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Hydrodebromination of Aromatic Bromides Catalyzed by Unsupported Nanoporous Gold: Heterolytic Cleavage of Hydrogen Molecule

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Abstract: Unsupported nanoporous gold (AuNPore) is a highly efficient, practically applicable, and recyclable catalyst for hydrodebromination of aromatic bromides. The AuNPore-catalyzed hydrodebromination of aromatic bromides proceeded smoothly at relatively low hydrogen pressure and temperature to achieve good to excellent yields of the corresponding non-bromine variants. The selective hydrodebromination reaction occurred exclusively in the coexistence of chlorine atom. For the first time, a mechanistic study revealed that the H–H bond splits in a heterolysis manner on the surface of AuNPore to generate Au–H hydride species.

(homolysis or heterolysis) on the surface of heterogeneous catalysts during the hydrodehalogenation of aromatic halides has not been explored.^[13b] Understanding the splitting manner of H₂ would help elucidate the reaction mechanism and the design of new catalysts for hydrodehalogenation.

The unsupported nanoporous gold (AuNPore) catalyst is an efficient, versatile, and reusable catalyst for oxidation,^[14] reduction,^[15] addition,^[16] annulation,^[17] and C–H bond oxidative coupling.^[18] In the course of our continuous research on AuNPore catalysis, we found that the AuNPore can also be used as a catalyst for selective hydrodebromination of aromatic bromides, revealing a new application for AuNPore catalyst.

Introduction

Development of convenient and efficient methods for the hydrodehalogenation of aromatic halides has attracted considerable attention.^[1] The hydrodehalogenation reaction can be used in environmental chemistry for degradation of halogen-containing anthropogenic and environmentally deleterious chemicals into their less noxious congeners^[2,3] and in organic synthesis for deprotection chemistry instead of sulfonic acid group by halogen atom as protecting group.^[4,5] Over the past decades, many types of homogeneous^[4,6] and heterogeneous^[7] catalyst systems have been developed for the hydrodehalogenation of aromatic halides. Among these catalyst systems, the heterogeneous catalyst systems based on transition metals Pd,^[8] Rh,^[9] Ru,^[10] Ni,^[11] and Co^[12] have emerged as extremely powerful tools for the hydrodehalogenation of aromatic halides using molecular hydrogen (H₂) as reductant. Furthermore, the activity of heterogeneous catalyst was reportedly improved by a bimetallic system consisting of Cu and Ni with H₂ as the reductant.^[13] However, to the best of our knowledge, no successful cases have been reported on the use of gold catalysts in the hydrodehalogenation of aromatic halides. Moreover, selective hydrodebromination of aromatic bromides simultaneously bearing fluorine and/or chlorine atoms on the aromatic ring has rarely been achieved.^[8b] In addition, the splitting manner of H₂

Results and Discussion

Preparation and Characterization of AuNPore. The unsupported nanoporous gold (AuNPore) catalyst was prepared according to a method described previously.^[15a] Pure gold (99.99%) and silver (99.99%) were melted with an electric arc-melting furnace under an argon atmosphere to form Au₃₀Ag₇₀ alloy, which was rolled down to thickness of 0.04 mm. The resulting foil was annealed at 850 °C for 20 h. The foil was cut into small pieces (5 × 2 mm square). Treatment of the resulting chips (100 mg) with 70 wt. % nitric acid (100 mL) for 18 h at room temperature in a shaking apparatus resulted in the formation of the nanoporous structure by selective silver leaching. The material was washed successively with a saturated aqueous solution of NaHCO₃, pure water, and acetone. Drying the material under reduced pressure gave the nanoporous gold. Ligaments and nanopore channels formed uniformly across the entire AuNPore, as shown by a scanning electron microscopy (SEM) image (Figure 1a). The structure of AuNPore was clearly shown with multiple layers of gold ligaments with convex and concave columnar curvatures, indicating that the nanoporous structure is a bicontinuous 3D network, as revealed by a transmission

electron microscopy (TEM) image (Figure 1b). The specific surface area of AuNPore was measured to be 28.3 m²/g by the Brunauer-Emmett-Teller method. The pore size distribution was also determined to be 4.78 nm from the adsorption branch of isotherms based on density functional theory (DFT) (Figure S1a). The dealloyed material was found to comprise Au_{>99}Ag_{<1} based on energy-dispersive X-ray spectroscopy (EDS) analysis (Figure 1c).

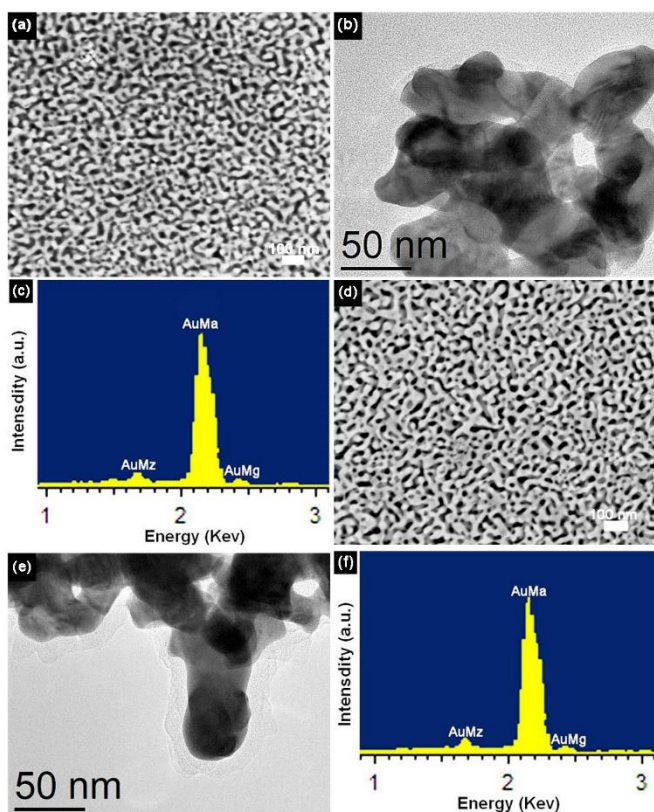


Figure 1. (a) SEM image of fresh AuNPore. (b) TEM image of fresh AuNPore. (c) EDS analysis of fresh AuNPore. (d) SEM image of AuNPore after five runs. (e) TEM image of AuNPore after five runs. (f) EDS analysis of AuNPore after five runs.

Further, the electronic states of AuNPore was measured by X-ray photoelectron spectroscopy (XPS) analysis (Figure 2). Figure 2a shows the XPS spectra of Au 4f in metallic gold (blue curve) and AuNPore (green curve). It was clearly shown that the binding energies of 84.01 and 87.78 eV for Au 4f_{7/2} and Au 4f_{5/2} in AuNPore were slightly greater than those (84.00 and 87.70 eV) found for Au 4f_{7/2} and Au 4f_{5/2} in metallic gold. Figure 2b presents the XPS spectra of Ag 3d in metallic silver (blue curve) and AuNPore (green curve). The XPS spectrum of Ag 3d in AuNPore showed two peaks with binding energies of 374.22 and 368.26 eV, which were slightly lower than those (374.45 and 368.44 eV) found for Ag 3d in metallic silver. These findings indicated that electron transfer from Au to Ag took place, leading to a partial positive charge on Au and negative charge on Ag.

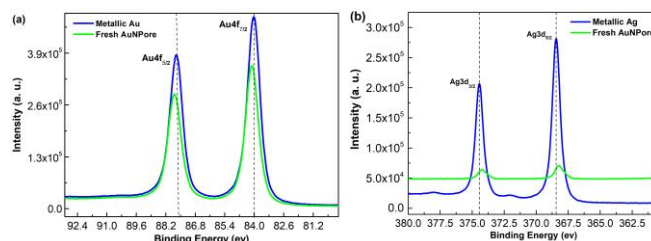


Figure 2. XPS spectra of (a) Au 4f and (b) Ag 3d of fresh AuNPore.

Hydrodebromination of Aromatic Bromides Catalyzed by AuNPore. In our initial studies, the hydrodebromination reaction of 4-butylphenyl bromide (**1a**) was selected as a model to optimize the reaction conditions, and the results are summarized in Table 1. The use of a base is necessary for the hydrodehalogenation reaction to neutralize hydrogen halide, a by-product. Therefore, the base was first screened in the presence of 10 mol% of AuNPore catalyst in MeOH at 100 °C for 24 h (entries 1–7). Among the bases tested, including organic [NEt₃ and HNEt₂] and inorganic [NaOH,

Table 1. Screening of reaction conditions.^[a]

Entry	Base (Equiv.)	Solvent	Time (h)	Yield (%) ^[b]
1	NEt ₃ (2)	MeOH	24	3
2	HNEt ₂ (2)	MeOH	24	6
3	NaOH (2)	MeOH	24	17
4	KOH (2)	MeOH	24	10
5	Ca(OH) ₂ (2)	MeOH	24	6
6	Ba(OH) ₂ (2)	MeOH	24	3
7	Cs ₂ CO ₃ (2)	MeOH	24	42
8	Cs ₂ CO ₃ (2)	MeOH	36	68
9	Cs ₂ CO ₃ (3)	MeOH	36	94
10	Na ₂ CO ₃ (3)	MeOH	36	10
11	K ₂ CO ₃ (3)	MeOH	36	40
12	CsOH (3)	MeOH	36	19
13	Cs ₂ CO ₃ (3)	EtOH	36	86
14	Cs ₂ CO ₃ (3)	iPrOH	36	12
15	Cs ₂ CO ₃ (3)	nBuOH	36	13
16	Cs ₂ CO ₃ (3)	cyclohexanol	36	15
17 ^[c]	Cs ₂ CO ₃ (3)	MeOH	36	73
18 ^[d]	Cs ₂ CO ₃ (3)	MeOH	36	75
19 ^[e]	Cs ₂ CO ₃ (3)	MeOH	36	55
20 ^[f]	Cs ₂ CO ₃ (3)	MeOH	36	NR ^[g]
21 ^[h]	Cs ₂ CO ₃ (3)	MeOH	36	NR ^[g]
22	none	MeOH	36	NR ^[g]

[a] Reaction conditions: 4-normal-butylphenyl bromide (**1a**, 0.5 mmol), base (2 or 3 equivalents), AuNPore catalyst (10 mol%) in solvent (2 mL) at 100 °C under 5 atm of hydrogen for 24 h or 36 h. [b] The yield was determined by NMR spectroscopy using CH₂Br₂ as the internal standard. [c] The reaction was conducted at 90 °C. [d] The reaction was conducted under 2 atm of hydrogen. [e] The reaction was conducted in the presence of 5 mol% of AuNPore catalyst. [f] Without AuNPore catalyst. [g] No reaction. [h] The reaction was conducted in the presence of 10 mol% of Au₃₀Ag₇₀ alloy.

KOH, Ca(OH)₂, Ba(OH)₂ and Cs₂CO₃] bases, Cs₂CO₃ proved to be the best base. The desired hydrodebromination product, butyl benzene (**2a**), was obtained in 42% yield (entry 7). An increased yield of **2a** was observed when the hydrodebromination reaction of **1a** was performed for prolonged period of time (entry 8, 36 h, 68% yield). Gratifyingly, the yield of **2a** was significantly increased by increasing the loading of Cs₂CO₃ (entry 9 vs. entry 8); substrate **1a** was almost completely converted into product **2a** when 3 equivalents of Cs₂CO₃ were used (entry 9, 94% yield). Subsequent investigations indicated that Cs cation and carbonate anion are important for the hydrodebromination reaction (entries 10–12). Solvents were subsequently screened using Cs₂CO₃ as the base. Alcohol solvents facilitate the hydrodehalogenation reaction.^[12,13] Therefore, different alcohol solvents, including MeOH, EtOH, ⁱPrOH, ⁿBuOH, and cyclohexanol, were investigated in the current study, and the obtained results suggested that MeOH was the optimal solvent (entry 9 vs. entries 13–16). The yield of **2a** decreased with decreasing reaction temperature, hydrogen pressure, and catalyst loading (entries 17–19). As expected, no reaction was observed in the absence of AuNPore catalyst (entry 20) and with Au₃₀Ag₇₀ alloy as a catalyst instead of AuNPore (entry 21). Surprisingly, no reaction was observed in the absence of base Cs₂CO₃ (entry 22). Cs₂CO₃ acted as a base to neutralize the by-product hydrogen halide and created an alkalic environment to facilitate the occurrence of target hydrodebromination reaction.^[19] Therefore, subsequent selective hydrodebromination reaction of aromatic bromides was conducted in the presence of AuNPore (10 mol%) and Cs₂CO₃ (3 equivalents) in MeOH at 100 °C under H₂ at 5 atm.

The scope and limitation of the AuNPore-catalyzed hydrodebromination reaction were investigated under the optimal reaction conditions. Table 2 shows the results obtained from the hydrodebromination reactions of various aromatic bromides **1a–1u**. Similarly, the hydrodebromination reaction of aryl bromide **1b** bearing a phenyl group on the *para*-position of benzene ring proceeded as smoothly as the reaction of **1a** to produce the corresponding product **2b** with an excellent yield (91%). Good yields were observed in the hydrodebromination reactions of amino-group-substituted aryl bromides **1c–1f** (**2c–2f**, 80%–86%). Good and excellent yields were observed again in the hydrodebromination reactions of aryl bromides **1g** and **1h** bearing an aminoethyl or a hydroxymethyl group on the *para*-position of benzene ring (**2g** and **2h**, 85% and 91% yields, respectively). The hydrodebromination reactions of 3,4,5-(trimethoxy)phenyl bromide (**1i**) and 4-(benzyloxy)phenyl bromide (**1j**) also proceeded smoothly to produce the corresponding products **2i** and **2j** with excellent yields (93% and 92%, respectively). Subsequent investigation demonstrated that the carboxyl-containing aromatic bromides **1k–1m** were also suitable substrates for the hydrodebromination reaction (**2k–2m**, 90%–93% yields). The C=C in aryl bromide **1m** was not reduced under the reaction conditions. Although aldehyde group could not be tolerated in the current hydrodebromination reaction, the aromatic bromide **1n** with a protected aldehyde group produced the product **2n** with a yield of 90%. The hydrodebromination product **2o** was obtained in 45% yield along with a by-product, 1-phenylethanol, in 19% yield when the substrate 4-acetylphenyl bromide (**1o**) was examined. The yield of **2o** increased to 70%

when the reaction temperature was decreased. The selective hydrodebromination reaction of chlorine-containing substrates **1p** and **1q** was observed; **2p** and **2q** were obtained in high yields and chlorine atoms were not reduced at all. The two bromine atoms in the substrate, 4,4'-dibromo-1,1'-biphenyl (**1r**), were completely removed by this catalytic method. Product **2b** was obtained with a yield of 93%. The substrates **1s–1u** having fused aromatic ring were finally examined, and the corresponding hydrodebromination products **2s** and **2u** were obtained with yields of 88% and 91%, respectively.

Table 2. Hydrodebromination reaction of various aromatic bromides^[a,b]

2a , 89%, 36 h	2b , 91%, 80 h	2c , 80%, 155 h
2d , 82%, 160 h	2e , 86%, 130 h	2f , 82%, 132 h
2g , 85%, 96 h	2h , 91%, 96 h	2i , 93%, 150 h
2j , 92%, 74 h	2k , 93%, 79 h	2l , 91%, 79 h
2m , 90%, 72 h	2n , 90%, 79 h	2o , 45%, 48 h ^c 70%, 48 h ^d
2p , 89%, 71 h	2q , 89%, 72 h	2b , 93%, 72 h
2s , 88%, 77 h	2s , 91%, 77 h	2u , 91%, 98 h

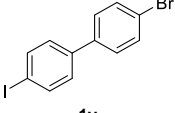
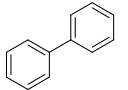
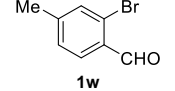
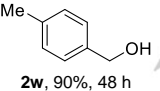
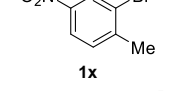
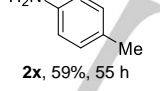
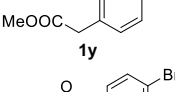
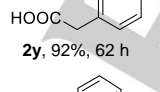
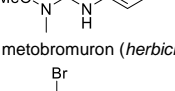
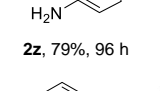
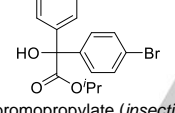
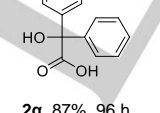

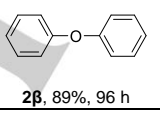
[a] Reaction conditions: aromatic bromide (**1**, 0.5 mmol), AuNPore (10 mol%), and Cs₂CO₃ (3.0 equiv.) in MeOH (2 mL) at 100 °C under 5 atm of hydrogen. [b] Isolated yield. [c] The by-product, 1-phenylethanol, was isolated in 19% yield. [d] The reaction was performed at 80 °C; the trace amount of the by-product, 1-phenylethanol, was isolated.

Table 3 shows the results obtained from the hydrodebromination reactions of some special aromatic bromides **1v–1β**. The bromine and iodine atoms in substrate **1v**

were simultaneously removed, and the corresponding product **2b** was obtained in 90% yield (entry 1). As described above, the aldehyde group in substrate **1w** was reduced to hydroxymethyl group and hydrodebromination reaction took place without any problem (entry 2). As expected, nitro group was reduced to amino group with the occurrence of the hydrodebromination reaction when the substrate 2-bromo-1-methyl-4-nitrobenzene (**1x**) was examined (entry 3).^[15b] Hydrolysis occurred in the hydrodebromination reactions of bromides **1y–1a**; this behavior is attributed to the basic reaction medium (entries 4–6). As expected, all the bromine atoms linked to the benzene rings of decabromodiphenyl oxide (**1β**, DBDPO) were completely removed to give the corresponding product **2β** with a yield of 89% (entry 7).

These results obtained from the reactions of bromide substrates **1z–1β** indicated that the current method can be practically applied for degradation of bromine-containing herbicide, insecticide, and fire retardant into their corresponding non-bromine variants (entries 5–7).^[20]

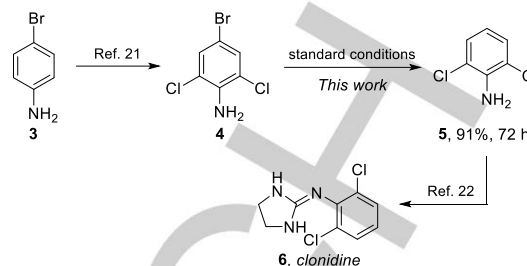
Table 3. Hydrodebromination reaction of some special aromatic bromides^[a,b]

Entry	Bromide 1	Product 2
1	 1v	 2b , 90%, 74 h
2	 1w	 2w , 90%, 48 h
3	 1x	 2x , 59%, 55 h
4	 1y	 2y , 92%, 62 h
5	 1z , metobromuron (herbicide)	 2z , 79%, 96 h
6	 1a , bromopropylate (insecticide)	 2a , 87%, 96 h
7	 1β , DBDPO (fire retardant)	 2β , 89%, 96 h

[a] Reaction conditions: aromatic bromide (**1**, 0.5 mmol), AuNPore (10 mol%), and Cs₂CO₃ (3.0 equiv.) in MeOH (2 mL) at 100 °C under 5 atm of hydrogen. [b] Isolated yield.

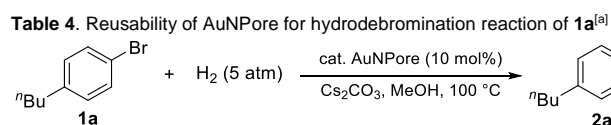
Application of This Method in Clonidine Synthesis. To further demonstrate practicability of the current method, we applied this method for deprotection chemistry. The result is shown in Scheme 1. 2,6-Dichloro-4-bromoaniline (**4**) can be synthesized through the chlorination of 4-bromoaniline (**3**);^[21] the bromine atom acted as a protecting group to block the *para*-position in this transformation. As expected, the key intermediate,

2,6-dichloroaniline (**5**), in the synthesis of clonidine (**6**),^[22] an antihypertensive drug,^[23] was obtained with a yield of 91% from the hydrodebromination reaction of **4** by using our method.^[24]



Scheme 1. Application in clonidine synthesis.

Reusability and Recovery of the AuNPore Catalyst. The efficiency and stability of the catalyst AuNPore were verified by recycling experiments under the standard conditions. The results are shown in Table 4. A high or excellent yield was obtained by repeated use of AuNPore catalyst when the model reaction was treated for prolonged period of time. The decrease in activity may be due to the adsorption of bromine ions on the surface of AuNPore. The almost unchanged catalyst nanostructure was confirmed by determinations of SEM, TEM, BET surface area, and pore size distribution (Figures 1d-1e and Figure S1b). The composition of the catalyst did not change as determined by EDS analysis (Figure 1f). The electron deficient characteristics of Au in AuNPore confirmed by XPS experiments may have facilitated the formation of Au–H species (Figure 2a). No gold leached from the AuNPore catalyst to the reaction solution as observed by conducting inductively coupled plasma mass spectrometry. These results clearly indicate that AuNPore catalyst is stable and can be used repeatedly for the hydrodebromination reaction.

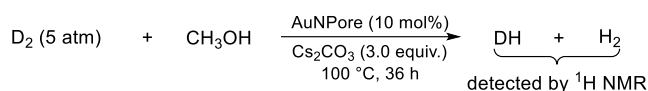


Run	1	2	3	4	5
Time (h)	36	40	72	90	95
Yield (%) ^[b]	94	92	93	89	82

[a] Reaction conditions: 4-butylphenyl bromide (**1a**, 0.5 mmol), AuNPore (10 mol%), and Cs₂CO₃ (3.0 equiv.) in methanol (2 mL) at 100 °C under 5 atm of hydrogen. [b] The yield was determined by NMR spectroscopy using CH₂Br₂ as an internal standard.

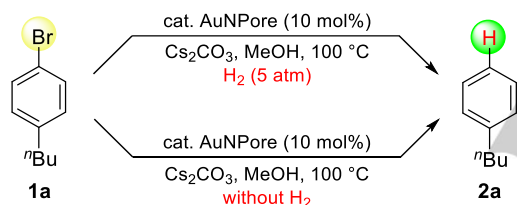
Deuterium-Hydrogen Exchange Reaction. Deuterium-hydrogen exchange reaction between D₂ and CH₃OH was performed under the standard conditions to clarify whether or not the current hydrodebromination involves Au–H species generated through the heterolytic cleavage of H₂ gas on the surface of AuNPore, which might act as a weak nucleophile (Scheme 2). As expected, the formation of DH and H₂ gas was clarified by proton nuclear magnetic resonance (¹H NMR) spectroscopy (Figure S2). The H₂ gas

is produced through the formation of DH generated via the heterolytic cleavage of D_2 (Figure S3). These observations clearly indicated that the H–H bond splits in a heterolysis manner on the surface of AuNPore in this kind of hydrodebromination reaction. The relatively large H/D kinetic isotope effect ($KIE_{H/D} = 2.3$) further indicated that the heterolytic dissociation of H_2 took place on the AuNPore (Figure S4).^[25] The generation of Au–H hydride species is the reason why the Br atom in polar C–Br bond was easily replaced by H atom.^[13,26]



Scheme 2. Deuterium-hydrogen exchange reaction.

Control experiments. Alcohol solvents serve two functions, namely, as solvent and as hydrogen donor, during the catalytic hydrogen transfer dehalogenation reaction.^[27] Therefore, control experiments were performed to clarify whether or not the solvent MeOH acted as a hydrogen donor in the current hydrodebromination reaction (Scheme 3 and Figure 3). Surprisingly, the hydrodebromination reaction of **1a** also proceeded with a relatively low reaction rate in the absence of H_2 gas. This observation indicated that the solvent MeOH acted as a hydrogen donor to produce Au–H hydride species,^[28] thereby promoting the occurrence of the hydrodebromination reaction. Figure 3



Scheme 3. Control experiments: hydrodebromination reaction was performed in the presence or in the absence of H_2 .

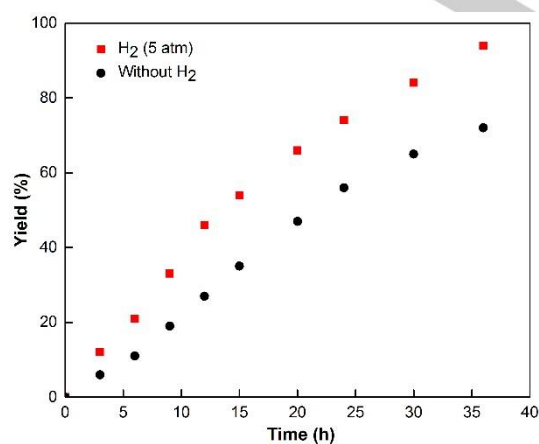


Figure 3. Time courses of dehalogenation of **1a**. The yield was determined by NMR spectroscopy using CH_2Br_2 as the internal standard.

clearly shows that the rate of hydrodebromination of **1a** was significantly elevated by using H_2 as a reductant. The target hydrodebromination reaction can be completed within 36 h.

Proposed Mechanism. On the basis of the above experimental outcomes and previous reports,^[7,13] a plausible catalytic cycle is proposed to account for the present hydrodebromination reaction (Figure 4). A H_2 molecule is adsorbed onto the surface of the AuNPore catalyst, and then heterolytic cleavage of the H–H bond occurred through the interaction of carbonate anion (CO_3^{2-}) producing Au–H^[29] species and HCO_3^- (right cycle). The coordination of Ar–Br to the surface of AuNPore catalyst and the nucleophilic substitution of Ar–Br with Au–H species successively occurred to provide the debromination product and Br⁻. In addition, a CH_3O^- anion was generated in situ from the reaction of CH_3OH with Cs_2CO_3 coordinated to the surface of AuNPore catalyst, and then Au–H species was produced via dehydrogenation reaction (left cycle); the formation of formaldehyde was verified by LC-MS determination (see SI for details). The coordination of Ar–Br to surface of AuNPore catalyst, followed by the nucleophilic substitution of Ar–Br with Au–H species, successively occurred to provide the debromination product and Br⁻.

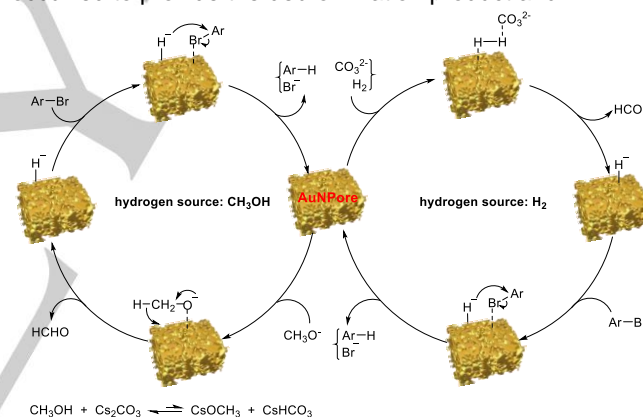


Figure 4. Proposed mechanism for hydrodebromination reaction.

Conclusion

In summary, we demonstrated for the first time that unsupported AuNPore catalyst is an efficient heterogeneous catalyst for the hydrodebromination reaction of aromatic bromides. The desired hydrodebromination products were obtained in good to excellent yields at relatively low hydrogen pressure and reaction temperature. The AuNPore catalyst can be practically applied for the degradation of bromine-containing herbicide, insecticide, and fire retardant. Moreover, it can be used for the deprotection chemistry in organic synthesis. The AuNPore catalyst can be easily recovered and reused several times. Mechanistic study revealed that the H–H bond splits in a heterolysis manner on the surface of AuNPore to generate Au–H species, which plays an important role in achieving efficient hydrodebromination. We revealed that the catalytic

hydrogen transfer dehalogenation reaction may also occur during a catalytic hydrodehalogenation reaction in the presence of an alcohol solvent.

Supporting Information

Full experimental details, characterization of catalyst, spectroscopic data for all products, as well as ^1H and ^{13}C NMR spectra.

Acknowledgements

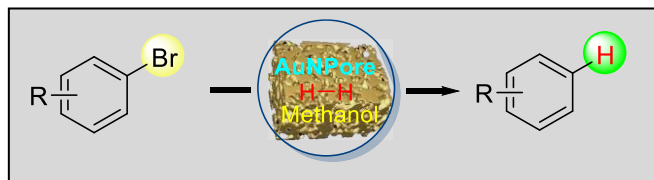
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Keywords: unsupported nanoporous gold • hydrodebromination • aromatic bromide • hydrogen gas • heterolysis

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AuNPore is demonstrated to be a highly efficient, practically applicable, and recyclable catalyst for hydrodebromination of aromatic bromides. Mechanistic study revealed for the first time that the H-H bond splits in a heterolysis manner on the surface of AuNPore to generate Au-H hydride species.