a) Rate of HD formation over various noble metal-based catalysts. (b) DRIFT spectra recorded on H₂-D₂ exchange of D₂ with the surface OH groups on the catalysts. Reproduced with permission from Ref. [43]. Copyright 2012, American Chemical Society.

tivity in the hydrogenation of quinoline compounds, the introduction of a second metal element using the Pt group elements has been regarded as an impressive strategy [112,113]. The obtained bimetallic hybrids are able to alter the catalytic reactivity and selectivity via electronic and geometric effects [114,115]. The Li's group have reported the facile synthesis of RuCu nanocages and core-shell Cu@Ru nanocrystals using a modified galvanic replacement reaction [116]. Interestingly, the addition of Cu atoms, unique nanocages and core-shell structures not only reduces the noble metal consumption, but also contributes to the significantly improved performance of the catalyst, especially its selectivity. Almost quantitative yields of the corresponding THQs were obtained at 80 °C and 20 bar H₂. The authors concluded that the synergistic effect and high atom-efficiency of Ru promoted the catalytic performance. This work successfully established a relationship between the mi-

crostructure of the catalyst and its corresponding catalytic properties. Another work reported by the Qu's group designed a Au-Pd bimetallic catalyst elaborately guided by DFT calculations [51]. The authors combined the advantages of the high efficiency of Pd in H₂ dissociation and the tilted orientation of halogenated quinolines on Au to afford high chemoselectivity towards halogenated py-THQ. This research highlights the synergistic effect of Pd and Au, meeting the requirements of heterogeneous catalysis in terms of activity, selectivity, and stability.

2.1.2. Selective hydrogenation of *N*-heterocycles using earth-abundant metal-based catalysts

Although a series of noble metal-based (Pd, Pt, Ru, etc.) catalysts can catalyze substituted quinoline derivatives efficiently and selectivity, the risk in supply and volatile price severely

Table 2

Representative data for recent selective hydrogenation reactions of quinoline using noble metal-based heterogeneous catalysts.

No.	Catalyst	Solvent	H-source	<i>T</i> (°C)	<i>P</i> _{H₂} (bar)	Conv. (%)	Yield (%)	TOF (h ⁻¹)	Ref.
1	Pd/Al ₂ O ₃	Isopropanol	H ₂	100	20	100	98	—	[19]
2	Pd/MgO	THF	H ₂	150	40	100	95	300	[20]
3	Pd/HS-NH ₂	Cyclohexane	H ₂	80	30	98	98	1084	[22]
4	Pd ⁰ HAP(30)	Toluene	H ₂	50	1	98	96	25	[25]
5	Pd@ompg-C ₃ N ₄	Ethanol	H ₂	40	1	100	100	7	[21]
6	Pd-BT-CF	H ₂ O	H ₂	60	20	99	99	165	[58]
7	BWT ₁₅ mg-Pd	<i>n</i> -Butanol	H ₂	90	20	98	98	192	[59]
8	Pd NP	H ₂ O	H ₂	25	1	99	98	—	[24]
9	Pd-pol	CH ₃ OH/H ₂ O	H ₂	80	10	99	98	22.2	[23]
10	Pd@CIL-900	CH ₃ OH	H ₂	80	1	98	98	—	[37]
11	PdNPore	CH ₃ CN	H ₂	25	5	100	93	0.5	[83]
12	Pd-Cu-Ni-P	H ₂ O	H ₂	80	5	100	100	—	[82]
13	SiO ₂ @RF/Pt	Toluene	H ₂	25	1	>99	>99	15.2	[26]
14 ^a	Pt/NR-CeO ₂	Toluene	H ₂	25	20	>99	>99	667	[38]
15	Pt/TiO ₂ -ED	Toluene	H ₂	30	10	>99	>99	5.8	[27]
16	Pt _{nano}	H ₂ O	H ₂	130	30	>99	>99	—	[86]
17	Ru/P4VPy	Toluene	H ₂	120	30	100	93	75	[92]
18	Ru/MgO	THF	H ₂	150	50	100	92	3400	[29]
19	Ru/SiO ₂	<i>n</i> -Octane	H ₂	100	30	—	—	185	[28]
20	Ru/HT-C ₁₂ A ₇	—	H ₂	80	10	99.2	97.8	—	[40]
21	RuSiO ₂ @mSiO ₂	H ₂ O	H ₂	90	20	100	100	29.9	[39]
22	Ru/OMNC-700	EtOH	H ₂	40	10	100	>99.5	48.6	[32]
23	Ru/CTAB-MMT	Methanol	H ₂	100	30	93.9	92.5	156.5	[94]
24	Ru/PIL	H ₂ O	H ₂	50	50	93	92	—	[95]
25	Ru/IL	IL	H ₂	80	10	100	99	—	[31]
26	Ru SAs/N-C	THF	H ₂	100	35	>99	>99	—	[96]
27 ^b	Ru/HAP	Ethanol	H ₂	90	30	92.2	88.7	266	[103]
28 ^b	Ru@hectorite	Cyclohexane	H ₂	100	30	99.6	>99	330	[104]
29 ^b	Ru/CSP	H ₂ O	H ₂	120	20	98.2	93.5	35	[105]
30	Rh/MgO	—	H ₂	100	10	100	100	2100	[106]
31	Rh/Fe ₃ O ₄	H ₂ O	THDB	80	—	>99	100	1632	[34]
32 ^b	Rh/AlO(OH)	<i>n</i> -Hexane	H ₂	125	8	100	99.6	—	[101]
33	Rh/[BMIM] [tppm]	[BMIM]PF ₆	H ₂	50	30	96	96	6.3	[107]
34	Rh/LAIL	[BMIM]BF ₄	H ₂	80	30	95	95	—	[42]
35	Rh/PEG	Toluene/ <i>n</i> -heptane	H ₂	100	30	97	97	320	[108]
36	Rh/rGO	[BMIM]BF ₄	H ₂	80	10	>99	>99	—	[36]
37	Ir/Si	H ₂ O/H ₂ SO ₄	HCOOH	80	—	>99	>99	65.3	[35]
38	IrO ₂	MeOH	H ₂	25	1	98	98	—	[41]
39 ^a	Au/HSA-TiO ₂	Toluene	H ₂	60	20	100	100	104	[43]
40	Au/TiO ₂ -R	Et ₃ N/DMF	HCOOH	130	—	99	95	—	[2]
41	Au/NH ₂ -SBA-15	Et ₃ N/DMF	HCOOH	130	—	100	79	—	[3]
42	AuNPore	Toluene	PhMe ₂ SiH	80	—	100	91	—	[117]
43	RuCu/C	THF	H ₂	80	20	99.6	99.6	—	[116]
44 ^a	AuPd/CeO ₂	Toluene	H ₂	100	20	100	91.6	—	[51]

^aThe substrate was 6-chloroquinoline. ^bThe main product was DHQ.

Table 3

Representative data for recent selective hydrogenation reactions of quinoline using earth-abundant metal-based heterogeneous catalysts.

No.	Catalyst	Solvent	H-source	<i>T</i> (°C)	<i>P</i> _{H₂} (bar)	Conv. (%)	Yield (%)	Ref.
1	Co ₃ O ₄ -Co/NGr@Al ₂ O ₃	Toluene	H ₂	120	20	100	98	[45]
2	CoO _x /CN	Methanol	H ₂	120	30	100	100	[72]
3	Co-Mo-S-0.83	Toluene	H ₂	150	12	>99	>99	[127]
4 ^a	Co/Melamine-6@TiO ₂ -800-5	Methanol	H ₂	160	60	>99	>99	[128]
5	Co/Melamine-2@C-700	Toluene	HCOOH	130	—	100	98	[130]
6	Co@OMNC-700	H ₂ O	HCOOH	140	—	99	>99	[131]
7	Fe(1)/L4(4.5)@C-800 (12)	H ₂ O	H ₂	140	50	96	85	[132]
8	Raney Ni	Ethanol	H ₂	60	30	—	88	[124]
9	QS Ni	THF	H ₂	100	15	>99	>99	[125]

^aThe substrate is pyridine.

hamper their industrial applications. For example, the earth reserves of Pt are only 4.1×10^3 ppm, and the world annual output is only about 1 kg, leading to a high price reaching up to 260 yuan/g or more [118]. In addition, noble metal residues often exist in the synthesis of key pharmaceutical intermediates and are generally not easily excreted from the body, which can have a serious impact on the physiological functions of the human body and is another urgent issue to be addressed [119]. Recently, inexpensive metal (e.g., Fe, Co, Ni)-based catalysts represent a promising alternative for the development of novel catalytic systems due to their distinctive electronic structures [120], low cost, and comparatively low toxicity [121,122]. Moreover, although the catalytic activities of non-noble metal catalysts are not as good as noble metal catalysts, their selectivity is excellent and easier to control, which is of growing importance for sustainability in modern society as high selectivity means less waste and simpler and cheaper separation units [123]. Actually, the use of inexpensive metal-based catalysts for the selective hydrogenation of quinolines has not progressed substantially over a long period of time with few works being reported, mainly on traditional Raney-Ni [124,125]. In recent years, non-noble metal catalysts, especially cobalt-based catalysts [45,72,126–131] and iron-based catalysts [132] have

made great progress in the selective hydrogenation of substituted quinoline compounds (Table 3). By changing the precursors and preparation methods of the catalysts, the problems of non-noble metal-based catalysts existing in the liquid phase reaction, such as facile metal leaching and aggregation, relatively low activity and so on, have been solved to some extent. For economical and ecological issues, the development of efficient and non-noble metal catalysts used to replace precious metal catalysts is of great importance and is the key to achieving sustainable chemistry.

2.1.2.1. Co-based heterogeneous catalysts

When it comes to the chemoselective hydrogenation reactions based on earth-abundant metal-based catalysts, great contributions have been made by the Beller group, who designed a series of Co- and Fe-based catalysts in 2013 [133–135]. In terms of the selective hydrogenation of quinoline compounds, the representative work was derived from cobalt catalysts constructed using a coordination-thermal decomposition strategy (Fig. 7) [45]. The authors first coordinated the cobalt salt with an N-containing organic molecule (in a molar ratio of 1:2), which was then organically combined with commercial Al₂O₃ as a support. Finally, the composite material con-

Fig. 7. Overall synthetic strategy (a), EDX elemental mapping (b–e), kinetic curves (f) of the hydrogenation of quinoline; (g) recycling experiments of $\text{Co}_3\text{O}_4\text{-Co/NGr@Al}_2\text{O}_3$. Reproduced with permission from Ref. [45]. Copyright 2015, American Chemical Society.

sisting of cobalt-based NPs, N-doped carbon, and Al_2O_3 ($\text{Co}_3\text{O}_4\text{-Co/NGr@Al}_2\text{O}_3$) was obtained via pyrolysis under an inert gas atmosphere (Fig. 7(a)). The cobalt NPs in the most active catalyst have a core-shell structure with a metallic cobalt core and Co_3O_4 surface (Fig. 7(b)–(e)). The catalyst smoothly catalyzed the hydrogenation of quinoline in 15 h with no by-products detected during the whole hydrogenation process (Fig. 7(f)). The recycling experiment demonstrated that the catalyst showed slight deactivation, achieving 76% yield of py-THQ after the sixth run (Fig. 7(g)). Although no leaching occurred into the reaction liquid, the reason for the slight deactivation was unclear. What should be mentioned is that the authors skillfully transplanted the concept of modulating active metal ligands in homogeneous catalysis to heterogeneous catalysis. These studies have shown that the type of organic ligands have a significant effect on the performance of the final catalyst, among which, 1,10-phenanthroline exhibits the best activity. In a subsequent work, the same group employed Co-based NPs supported on N-modified titanium ($\text{Co/Melamine-6@TiO}_2\text{-800-5}$) for the selective hydrogenation of more challenging pyridines in water. The catalyst delivered a broad scope, including pyridines bearing phenyl, benzyl, amide and carboxylic acid groups. The researchers concluded that the generation of an N-modified TiO_2 structure in the final catalyst plays a vital role in the improved hydrogenation activity [128].

Even though great progress in quinoline hydrogenation has been achieved by the initial $\text{Co}_3\text{O}_4\text{-Co/NGr@Al}_2\text{O}_3$ catalyst, the use of expensive organic ligands during the preparation of the catalyst, long term costing of the reaction, and the slight deactivation observed during the recycling experiments have limited its industrial application. The development of more easily accessible and stable Co-based catalytic systems that can be handled under milder reaction conditions are highly desirable. To this end, the Wang group has fabricated porous N-doped graphene layers-coated cobalt NPs ($\text{CoO}_x\text{@CN}$) using a simple and efficient pyrolysis of D-glucosamine hydrochloride, melamine, and $\text{Co(OAc)}_2\cdot 4\text{H}_2\text{O}$ (Fig. 8) [72]. The starting materials have a wide selection of sources and were inexpensive, building

an economical and environmentally friendly catalytic system. The HRTEM images show that metallic cobalt and Co_3O_4 NPs were surrounded by a few graphene layers with obvious defects, such as small channels (Fig. 8(a)). Notably, an almost 100% yield of target product was achieved in 3 h at 120 °C and 30 bar H_2 with a relatively high TOF of 4.1 h^{-1} among the non-noble metal catalysts (Fig. 8(b)). The authors found that $\text{CoO}_x\text{@CN}$ was relatively stable during the reuse tests and could be recycled 12 times, but the trend in the catalytic performance was “down-up-down” with a final yield of 57% (Fig. 8(c)). The slight leaching of cobalt was the main reason for the decreased activity during the reuse process. When combined with the XRD results, the Co_3O_4 NPs in $\text{CoO}_x\text{@CN}$ were readily converted to CoO and then to metallic Co, which can enormously promote the dissociation of H_2 and improve the catalytic activity, corresponding to the recovered activity during the reuse process (Fig. 8(e)). Interestingly, a remarkable deactivation occurred during the reuse process with CoO_x NPs deposited on the outer surface of CN ($\text{CoO}_x\text{-CN}$) (Fig. 8(d)). The obviously better reusability of $\text{CoO}_x\text{@CN}$ was attributed to its specific encapsulated structure, which not only inhibits the aggregation and leaching of cobalt NPs, but also greatly weakened the strong coordination between N atoms in heterocycles and the active metal NPs.

Although the catalytic performance of $\text{CoO}_x\text{@CN}$ was improved in the hydrogenation of quinoline and the catalyst cost was reduced, catalysts with a high tolerance to more challenging groups, such as alkenes, ketones, cyanides and so on, were not investigated and should be addressed. In a related work, Corma and co-workers [127] constructed nanolayered cobalt-molybdenum sulfide hybrids via a hydrothermal process using earth-abundant metal precursors (Fig. 9). The compositions of cobalt-molybdenum sulfide were tunable by simply changing the molar ratio of the metal precursors. The optimal Co-Mo-S-0.83 catalyst presented more interlaced MoS_2 and cobalt sulfide (CoS_2 and Co_3S_4) species, forming more Co-Mo-S active sites (Fig. 9(a)). The kinetic curves showed that quinoline was efficiently hydrogenated to py-THQ in 6 h using Co-Mo-S-0.83 at 150 °C and 12 bar H_2 (Fig. 9(b)). Unfortunately,

Fig. 8. (a) HRTEM images of $\text{CoO}_x\text{@CN}$. (b) The conversion with reaction time using $\text{CoO}_x\text{@CN}$. (c–d) Recycling experiments of $\text{CoO}_x\text{@CN}$ and $\text{CoO}_x\text{-CN}$, respectively. (e) XRD patterns of $\text{CoO}_x\text{@CN}$ after one use and 12 uses. Reproduced with permission from Ref. [72]. Copyright 2016, American Chemical Society.

Fig. 9. (a) HRTEM images and (b) catalytic performance of Co-Mo-S-0.58, Co-Mo-S-0.66, Co-Mo-S-0.83, and Co-Mo-S-0.91. (c) Recycling experiments of Co-Mo-S-0.83 before and after reactivation. (d) XRD patterns of the different catalysts. (e) Square wave voltammograms of Co-Mo-S-0.83, Co-Mo-S-0.83-R1, Co-Mo-S-0.83-R3, Co-Mo-S-0.83-R6, and Co-Mo-S-0.83-React catalysts from top to down in the image. Reproduced with permission from Ref. [127]. Copyright 2018, American Chemical Society.

ly, the reusability of the Co-Mo-S-0.83 catalyst was not satisfactory despite the catalytic activity being recovered to some extent via a hydrothermal treatment of the recovered catalyst (Fig. 9(c)). The experiment results indicate that the active component of Co-Mo-S-0.83 changed during the reaction. The unstable Co-Mo-S active structures vanished during the first reaction and the activity of the different cobalt sulfides ranked in the order of $\text{Co}_3\text{S}_4 > \text{CoS}_2 > \text{Co}_9\text{S}_8$ (Fig. 9(d)–(e)). Additionally, the Co-Mo-S-0.83 catalyst was versatile and allowed for the efficient hydrogenation of more than 20 functionalized *N*-heteroarenes. The challenging substituents such as alkenes, ketones, nitriles, aldehydes, and amides were all tolerated during the hydrogenation reaction.

2.1.2.2. Fe and Ni-based heterogeneous catalysts

When compared with Co, Fe is richer in reserves with an annual output of about 3.3×10^9 tons and whose price is more advantageous [50]. Moreover, Fe has good biocompatibility and is an essential trace element for the human body. In nature, iron-iron hydrogenase can realize H_2 activation and transfer. Therefore, it is possible to apply Fe-based catalysts in the hydrogenation of quinolines. Unfortunately, Fe-based heterogeneous catalysts have shown very limited development in this area. The development of high efficiency and well-structured iron-based catalysts for the selective hydrogenation of *N*-heteroarenes are highly desirable, and will have great potential application in pharmaceutical manufacturing. Up until recently, a great breakthrough was made by the Beller group with the pyrolysis of $\text{Fe}(\text{OAc})_2$ and *N*-aryliminopyridines used to obtain a mixed phase of Fe species (Fe_3C , metallic Fe, and FeN_x) and *N*-doped carbon [132]. A variety of quinolines with

diverse functional groups can be successfully converted to their corresponding py-THQ derivatives in moderate to good yield at 140 °C and 5 MPa H_2 . The authors elaborated a series of nitro-containing organic molecules and found that the structure was heavily related to the catalytic behavior of the final catalysts. This was the first report on a Fe-based heterogeneous catalyst employed in the selective hydrogenation of quinolines and (iso)quinolines, however, harsh reaction conditions and long reaction times were needed. Besides, the composition of the active sites were complicated and the real active sites are still ambiguous. The development of more efficient Fe-based catalysts is still a challenging task. Moreover, the real catalytic active sites and reaction mechanism should also be further investigated.

Ni-based heterogeneous catalysts generally show higher catalytic activity when comparing with Fe and Co-based catalysts [136]. Due to the strong adsorption ability of H_2 , high catalytic activity and thermal stability of the Raney-Ni catalyst, it was widely used in catalytic hydrogenation for many industrial processes. Although Ni is toxic to humans, it cannot accumulate and is easily excreted from the human body. In an early work by Wangelin and co-workers [124], Raney-Ni was employed as an efficient and reusable catalyst for the selective hydrogenation of 8-hydroxyquinoline, affording an 88% yield of the corresponding py-THQ derivative. The catalysts were easily recovered using an external magnetic stirrer bar and provide a useful tool for lab-scale hydrogenation reactions. When compared with Raney-Ni, the skeletal Ni prepared via a quenching technique (QS Ni) exhibited higher catalytic performance in the selective hydrogenation of quinolines due to the abundant low-coordination sites and defects [125]. However, the catalyst-

ic stability and feasibility of reuse were not mentioned. Although some Ni-based catalysts can be recycled several times under relatively mild reaction conditions, the recycling protocol is limited. Upon elevating the reaction temperature and/or extending the reaction time, apparent leaching and deactivation of the catalyst were observed.

2.2. Selective transfer hydrogenation of *N*-heterocycles using a hydrogen donor

Catalytic transfer hydrogenation (CTH) using hydrazine hydrate, NaBH_4 , formic acid and alcohol as hydrogen donors provides an attractive alternative to catalytic hydrogenation using H_2 . Most CTH processes can be carried out under mild conditions instead of using high-pressure devices and flammable hydrogen gas [137]. Generally speaking, the selectivity is easier to control in the hydrogenation of substrates bearing multi-reducible groups under CTH conditions when compared to using H_2 . However, the hydrogen donors used in CTH are often highly corrosive and higher requirements for the reaction equipment are needed. Ir-, Au-, and Co-based heterogeneous catalysts have been successfully applied in the transfer hydrogenation of quinolines. Immobilization of an active homogeneous catalyst onto a solid support can combine the advantages of homogeneous and heterogeneous catalysis, which not only expose the active sites for catalytic transformations, but also allows the catalyst to be employed in successive reactions [33]. Recently, Ir complexes immobilized on SBA-15 (Ir/Si) have been fabricated, which show a good performance in the transfer hydrogenation of quinolines [35]. Notably, the catalyst is also reusable due to its immobilization. Subsequent studies by the Cao group investigated the catalytic transfer hydrogenation reaction and showed that Au NPs supported on single phase rutile titania ($\text{Au}/\text{TiO}_2\text{-R}$) acts as an efficient and versatile catalyst for the regioselective transfer hydrogenation of quinoline derivatives to their corresponding py-THQ using HCOOH as a safe and convenient hydrogen source [2]. Sub-nanometric Au clusters supported on amino-functionalized SBA-15 [3] and unsupported nanoporous Au catalysts [117] both catalyze the hydrogenation of quinolines selectively using HCOOH as the hydrogen source in an organosilane/water system, respectively. An earth-abundant catalyst created from $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ and melamine or waste melamine resins displays high performance and broad substrate scope in the transfer hydrogenation of *N*-heteroarenes using HCOOH in the absence of any base, which avoided the need of high H_2 pressure and allowed a facile operational set-up [129,130]. The high catalytic activity arose from the efficient dehydrogenation of formic acid to form H_2 selectively. Recently, another example reported by Huang *et al.* [131] employed ordered mesoporous N-doped carbon (OMNC) encapsulating Co NPs (Co@OMNC-700) in the catalytic transfer hydrogenation of quinoline using HCOOH as the hydrogen source, presenting an acid-tolerant, efficient, and reusable catalytic system. Similar to CoO_x/CN , the encapsulated structure was essential to improve the stability of Co@OMNC-700 , which enormously protected the Co NPs from etching under the acidic reaction conditions. There were three conclusions regarding

the high catalytic performance of Co@OMNC-700 : (1) The ordered mesoporous structure greatly inhibits the limitation of mass transfer, thus promoting the free diffusion of molecules to access the active sites and improving the catalytic activity, (2) the strong interactions between quinoline and the catalyst result in a high quinoline concentration on the catalyst surface, and (3) the high density of basic sites on the surface of the catalyst are beneficial for the adsorption of HCOOH and its further dehydrogenation to H_2 during the catalytic transfer hydrogenation process.

3. Reversible dehydrogenation and hydrogenation of *N*-heterocycles using a single catalyst

The catalytic dehydrogenation of *N*-heterocycles also constitutes a key step in organic synthesis, as the achieved unsaturated heterocycles are important synthetic intermediates for various biologically active compounds and pharmaceuticals [134]. To date, heterogeneous noble metal-based catalysts (Au [138], Rh [139], Pt [140–142], and Pd [143,144] NPs), earth-abundant metal-based catalysts (Cu [44,145], Co [146–148], Fe [134], MgO [149], and NiMn [150] NPs or isolated single-atoms) and metal-free catalytic systems [151–153] have been applied in the catalytic dehydrogenation process. Generally speaking, oxidative dehydrogenation reactions and acceptorless dehydrogenation reactions constitute the dehydrogenation process of *N*-heterocycles and both have their own advantages and disadvantages. In terms of the oxidative dehydrogenation reaction, the introduction of external oxidants as hydrogen scavengers, such as O_2 or stoichiometric oxidants, can significantly decrease the thermodynamic energy barriers of dehydrogenation [154], which enable the reaction to occur under mild conditions. Nevertheless, the use of oxidants often causes a lot of waste and potentially limited selectivity and substrate scope [141]. The acceptorless dehydrogenation of *N*-heterocycles presents a straightforward and atom-efficient process to generate unsaturated *N*-heterocycles and H_2 in the absence of oxidants. Unfortunately, the acceptorless dehydrogenation process is thermodynamically unfavorable and requires high reaction temperatures.

H_2 has been proposed as a clean energy source, which acts as an alternative to fossil fuels for automobile and fuel cells. The reverse hydrogenation/dehydrogenation of organic molecules is regarded as a promising strategy in the field of liquid organic hydrogen storage systems. The above-mentioned works demonstrate that the selective hydrogenation and dehydrogenation of *N*-heterocycles are both possible with the aid of catalysis. The combination of dehydrogenation of *N*-heterocycles (release of H_2) and the reverse hydrogenation (storage of H_2) constitutes a perfect liquid organic hydrogen system. Actually, the two types of reactions involved use two different catalysts, which are not convenient in practical use. A single catalyst that can catalyze both processes have been rarely reported and will be summarized in the following section (Table 4). It is believed that the development of versatile catalysts with catalytic ability in the reversible dehydrogenation/hydrogenation of *N*-heterocycles will become more and

Table 4

Representative data for recent selective hydrogenation reactions of quinoline and the reverse dehydrogenation process using heterogeneous catalysts.

No.	Catalyst	Reaction	Solvent	H/O source	<i>T</i> (°C)	<i>P</i> (bar)	Conv. (%)	Yield (%)	Ref.
1	Pt NW	1-2	H ₂ O	H ₂	80	1	97.9	94.1	[140]
		2-1	Methanol	O ₂	40	1	>99	>99	
2	PtC	1-2	Methanol	H ₂	160	3	100	84	[141]
		2-1	<i>o</i> -Xylene	N ₂	144	1	>99	96	
3	PdNPs/SBA-15	1-2	Tol- <i>d</i> ₈	H ₂	60	1	>99.9	>99.9	[46]
		2-1	Tol- <i>d</i> ₈	N ₂	130	1	>99.9	92	
4	PdNi@MIL-100(Fe)	1-2	H ₂ O	H ₂	60	4	100	100	[143]
		2-1	H ₂ O	Ar	130	1	100	100	
5	Cu/TiO ₂	1-2	Mesitylene	H ₂	150	1	95	100	[44]
		2-1	Mesitylene	Ar	150	1	>99	>99	
6	Co@NGS-800	1-2	Isopropanol	H ₂	140	40	84	82	[146]
		2-1	Methanol	O ₂	80	1	90	88	
7	ISAS-Co/OPNC	1-2	Toluene	HCOOH	120	—	99	99	[147]
		2-1	Mesitylene	Air or Ar/BHT	120	1	99	99	
8	Ni-phen@SiO ₂ -1000	1-2	H ₂ O/MeOH	H ₂	120	50	—	90	[155]
		2-1	Triglyme	Ar	200	1	—	93	

more prevailing nowadays.

Noble metal-based heterogeneous catalysts, such as Pt, Pd and Rh, can achieve the reversible dehydrogenation/hydrogenation of *N*-heterocycles. Pt nanowire (NW) reported by the Gu group showed equally high catalytic activity, selectivity, and stability in the hydrogenation (80 °C, 1 bar H₂) and oxidative dehydrogenation (40 °C, 1 bar O₂) reactions of *N*-heterocycles under mild reaction conditions [140]. This was the first example of a single catalyst successfully enabling the reversible oxidative dehydrogenation/hydrogenation of *N*-heterocycles. A subsequent work based on a Pt catalyst involved Pt NPs supported on carbon (PtC). PtC showed the highest activity in the acceptorless dehydrogenation of *N*-heterocycles among 20 types of catalysts [141]. Upon detailed analysis of the catalytic activity of different noble metal NPs supported on carbon, the authors found that there was a typical volcano-type dependence between the catalytic activity and the d-band center. Pt, Ir, Pd, Rh, and Ru with an intermediate d-band center exhibit higher catalytic activity than metals with a deep ε_d level (Ag, Cu) or the metals with d-band centers close to the Fermi energy level (Ni, Co). Meanwhile, the catalyst was also active in the opposite selective hydrogenation of quinoline at 160 °C and 3 bar H₂.

Although PtC serves as a versatile catalyst for reversible transformation in the absence of hydrogen scavengers, the high reaction temperature impedes its extensive use in liquid organic hydrogen storage systems. As a response, recent work by Somorjai and co-workers employed Pd, Pt, Rh NPs with G4OH PAMAM dendrimers supported in SBA-15 (MNP/SBA-15) in the acceptorless dehydrogenation and reverse hydrogenation of heterocycles (Fig. 10) [46]. The preparation of the catalyst comprised the following three steps: (1) Coordination of the metallic ions with the tertiary amines in the G4OH PAMAM dendrimers, (2) reduction of the metallic ions into their corre-

sponding NPs using NaBH₄, and (3) heterogenization of the NPs/G4OH PAMAM upon stirring with a mesoporous SBA-15 support under ultrasonication (Fig. 10(a)). The NPs were uniformly distributed in SBA-15 with a mean particle size of 1.5 nm due to the strong coordination effect of the tertiary amines and the confined effect of the ordered mesopores (Fig. 10(b)–(e)). PdNPs/SBA-15, PtNPs/SBA-15, and RhNPs/SBA-15 were all active in the acceptorless dehydrogenation of 2-methyl-py-THQ, affording an almost 100% yield of the target product at 130 °C. In addition, PdNPs/SBA-15 and PtNPs/SBA-15 were also employed as efficient catalysts in the hydrogenation reaction at 60 °C and 1 bar H₂, showing higher catalytic activity than RhNPs/SBA-15 (Fig. 10(f)). This catalytic system is very active and recyclable, which shows potential in hydrogen storage using reversible dehydrogenation/hydrogenation processes.

Another efficient reversible catalytic system fabricated by Cai and co-workers used PdNi bimetallic NPs encapsulated in MIL-100(Fe) (PdNi@MIL-100(Fe)) in the reversible dehydrogenation/hydrogenation of *N*-heterocycles in water [143]. The synergistic effect between Pd and Ni, the Lewis acidity, and special structure (micro-mesopore size distribution) of the support boosted the catalytic performance.

Recently, great progress has been made on earth-abundant metal-based catalysts used for the reversible dehydrogenation/hydrogenation of *N*-heterocycles, especially Co- and Ni-based catalysts [147,155]. Cu/TiO₂ reported by Kaneda *et al.* [44] in 2011 was the first catalyst that enabled the acceptorless dehydrogenation of py-THQ and the hydrogenation of quinoline. This catalytic system was so active and robust that both reversible reactions could be carried out under an atmospheric pressure of N₂ or H₂.

Co-based heterogeneous catalysts are regarded as a potential substitute for Pt-group metal catalysts in the selective hy-

Fig. 10. (a) Synthetic route used to prepare NPs/G4OH PAMAM. (b–e) Representative TEM images and the corresponding metal particle size distribution histograms of PdNPs/SBA-15, RhNPs/SBA-15, and PtNPs/SBA-15. (f) Catalytic results obtained for PdNPs/SBA-15 in the reversible dehydrogenation and selective hydrogenation of *N*-heterocycles. Reproduced with permission from Ref. [46] (<https://pubs.acs.org/doi/abs/10.1021%2Fjacs.7b10768>). Copyright 2017, American Chemical Society. Further permissions related to the material excerpted should be directed to the ACS.

drogenation and oxidative dehydrogenation reactions. Yet, the real active sites are ambiguous and need to be explored in detail. In this respect, the Li's group [154] employed Co NPs encapsulated N-doped graphene shells (Co@NGS) as a bifunctional catalyst in the oxidative dehydrogenation and reverse hydrogenation of quinolines (Fig. 11). Using O₂ as a clean oxidant, Co@NGS shows excellent activity in the oxidative dehydrogenation of py-THQ at 80 °C (Fig. 11(a)). In addition, Co@NGS also promote the selective hydrogenation of quinoline to py-THQ at 140 °C and 40 bar H₂ (Fig. 11(b)). The experiments confirmed that N-doped graphene layers modified with Co NPs act as the active sites for O₂ activation in the oxidative dehydrogenation reaction. In addition, FTIR spectroscopy provided direct evidence for O₂ activation as two characteristic peaks assigned to peroxide species were recorded (Fig. 11(d)). Meanwhile, poisoning with KSCN did lead to an obvious activity delay of Co@NGS, but negligible deactivation of NGS (Fig. 11(g)), confirming that the coordination of Co sites with SCN ions inhibited the electron transfer between the Co NPs and N-doped graphene layers. That is, the N-doped graphene layers are the real active sites for the oxidative dehydrogenation process. In contrast, a significantly decrease in the conversion of the hydrogenation of quinoline was observed after the poisoning experiments (Fig. 11(h)), clearly unveiling that the active sites for the hydrogenation process were the underlying Co NPs. This work was reasonable and helpful to understand the dehydrogenation and hydrogenation processes.

To further improve the catalytic activity of Co-based catalysts, isolated cobalt single-atoms supported on ordered porous N-doped carbon (ISAS-Co/OPNC) were fabricated based on a template-assisted pyrolysis method (Fig. 12) [147]. TEM and HAADF-STEM images confirmed the ordered structure and the formation of isolated cobalt single-atoms (Fig. 12(f)–(g)). The

valence of the Co atoms was determined between Co⁰ and Co²⁺ using XANES spectra. As confirmed by EXAFS spectra, no Co-Co bonds were formed in ISAS-Co/OPNC and the coordination number of Co was about four with a mean bond length of 1.92 Å (Fig. 12(f)–(i)), further confirming the atomically dispersed Co in the catalyst. Gratifyingly, ISAS-Co/OPNC offered efficient performance in the dehydrogenation of py-THQ, affording a 99% yield of quinoline at 120 °C in air or under an argon atmosphere in the presence of butylated hydroxytoluene (BHT). Simultaneously, the catalyst also efficiently catalyzed the selective transfer hydrogenation reaction of quinoline to give py-THQ at 120 °C. The authors proposed that the Eley–Rideal mechanism was the dominant mechanism, which was verified using DFT calculations.

As mentioned in section 2.2.2, Raney-Ni catalysts are considered to be the state-of-the-art hydrogenation catalysts used in industry and show encouraging activity in the selective hydrogenation of quinoline. However, its pyrophoric properties require careful handling in practical use, usually under an inert atmosphere. To date, no works on the reverse dehydrogenation of *N*-heterocycles using Raney-Ni have been reported. Recently, nickel silicide (Ni₃₁Si₁₂ and Ni₂Si) NPs encapsulated in graphitic layers were created by Beller and co-workers via the pyrolysis of nickel(II)acetate, 1,10-phenanthroline, and SiO₂ [155]. The synthetic method was facile in operation, overcoming the traditional multi-step methods used for the synthesis of intermetallic Ni-Si catalysts. Ni-phen@SiO₂-1000 shows high activity in the selective hydrogenation and reverse dehydrogenation reactions of a wide range of *N*-heterocycles. Notably, the authors found that the introduction of silicon in the nickel metal lattice plays a vital role in the improved catalytic activity. This highly active and stable catalyst with low cost, safe and convenient handling may be an attractive alternative to Raney nickel and

Fig. 11. The catalytic performance observed in the oxidative hydrogenation (a) and selective hydrogenation reaction (b) for a series of catalysts. (c) XPS spectra of NGS and Co@NGS-800. (d) FT-IR spectra of Co@NGS-800 upon treatment with O₂ (red) and N₂ (black). (e–f) Line scanning of the poisoned Co@NGS-800 catalyst. (g–h) A comparison of the catalytic performance of Co@NGS-800 and NGS with and without KSCN in the oxidation dehydrogenation of py-THQ and hydrogenation of quinoline. Reproduced with permission from Ref. [154]. Copyright 2017, Elsevier.

other heterogeneous catalysts for industrial applications.

4. The reaction mechanism for the selective hydrogenation/dehydrogenation of *N*-heterocycles

For homogeneous catalysis in the hydrogenation reaction of quinolines, it has been generally accepted that quinoline is formed via an ionic and cascade reaction pathway (Noyori's mechanism), including 1,4-addition, isomerization, and 1,2-addition [8]. In particular, hydrogen addition undergoes a stepwise H⁺/H⁻ transfer pathway outside the coordination sphere [10]. In terms of the heterogeneous hydrogenation of quinolines toward py-THQs, there are few investigations on the reaction mechanism and the pathways are strongly related to the solvents and supports used. Deuterium labeling experiments are usually used to explore the mechanism of the hydrogenation process. First, the quinolines are adsorbed on the surface of the catalysts in a tilted orientation through hydrogen bonds between the pyridine ring and support [39,51]. At the same time, H₂ can be activated to form active hydrogen species via an heterolytic H₂ splitting or homolytic H₂ splitting process [38,83]. Subsequently, the activated hydrogen species transfer to the quinoline molecules mainly via a 1,2-addition pathway, while the 1,4-addition proceeds to a minor extent [3,26]. Finally, the generated py-THQ leaves the surface of the catalyst quickly, being replaced by the more strongly binding quinoline molecule and avoids further hydrogenation to DHQ.

For the dehydrogenation of quinolines, the oxidation dehydrogenation of py-THQ usually involves a free radical mecha-

nism. The reaction cannot proceed effectively in the presence of a radical scavenger [134]. The direct formation of a C=C linkage is difficult and the oxidation process begins with the formation of the corresponding imine (C=N) [152]. For acceptorless dehydrogenation of quinolines, the reaction mechanism is rarely reported and should be strengthened in the future. As the basic reactions of hydrogenation and dehydrogenation of *N*-heterocycles are similar, the dehydrogenation pathways can be understood according to the hydrogenation mechanism [147].

5. Conclusions and outlook

The selective hydrogenation of quinolines offers straightforward and efficient access to a wide range of py-THQs, which is important as they were widely present in many bioactive natural products, pharmaceuticals, or agrochemicals. However, several key issues, including low activity, unsatisfactory selectivity, poor stability, and harsh reaction conditions are posing challenges for practical use. In the past few decades, great progress had been made on the design and fabrication of heterogeneous catalysts for the selective hydrogenation of substituted quinoline compounds. In this review, we introduced a series of catalytic systems spanning from noble metal-based catalysts (Pd, Pt, Ru, Rh, Ir, Au, RuCu, AuPd, and PdNi) to earth-abundant catalysts (Fe, Co, Ni and Cu), discussing the overall fabrication strategies for the catalysts and correlating the catalytic performance with the microstructures and characters of the catalysts. Subsequent discussions were based on the reverse dehydro-

Fig. 12. (a) The overall synthetic strategy, (b–e) TEM images, HAADF-STEM images, and corresponding EDX elemental mapping of ISAS-Co/OPNC. (f) XANES spectra, (g) Fourier transform (FT) at the Co K-edge, (h–i) the corresponding EXAFS fitting curves in the *k* space and in the *R* space of ISAS-Co/OPNC. (j) The dehydrogenation of py-THQ using Co-based catalysts. (k) Transfer hydrogenation of quinoline using Co-based catalysts. Reproduced with permission from Ref. [147]. Copyright 2018, WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

generation of *N*-heterocycles toward quinolines, which represents a perfect liquid organic hydrogen system.

It was concluded that the property of the support and metal-support interaction, electronic structure of active metals, bimetallic or multi-metallic effects, core-shell structure, and particle size of the NPs played an important role in the final catalytic behavior. A highly active catalytic system with encouraging selectivity and reusability could be achieved by altering the reaction medium or rationally tuning the structure of the catalyst, including: (1) modification of the surface properties of supports (acid, base, etc.) to enhance the interaction of metal and support; (2) modulation of the electronic property by decreasing the mean particle size, even to that of a single atom or alloying with one or more additional metals; and (3) tuning the structure of the catalysts, to an encapsulated struc-

ture, core-shell, or yolk shell structure. The ultimate purpose was to induce the heterolytic splitting of H₂ and enhance the interaction of the substrates with catalytic active sites. Nevertheless, this interaction should not be too strong; else, it may cause contamination of the active sites, resulting in poor reusability.

Despite the promising results obtained in the selective hydrogenation of quinolines and the reverse dehydrogenation of *N*-heterocycles, it is important to note that there are still some challenges. Most state-of-the-art of noble metal-based catalysts achieved selective hydrogenation under mild reaction conditions. However, the drawbacks of supply, high price, and limited substrate scope (unsatisfactory selectivity in quinolines bearing with reducible groups) hinder their industrial applications. Earth-abundant metal catalysts proved a promising al-

ternative to noble-metal catalysts due to their encouraging catalytic activity and selectivity. However, a high reaction temperature, high H₂ pressure, and long reaction time were required. Moreover, the stability of the catalysts should also be improved. Most nanomaterials toward selective hydrogenation and reverse dehydrogenation were fabricated by a purely trial-and-error and/or a combinatorial strategy. A comprehensive understanding of the intrinsic, atomic-scale catalytic properties of the achieved hybrids is required. Therefore, researchers should concentrate on the mechanistic and fundamental insights of the catalysts via the following aspects:

(1) Development of *in situ* spectroscopic measurement techniques to probe into the catalytic active sites during the reaction will aid in identifying the real active sites and gaining more insight into the reaction mechanisms. Some catalytic systems are relatively complicated. The real active site is ambiguous and there is no direct evidence. Consider Fe-based catalysts as an example. Due to the large variety and the mixed phases of the synthesized Fe-based catalysts, the catalytic active sites in the selective hydrogenation of quinolines are not yet established, and this can serve as a key topic for future studies.

(2) To date, the reported works have mainly focused on improving the catalytic performance; the reaction mechanisms have rarely been explored in detail. A deeper understanding of the reaction pathway by combination experimental tests and theoretic computation will help us better understand the reaction mechanism, which in turn may provide practical guidance for designing highly active, selective, and reusable catalysts.

(3) To achieve industrial application, further improvement in the stability of the catalysts is imperative. Although some catalytic systems have enabled reuse in successive runs for the selective hydrogenation of quinolines, the synthesis processes were relatively complex. Exploration of easy-to-handle methods for the scalable production of multi-component hybrids with specific structures may prove useful for industrial applications. The possibility of synergistic effects among the different components in the catalysts may also enable satisfactory catalytic performance.

(4) From the economic and ecological point of view, it is

highly imperative suggested to design more efficient earth-abundant metal catalysts, owing to their distinctive electronic structures, low cost, and comparatively low toxicity. Notably, Fe-based nanomaterials have recently emerged as valuable potential catalysts for the selective hydrogenation and reverse dehydrogenation of *N*-heterocycles. It is believed that much progress will be made on this respect.

(5) One single catalyst that can allow the reversible selective hydrogenation/dehydrogenation of *N*-heterocycles is essential to the field of liquid organic hydrogen storage systems and commercial fuel cells. The rational design of more versatile catalytic systems will be very important in future.

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Graphical Abstract

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Recent advances in heterogeneous catalytic hydrogenation and dehydrogenation of *N*-heterocycles

Zhongzhe Wei, Fangjun Shao, Jianguo Wang*
Zhejiang University of Technology

An overview summarizes the recent progress on the heterogeneous catalytic hydrogenation and reverse dehydrogenation of *N*-heterocycles spanning from noble metal catalysts to earth-abundant catalysts, and discusses their overall fabrication strategies and microstructure-reactivity relationships.

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氮杂环化合物的多相催化加氢反应及其可逆脱氢反应的最新进展

魏中哲, 邵方君, 王建国*

浙江工业大学绿色化学合成技术国家重点实验室培育基地, 化学工程学院, 工业催化研究所实验室, 浙江杭州310032

摘要: 功能化1, 2, 3, 4-四氢喹啉类化合物在医药、生物碱、农药和许多精细化学品的生产中作为具有生物活性的构筑单元和关键中间体, 其合成越来越受到人们的关注. 通过喹啉化合物的选择性加氢得到py-THQs具有高的原子效率, 是一种直接和有效的方法. 喹啉化合物的选择性加氢常面临以下问题和挑战: (1)喹啉类化合物的加氢反应具有较高的反应能垒, 使得反应需要在苛刻的反应条件下进行; (2)加氢反应过程通常涉及多个中间体, 可能会产生副产物; (3)取代喹啉类化合物如乙烯基、酮基、腈基、醛基、氨基、卤素等易还原取代基也可能发生氢化反应, 导致选择性下降; (4)由于N-杂环中金属与N原子的强配位效应, 催化活性位点易中毒, 导致催化剂的可重用性较差. 新型、高性能非均相催化剂的开发得到了持续关注, 近期取得了一系列进展.

氮杂环化合物的催化脱氢也是有机合成的关键步骤, 所得到的不饱和氮杂环化合物是各种生物活性化合物和药物的重要合成中间体. 同时, 从氢气存储的角度出发, 有机分子的可逆加氢/脱氢被认为是液体有机储氢系统中一个很有前途的策略. 氮杂环化合物的脱氢(释放氢气)和加氢(储存氢气)相结合, 构建了一个有效的液态有机氢存储体系. 研制一种能够实现氮杂环化合物可逆脱氢/加氢的催化剂越来越受到人们的关注.

近几十年来, 功能化喹啉化合物选择性加氢高效多相催化剂的可控合成取得了重大突破, 使人们能够从整体上关联结构-性能关系. 本文综述了近年来该领域在催化剂合成策略、微观结构和化学特性、催化性能评价及其内在关系等方面取得的重要进展. 本文首先介绍了单贵金属催化剂(Pd, Pt, Ru, Rh, Ir, Au)和双/多金属催化剂(RuCu, AuPd, PdNi)的研究现状, 然后对储量丰富的廉价金属催化剂(Co, Fe, Ni, Cu)进行了综述. 综合文献结论, 反应介质、载体的性质、金属-载体相互作用、活性金属的电子结构、双金属或多金属协同效应、微观结构(核壳、包覆、蛋黄结构)以及纳米粒子的粒径大小对催化剂的最终催化行为起着重要作用. 最后, 引入氮杂环化合物的脱氢反应, 形成一个可逆的加氢/脱氢体系用于液相有机氢储存系统, 并对其反应机理及今后的研究方向进行了探讨. 本综述将加深我们对氮杂环化合物催化转化的认识, 为研究人员合理设计催化剂提供指导.

关键词: 氮杂环化合物; 选择性加氢; 脱氢反应; 多相催化剂; 构-效关系

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*通讯联系人. 电话/传真: (0571)88871037; 电子信箱: jgw@zjut.edu.cn

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