Heterogeneous catalytic hydrogenation is a powerful tool for achieving controlled reduction of many types of organic compounds under mild conditions. The importance of this reductive transformation has been originally highlighted by the catalytic hydrogenation of functionalized quinolines with $\text{H}_2$ under mild reaction conditions. Our results point toward an unexpected role for quinolines in gold-mediated hydrogenation reactions, namely that of promoter; this is in stark contrast to what prevails in the traditional noble metal Pt-, Pd-, and Ru-based catalyst systems, in which quinolines and their derivatives typically act as poisons. As a result of the remarkable promotional effect of quinoline molecules to $\text{H}_2$ activation over supported gold, the transformation can proceed smoothly under very mild conditions (even at temperatures as low as 25 °C). Of practical significance is that various synthetically useful functional groups including halogens, ketone, and olefin remain intact during the hydrogenation of quinolines. Moreover, the protocol also shows promise for the regiospecific hydrogenation of the heterocyclic ring of a variety of other biologically important heteroaromatic nitrogen compounds, such as isoquinoline, acridine, and 7,8-benzoquinoline, in a facile manner. Apart from its importance in catalytic hydrogenation, we believe that this intriguing self-promoted effect by reactant molecules may have fundamental implications for the broad field of gold catalysis and form the basis for development of new catalytic procedures for other key transformations.
magnitude lower than those of the traditional platinum group metal (PGM)-based catalysts.\textsuperscript{10,11} Hence, the development of new effective Au-based hydrogenation processes that can deliver high activity while preserving high selectivity under mild conditions constitutes a major challenge.

1,2,3,4-Tetrahydroquinolines are ubiquitous in numerous biologically active natural products and pharmacologically relevant therapeutic agents.\textsuperscript{12} While Au-catalyzed approaches to tetrahydroquinoline derivatives have been reported,\textsuperscript{13} a chemo- and regioselective hydrogenation approach would be superior. The direct hydrogenation of readily available quinolines offers a straightforward and promising approach to access tetrahydroquinolines in terms of its simplicity and high atom efficiency.\textsuperscript{14} Unfortunately, the use of this truly green tool has proven extremely difficult, due to the aromatic nature of the quinoline ring and the potential poisoning of the catalysts. Until now, relevant protocols are largely based on several Ir, Ru- and Rh-based homogeneous systems.\textsuperscript{15} Despite their utility, these procedures still suffer from the inherent problems associated with the reusability and/or the indispensable use of cocatalysts. Recently, a handful of heterogeneous catalytic systems based on traditional noble metals (Pd, Pt, Ru etc.) have been developed.\textsuperscript{16} These catalysts need to be used with caution because they are vulnerable to the poisoning effect of strongly adsorbed quinolines and/or their hydrogenated derivatives. Moreover, clear drawbacks of these systems are their low tolerance for functional groups and limited substrate scope. Given the vital importance of this type of transformation, the search for new simple, efficient, and general catalytic system that can facilitate selective quinoline hydrogenation under mild and ligand-free conditions remains a challenging but rewarding task.

We report herein an unusual chemo- and regioselective hydrogenation of quinolines to the corresponding 1,2,3,4-tetrahydroquinolines using supported Au NPs. As a result of the remarkable reactant-promoted effect of quinoline compounds to hydrogen activation over highly dispersed Au NPs, the transformation can proceed smoothly under mild conditions (even at temperatures as low as 25 °C). Furthermore, a wide range of substituted quinolines can be exclusively hydrogenated to the desired products, keeping various synthetically useful functional groups including halogens, ketone, and olefin intact. The excellent performance of the present catalytic system has allowed us to extend this methodology to the regioselective hydrogenation of the heterocyclic ring of various other biologically important heteroaromatic nitrogen compounds, such as isoquinoline, acridine, in a facile manner.

**RESULTS AND DISCUSSION**

In exploratory experiments, we selected the hydrogenation of 6-chloroquinoline (1) to corresponding 6-chloro-1,2,3,4-tetrahydroquinoline (2) as the model reaction to study the catalytic activity and selectivity of several commercially available noble metal-based catalysts (Table 1, entries 1–5). The hydrogenation of 1 without C−X bond cleavage (X = halogen, by hydrogenolysis) is of critical importance, as the aryl halide products obtained are useful reagents in metal-catalyzed cross-coupling reactions.\textsuperscript{17} Under 2 MPa H\textsubscript{2} at 80 °C, the benchmark Au/TiO\textsubscript{2}-WGC catalyst (with a Au particle mean diameter of 3.5 nm, supplied by World Gold Council, Figure S3), can afford exclusive formation of 2 with moderate activity (43% conversion) within 4 h (Table 1, entry 1). To our delight, Au/TiO\textsubscript{2}-M (supplied by Mintek) catalyst with smaller Au particle size (average size ca. 2.7 nm, Figure S3) facilitated the complete conversion of 1 under identical conditions (Table 1, entry 2). Applying Pd/C, Pt/C, or Ru/Al\textsubscript{2}O\textsubscript{3} (provided by Alfa Aesar), the desired halo-substituted 1,2,3,4-tetrahydroquinoline was also formed (Table 1, entries 3–5). Nevertheless, in these cases, an unavoidable concomitant formation of dehalogenation products readily occurs. Given the fact that the rate of nitro or carbonyl group reduction over Au (<5 nm) was significantly lower than those over traditional PGM-based catalysts, the comparable or even superior performance obtained in the present Au-catalyzed hydrogenation of substituted quinolines was remarkable.

After these initial promising results, we further examined a series of Au deposited on other mineral supports, such as Al\textsubscript{2}O\textsubscript{3}, ZnO, CeO\textsubscript{2} and activated carbon. These catalysts, however, were not found to be particularly active, although in all cases the desired chloro-substituted 1,2,3,4-tetrahydroquinoline can be exclusively produced (Table S1, entries 2–5). Considering that TiO\textsubscript{2} (P25) in both Au/TiO\textsubscript{2}-WGC and Au/TiO\textsubscript{2}-M has rather low surface areas (45 m\textsuperscript{2} g\textsuperscript{−1}), the desired halo-substituted 1,2,3,4-tetrahydroquinoline was also formed (Table 1, entries 3–5). Nevertheless, in these cases, an unavoidable concomitant formation of dehalogenation products readily occurs. Given the fact that the rate of nitro or carbonyl group reduction over Au (<5 nm) was significantly lower than those over traditional PGM-based catalysts, the comparable or even superior performance obtained in the present Au-catalyzed hydrogenation of substituted quinolines was remarkable.

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<table>
<thead>
<tr>
<th>entry</th>
<th>catalysts</th>
<th>T (°C)</th>
<th>t (h)</th>
<th>conv (%)</th>
<th>select (%)</th>
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<td>Pd/TiO\textsubscript{2}-HAP</td>
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<td>− − −</td>
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<td>17\textsuperscript{f}</td>
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<td>3</td>
<td>98</td>
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\textsuperscript{a}6-chloroquinoline (0.5 mmol), toluene (3 mL), catalyst (metal: 1 mol %), 2 MPa H\textsubscript{2}. n.r. = no reaction. \textsuperscript{b}Au/TiO\textsubscript{2}-WGC sample was provided by the World Gold Council. \textsuperscript{c}Au/TiO\textsubscript{2}-M was supplied by Mintek. \textsuperscript{d}Pd/C, Pt/C, and Ru/Al\textsubscript{2}O\textsubscript{3} were provided by Alfa Aesar. \textsuperscript{e}6-chloroquinoline (0.5 mmol), toluene (3 mL), catalyst (metal: 5 mol %), 2 MPa H\textsubscript{2}. \textsuperscript{f}Fifth run. \textsuperscript{g}Conversion (Conv.) and selectivity (Select.) were based on 6-chloroquinoline consumption (GC analysis).
(entry 7). Most remarkably, at temperatures as low as 25 °C, the hydrogenation of 1 proceeds smoothly, although a longer reaction time and relatively larger amounts of the Au catalyst were required (Table 1, entry 8). Nevertheless, the performance is encouraging since it represents the mildest condition in the Au-based hydrogenation process to date.

In subsequent experiments performed under 2 MPa H₂ at 60 °C, a clear advantage of the Au/HSA-TiO₂ catalyst in terms of conversion and selectivity over other noble metals (Pd, Pt, Ru) with identical particle size₁⁹ supported on HSA-TiO₂ was also noticed (Table 1, entries 9–11). Note that previously reported solid catalysts, such as hydroxyapatite (HAP)-supported Pd NPs (Pd/HAP),₁⁶a showed good activity but much inferior selectivity relative to Au/HSA-TiO₂ under the present reaction conditions (Table 1, entry 12). Blank experiments without catalyst or using the Au-free HSA-TiO₂ gave no conversion, thus further confirming that the highly dispersed Au NPs were indispensable for the desired transformation (Table 1, entry 13). In addition, the use of the catalyst precursor HAuCl₄ as well as with other Au compounds, including Au₂O₃ and Au₀ powder (average particle size of ca. 150 nm), did not promote the reaction at all (Table 1, entries 14–16).

To verify whether the observed catalysis is truly heterogeneous or not, the reaction mixture was hot filtered at 40% conversion of 1 at 60 °C. Further stirring of the filtrate under the above reaction conditions did not yield any additional product. An inductively coupled plasma method with detection limit of 0.007 ppm was used to confirm that no Au leached into the filtrate.²⁰ Furthermore, the recovered Au/HSA-TiO₂ catalyst could be reused at least five runs without appreciable loss of the original catalytic activity (Table 1, entry 17). These results rule out any possible contribution of homogeneous catalysis by leached Au species.

Having established that Au/HSA-TiO₂ was an efficient catalyst for the hydrogenation of quinolines, we extended our studies to various structurally different substituted quinolines. The results were summarized in Table 2. The hydrogenation of quinoline was highly regioselective, producing 1,2,3,4-tetrahydroquinoline exclusively (Table 2, entry 1). No trace of 5,6,7,8-tetrahydroquinoline or decahydroquinoline, byproducts frequently formed under hydrogenation catalysis,²¹ was observed. Reactions of quinolines bearing a methyl group at the 2- and 4-position proceeded successfully to give the corresponding 1,2,3,4-tetrahydroquinolines (Table 2, entries 2 and 3). Quinolines with electron-donating groups (−OMe and −NH₂) on the benzene ring react smoothly (Table 2, entries 4 and 5). Remarkably, the hydrogenation of 8-hydroxyquinolines afforded the corresponding biologically active 1,2,3,4-tetrahydro-8-hydroxyquinolines (Table 2, entries 6–8), which can inhibit leukotriene formation in macrophages.²² Furthermore, in the more challenging reactions, where quinolines with other reducible groups (halogens, ketone, and olefin) were employed, the corresponding valuable functional tetrahydroquinolines were obtained in excellent yield (Table 2, entries 9–12), which has no precedent in heterogeneous quinoline hydrogenation.

Encouraged by these results, we applied this attractive protocol to the regioselective hydrogenation of heterocyclic ring of a series of other biologically important heteroaromatic nitrogen compounds. Isoquinoline, acridine, and 7,8-benzoquinoline were tested. As depicted in Table 3, nearly quantitative hydrogenation of 1,2,3,4-tetrahydro-8-hydroxyquinolines (Table 2, entries 6–8), which can inhibit leukotriene formation in macrophages.²² Furthermore, in the more challenging reactions, where quinolines with other reducible groups (halogens, ketone, and olefin) were employed, the corresponding valuable functional tetrahydroquinolines were obtained in excellent yield (Table 2, entries 9–12), which has no precedent in heterogeneous quinoline hydrogenation.

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yields were obtained in most cases. Isoquinoline was reduced to the corresponding tetrahydroisoquinoline (Table 3, entry 1). 6-bromoisoquinoline was converted to the corresponding 6-bromotetrahydroisoquinoline without any dehalogenation (Table 3, entry 2). More complex fused ring compounds including acridine and 7,8-benzoquinoline were hydrogenated to their corresponding tetrahydroderivatives (Table 3, entries 3 and 4). Note that the order of individual initial rate was acridine > quinoline > 7,8-benzoquinoline > isoquinoline, which reflects both steric and electronic effects. Similar tendencies were observed and explained in the previous reported homogeneous reduction of polynuclear heteroaromatic compounds using (Ph3P)3RhCl complexes.23

A heterogeneous direct hydrogenation without solvents would be more desirable for practical applications. Notably, this Au/HSA-TiO2-catalyzed system can facilitate the 100 mmol scale hydrogenation of quinoline under neat conditions at 140 °C (Scheme 1). The hydrogenation was complete within 48 h with 100% selectivity in the presence of 0.02 mol % Au, in which the turnover number (TON, based on total Au) of the Au catalyst approached 5000 with an excellent average turnover frequency (TOF) of approximately 104 h⁻¹. When the reaction was carried out on this scale, the Au/HSA-TiO2 catalyst can also be reused without loss of activity.

At this stage, we became interested in elucidation of the nature of active Au in Au/HSA-TiO2 sample, since the chemical state of Au was generally assumed as one of the key factors in determining the catalytic activity.24 Detailed spectroscopic characterizations of the Au/HSA-TiO2 sample were done with X-ray photoelectron spectroscopy (XPS) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) as well as X-ray absorption near-edge structure (XANES) studies.25 From XPS data presented in Figure S5, only metallic Au was identified on the surface of the Au/HSA-TiO2 catalyst. The fact that no bands for Au⁺ or Au⁺ were seen in the DRIFT spectrum (Figure S6) of adsorbed CO further confirmed the sole presence of metallic Au species in this material. Moreover, Au L₃-edge XANES data (Figure 2) of the Au/HSA-TiO2 were clearly different from that of HAuCl₄ (as a reference compound for ionic Au³⁺ species) but rather similar to that of Au foil, which further indicated that Au species in the Au/HSA-TiO2 sample exists in its elemental state.

To clarify the origin of the superior activity achieved in present Au0-mediated hydrogenation system, we studied the H₂−D₂ exchange reaction over a variety of catalysts.26 For the sake of comparison, the measurements were applied as close to the reaction conditions as possible. Thus, the rates of HD formation in terms of the TOF values were estimated at 60 °C over the samples with and without the presence of preadsorbed quinoline or its hydrogenated derivatives (Figure 3).27 It is revealed that, as opposed to the case without preadsorption or in presence of preadsorbed tetrahydroquinoline, the H₂−D₂ exchange proceeds much more rapidly over the Au/HSA-TiO2.

Table 3. Au/HSA-TiO₂-Catalyzed Hydrogenation of Heteroaromatic Nitrogen Compounds

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<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
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<th>Yield (%)</th>
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<td>7</td>
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</tbody>
</table>

“Substrate (0.5 mmol), toluene (3 mL), Au/HSA-TiO₂ (Au: 1 mol %), 60 °C, 2 MPa H₂. b80 °C. cConversion was based on heteroaromatic nitrogen compounds consumption. dNumbers in parentheses refer to yields of isolated products.

Scheme 1. Au/HSA-TiO₂-Catalyzed 100 mmol Scale Hydrogenation of Quinoline

Figure 2. Au L₃-edge XANES spectra of the (a) HAuCl₄, (b) Au foil, and (c) Au/HSA-TiO₂.

Figure 3. Rate for HD formation over various noble metal-based catalysts. The TOF values were calculated based on the mol of HD molecules formed per mol metal (Au, Pd, Pt, or Ru) per min. The error bars represent the standard deviation of triplicate tests.
catalyst preadsorbed with quinoline molecules. This is in strong contrast to that occurs with the corresponding traditional Pd-, Pt-, and Ru-based catalysts, in which the rate of HD formation was heavily decreased when the samples were preadsorbed with relevant N-heterocyclic compounds. These results unambiguously demonstrate that quinoline, a poison for traditional noble metal-containing hydrogenation catalysts, can act as a promoter for the Au-catalyzed hydrogenation processes via facilitating the activation of H2.

As for the activation of H2 for chemoselective reduction of polar bonds (C=O or C≡N) with homogeneous metal–ligand bifunctional catalysts, it is widely accepted that the reaction initiates with the heterolytic cleavage of H2 to yield H+ in a OH or NH ligand and H− in metal hydrides, and the resulting H+/H− pair preferentially transfers to the polar bonds. This type of ionic mechanism might be applicable also for heterogeneous metal catalysts. Very recently, Garcia and coworkers showed direct IR evidence on heterolytic dissociation of H2 on ceria-supported Au NPs at 150 °C, leading to a proton bonded to a ceria oxygen and a hydride attached to Au. On the other hand, it is well established that on exposure of H2 to metal particles dispersed on oxide materials, such as Pt/Al2O3 and Rh/Al2O3, the formation of additional OH groups on the support via hydrogen spillover will readily occur. Adopting these models, the dissociation of H2 over Au/HSA-TiO2 would yield H+ on the support and H− species on Au NPs, albeit the characteristic vibrations associated with the Au hydrides were not detected by IR spectroscopy in our case.

To measure the rate of H2 cleavage step over various Au-based catalysts, H2–D2 exchange of D2 with surface OH groups of the catalysts at 60 °C was monitored by DRIFTS. The results are shown in Figure 4. For Au/HSA-TiO2, a simultaneous loss and gain in the IR band intensity for the Ti–OH (3686 cm−1) and Ti–OD (2694 cm−1) stretching vibrations were observed. The OD formation rate for Au/HSA-TiO2 was 3 orders of magnitude higher than that for HSA-TiO2 (result not shown). This gives direct evidence of the Au NPs-catalyzed cleavage of the H–H bond. From the kinetic curves, the initial rate of the OD formation decreased significantly when Au particle size increased from 2 to 3.5 nm. For the catalysts with the same Au loading (0.5 wt %) and identical mean Au particle size (1.9–2.1 nm), the OH–D2 exchange reaction rate ranks in the order of Au/HSA-TiO2 (124 m2 g−1) > Au/TiO2–P25 (45 m2 g−1) > Au/Al2O3 (50 m2 g−1). This trend is in line with the catalytic data for quinoline hydrogenation, as shown in Tables S1 and S2, suggesting that a high abundance of surface hydroxyl groups on HSA-TiO2 is beneficial for D2 dissociation.

Based on the above-mentioned facts and bearing in mind that basic ligands of transition-metal complexes promote heterolytic cleavage of H2 to give metal–hydride species, we propose a concerted effect between quinoline molecules and the supported Au NPs. As depicted in Scheme 2, the key aspect of quinoline is to facilitate the crucial heterolytic H2 activation at the Au-support interface. Namely, the quaternizable nitrogen atom of quinoline can serve as a basic ligand to promote the heterolytic H2 cleavage, providing a favorable situation for provoking hydrogen activation under very mild conditions. Although the precise way by which the quinoline-assisted H2 cleavage at the Au-support interface occurs remains to be clarified at this stage, it is important to emphasize that the moderate interaction between quinoline and Au could be the key factor accounting for the essential role of quinolines in the present Au-mediated hydrogenation reactions. Recent density functional theory (DFT) calculations have confirmed that flat and tilted orientations of the quinoline ring have lower adsorption energy on Au (7 and 10 kcal·mol−1 for flat and tilted species, respectively) compared to adsorption on Pt (ca. 40 kcal·mol−1 for flat species). These facts, coupled with the findings in the present study, suggest that self-cooperation of Au surface and functional reactants may open new possibilities for development of new catalytic procedures for other key transformations.
**CONCLUSIONS**

In conclusion, we have described an exceedingly efficient approach for mild and clean hydrogenation of a wide range of quinolines and related heteroaromatic nitrogen compounds to the corresponding tetrahydroderivatives using supported Au NPs. Of practical significance is that various synthetically useful functional groups including halogens, ketones, and olefins remain intact during quinoline hydrogenation. Quinoline compounds, a class of well-known poisons for the traditional noble metal-based hydrogenation catalysts, can act as promoters for the Au catalysts, contributing to the superior activity and selectivity achieved with these processes. We believe this intriguing and remarkable promotional effect by reactants may have fundamental implications for the broad field of Au catalysis and be useful to design new powerful catalytic systems for green and sustainable organic synthesis.

**EXPERIMENTAL SECTION**

**Preparation of HSA-TiO₂ Support.** HSA nanocrystalline TiO₂ powders predominantly in the anatase phase were prepared by the hydrolysis of tetrabutyl titanate [TTBT, Ti(Obu)₄]. Typically, 17.2 g Ti(Obu)₄ was dropwise added to 800 mL water under vigorous stirring at room temperature, and then the mixture was further stirred for 2 h. The precipitate obtained was filtered and washed with water. The resultant powder was dried at 100 °C for 12 h and then calcined in a tubular oven at 400 °C in air for 4 h. The BET surface area of the resultant material was 124 m² g⁻¹.

**Preparation of Au/HSA-TiO₂.** Using a routine deposition precipitation (DP) method, 0.5 wt % Au/HSA-TiO₂ catalyst was prepared. An appropriate amount of aqueous solutions of chloroauric acid (H[AuCl₄]) was heated to 80 °C under vigorous stirring. The pH was adjusted to 8.0 by dropwise addition of NaOH (0.2 M), and then 1.0 g of HSA-TiO₂ was dispersed in the solution. The mixture was stirred for 2 h at 80 °C, after which the suspension was cooled to room temperature. Extensive washing with deionized water was then followed until it was free of chloride ions. The samples were dried under vacuum at room temperature for 12 h and calcined in air at 250 °C for 2 h.

**General Procedure for Catalytic Hydrogenation of Quinolines.** A mixture of substrate (0.5 mmol), catalyst (metal: 1 mol %), and toluene (3 mL) was charged into a Parr autoclave (25 mL capacity, SS-316). Then the autoclave was sealed, and 2 MPa H₂ was charged into it after internal air being degassed completely. The resulting mixture was vigorously stirred (1200 rpm with a magnetic stir bar) at a given temperature. The products were confirmed by the comparison of their GC retention time, mass, and ¹H NMR spectroscopy. The conversion and product selectivity were determined using a routine gel chromatography (hexanes/ethyl acetate).

**Isotope H₂−D₂ Exchange Reaction.** The H₂−D₂ exchange reaction was carried out in a fixed bed quartz reactor with an inner diameter of 4 mm at 60 °C. The feed gas containing 20 vol% H₂, 20 vol% D₂, and balancing He at a total flow rate of 60 mL min⁻¹, corresponding to a gas hourly space velocity (GHSV) of 1.8 × 10⁶ mL h⁻¹ gcat⁻¹. Under these conditions, the H₂−D₂ exchange conversions were always kept below 15% to avoid mass-transfer limitations. Reaction products (H₂, HDm, and D₂) were analyzed by online mass spectrometer (Balzers, QMS 200 Omnistar). Trace amounts of HD formed in the experimental setup without catalyst and the product concentrations were corrected for this. Prior to catalytic test, the catalysts were heated in He flow (10 mL min⁻¹) at 200 °C for 0.5 h, followed by cooling to the desired temperature under He flow. For the introduction of quinoline or tetrahydroquinoline to the samples, the liquid compound (25 μmol) was injected under the He flow.

**DRIFT Spectroscopic Measurements.** The DRIFTS experiments were carried out on a Nicolet Magna-IR 760 Fourier transform spectrometer (ThermoNicolet, Madison, WI) using an MCT detector. Prior to the chemisorption (10 vol% D₂/He), the sample (typically 20 mg) was pretreated in a stream of He (35 mL min⁻¹) at 250 °C for 2 h and then cooled under He to 25 °C. Unless stated otherwise, infrared (IR) spectra were recorded against a background of the sample at the reaction temperature under flowing He. IR spectra were recorded with coaddition 64 scans in single-beam spectra or absorbance spectra by applying a resolution of 4 cm⁻¹.

**REFERENCES**


