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(54) **SOLID SUPPORTED GOLD NANOPARTICLES, METHODS OF USE THEREOF, AND METHODS FOR MAKING SAME**

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**B01J 21/00** (2006.01)  
**B01J 23/02** (2006.01)  
**B01J 23/04** (2006.01)

(52) **U.S. Cl.**  
USPC ..... **502/243**; 502/344; 977/777

(58) **Field of Classification Search**  
USPC ..... 502/243, 344; 977/777  
See application file for complete search history.

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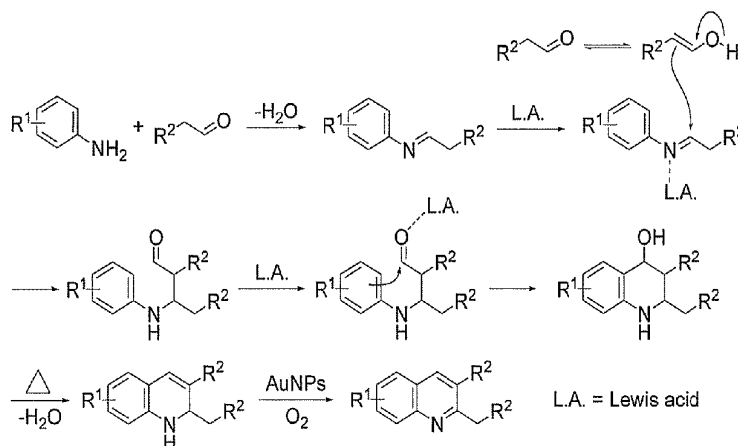
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(57) **ABSTRACT**

Solid-supported gold nanoparticles for use as a catalyst for the synthesis of quinolines from anilines and aldehydes using oxygen as an oxidant are provided. Also provided are a method for the preparation of SiO<sub>2</sub>-supported gold nanoparticles by in situ deposition of gold nanoparticles to silica gel and a method for synthesizing quinolines from anilines and aldehydes using oxygen as an oxidant.

**8 Claims, 8 Drawing Sheets**



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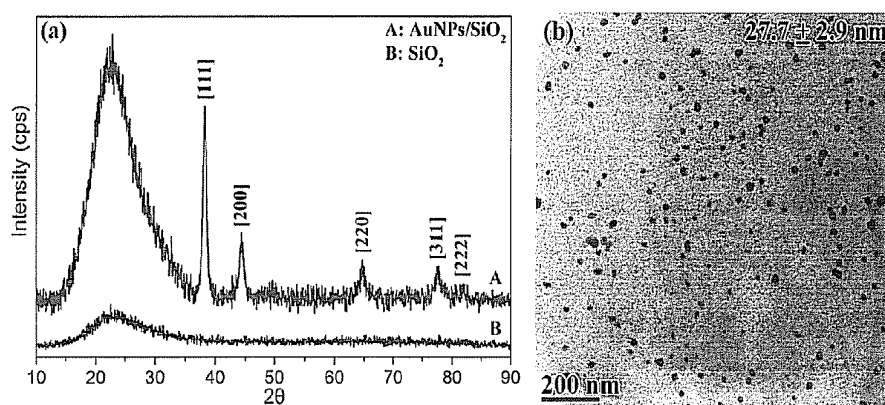


FIG. 2

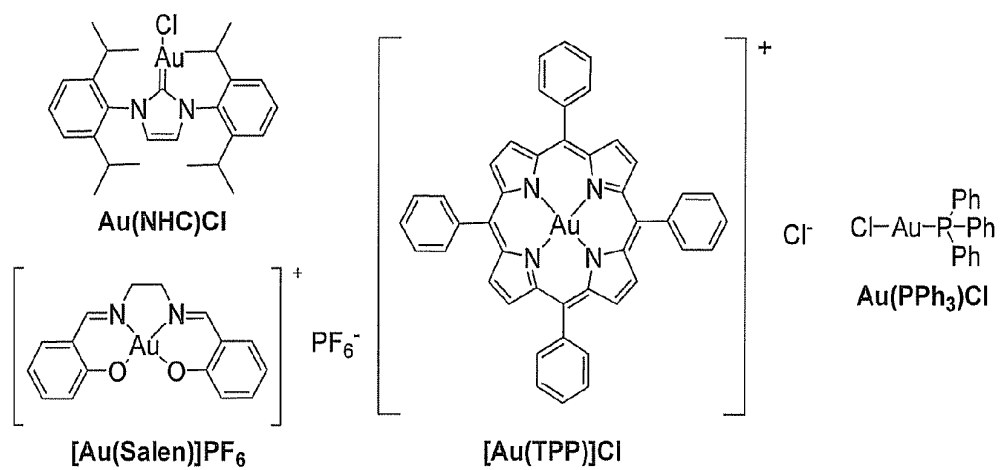


FIG. 3

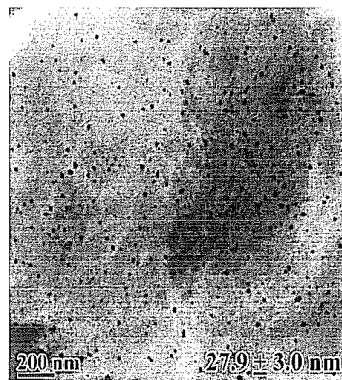


FIG. 4

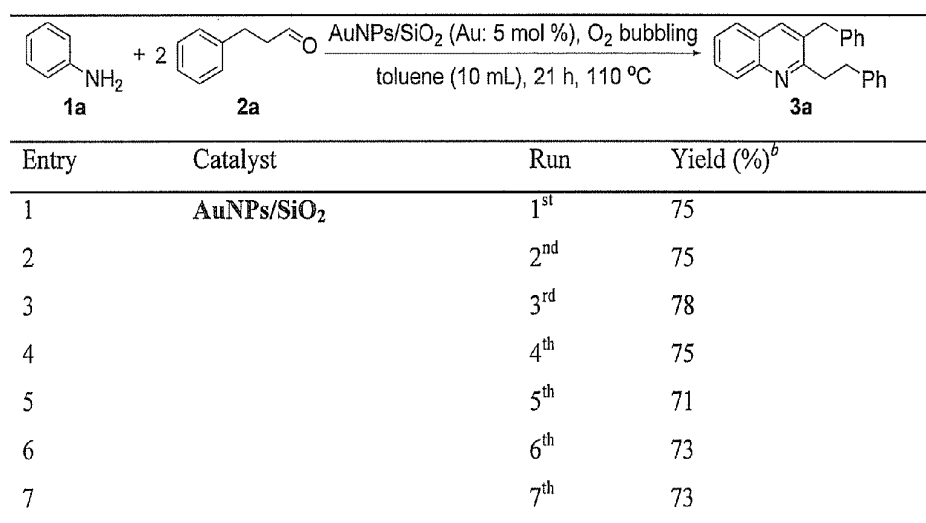
Reaction scheme: Nc1ccccc1 (1a) + 2 O=CCc1ccccc1 (2a)  $\xrightarrow[\text{toluene (10 mL), 21 h, 110 }^\circ\text{C}]{\text{catalyst (Au: 5 mol \%), O}_2 \text{ bubbling}}$  C1=CC=C(C=C1)C2=CC=CC=C2C3=CN(C3)CCc4ccccc4 (3a)

Entry	Catalyst	Yield (%) <sup>b</sup>
1	AuNPs/SiO <sub>2</sub>	75
2	AuNPs/SiO <sub>2</sub> -1	66
3	AuNPs/Al <sub>2</sub> O <sub>3</sub>	38
4	AuNPs/C	35
5	AuNPs/Fe <sub>2</sub> O <sub>3</sub>	<5
6	AuNPs/TiO <sub>2</sub>	<5
7	AuNPs/HAP	<5
8 <sup>c</sup>	Au powder	<5
9	KAuCl <sub>4</sub>	60
10	AuCl	35
11 <sup>d</sup>	SiO <sub>2</sub>	38
12	-	Nil
13	Au <sup>III</sup> (NHC)Cl	<5
14	[Au <sup>III</sup> (Salen)]PF <sub>6</sub>	<5
15	[Au <sup>III</sup> (TPP)]Cl	<5
16	Au <sup>I</sup> (PPh <sub>3</sub> )Cl	<5
17 <sup>e</sup>	AgNO <sub>3</sub>	<5
18 <sup>f</sup>	CuI	<5

<sup>a</sup> Reaction conditions: **1a** (0.2 mmol), **2a** (0.5 mmol), catalyst (Au: 5 mol %), toluene (10 mL), O<sub>2</sub> bubbling, 110 °C, *t* = 21 h, unless otherwise stated. <sup>b</sup> Yield was determined by <sup>1</sup>H-NMR using Ph<sub>2</sub>C=CH<sub>2</sub> as the internal standard and calculated based on the amount of **1a** added. <sup>c</sup> Au powder (2.0 mg) was used. <sup>d</sup> Acid washed SiO<sub>2</sub> (100 mg) was used. <sup>e</sup> AgNO<sub>3</sub> (1.7 mg; Ag: 5 mol %) was used. <sup>f</sup> CuI (2.0 mg; Cu: 5 mol %) was used.

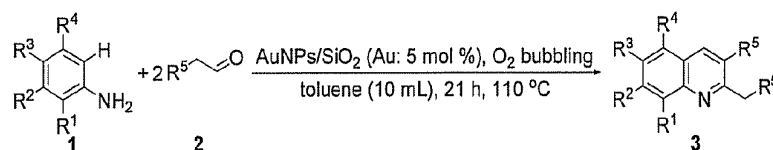
FIG. 5





<sup>a</sup> Reaction condition: **1a** (0.2 mmol), **2a** (0.5 mmol), AuNPs/SiO<sub>2</sub> (Au: 5 mol %), toluene (10 mL), O<sub>2</sub> bubbling, 110 °C, *t* = 21 h, unless otherwise stated. <sup>b</sup> Yield was determined by <sup>1</sup>H-NMR using Ph<sub>2</sub>C=CH<sub>2</sub> as the internal standard and calculated based on the amount of **1a** added.

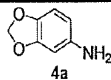
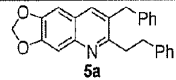
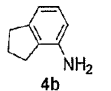
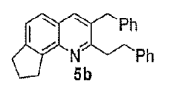
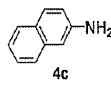
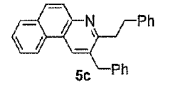
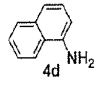
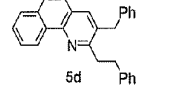
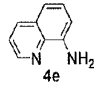
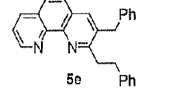
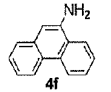
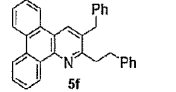
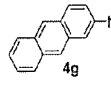
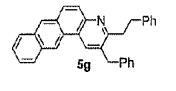
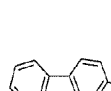
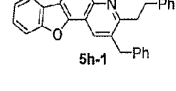
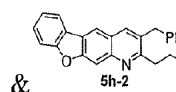
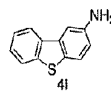
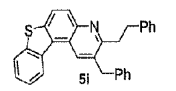
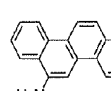
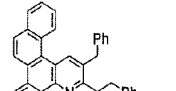
FIG. 6



Entry	Aniline				Aldehyde	Product	Yield (%) <sup>b</sup>
	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	R <sup>5</sup>		
1	H	H	H	H	<b>1a</b> PhCH <sub>2</sub>	<b>2a 3a</b>	75
2	H	H	<i>i</i> -Pr	H	<b>1b</b> PhCH <sub>2</sub>	<b>2a 3b</b>	72
3	H	H	Me	H	<b>1c</b> PhCH <sub>2</sub>	<b>2a 3c</b>	66
4	H	Me	H	H	<b>1d</b> PhCH <sub>2</sub>	<b>2a 3d-7 &amp; 3d-5</b>	92 <sup>c</sup>
5	Me	H	H	H	<b>1e</b> PhCH <sub>2</sub>	<b>2a 3e</b>	66
6	Me	H	H	Me	<b>1f</b> PhCH <sub>2</sub>	<b>2a 3f</b>	65
7	Me	H	Me	H	<b>1g</b> PhCH <sub>2</sub>	<b>2a 3g</b>	70
8	Me	Me	H	H	<b>1h</b> PhCH <sub>2</sub>	<b>2a 3h</b>	82
9	H	H	OMe	H	<b>1i</b> PhCH <sub>2</sub>	<b>2a 3i</b>	45
10	H	OMe	H	H	<b>1j</b> PhCH <sub>2</sub>	<b>2a 3j-7 &amp; 3j-5</b>	83 <sup>d</sup>
11	H	OMe	OMe	OMe	<b>1k</b> PhCH <sub>2</sub>	<b>2a 3k</b>	95
12	Ph	H	H	H	<b>1l</b> PhCH <sub>2</sub>	<b>2a 3l</b>	82
13 <sup>e</sup>					PhCH <sub>2</sub>	<b>2a</b>	60
14	H	H	Cl	H	<b>1n</b> PhCH <sub>2</sub>	<b>2a 3n</b>	17
15 <sup>f</sup>	H	H	H	H	<b>1a</b> CH <sub>3</sub>	<b>2b 3o</b>	54
16 <sup>f</sup>	Me	Me	H	H	<b>1h</b> CH <sub>3</sub>	<b>2b 3p</b>	64
17 <sup>f</sup>	H	OMe	OMe	OMe	<b>1k</b> CH <sub>3</sub>	<b>2b 3q</b>	81
18 <sup>f</sup>	H	OMe	OMe	OMe	<b>1k</b> CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub>	<b>2c 3r</b>	91
19	H	H	H	H	<b>1a</b> CH <sub>3</sub> (CH <sub>2</sub> ) <sub>9</sub>	<b>2d 3s</b>	71
20	H	OMe	OMe	OMe	<b>1k</b> CH <sub>3</sub> (CH <sub>2</sub> ) <sub>9</sub>	<b>2d 3t</b>	92

<sup>a</sup> Reaction condition: **1** (0.2 mmol), **2** (0.5 mmol), AuNPs/SiO<sub>2</sub> (Au: 5 mol %), toluene (10 mL), O<sub>2</sub> bubbling, 110 °C, *t* = 21 h; unless otherwise stated. <sup>b</sup> Yield was determined by <sup>1</sup>H-NMR using Ph<sub>2</sub>C=CH<sub>2</sub> as the internal standard and calculated based on the amount of **1** added. <sup>c</sup> The ratio of 7-isomer (**3d-7**) and 5-isomer (**3d-5**) was 6:1. <sup>d</sup> The ratio of 7-isomer (**3j-7**) and 5-isomer (**3j-5**) was 9:1. <sup>e</sup> **2a** (1 mmol) and AuNPs/SiO<sub>2</sub> (Au: 10 mol %) was used. <sup>f</sup> **2** (1 mmol) was used. Reaction was performed under O<sub>2</sub> atmosphere (1 atm) instead of O<sub>2</sub> bubbling.

FIG. 7

Entry	Polycyclic aniline	Aldehyde	Product	Yield (%) <sup>b</sup>
1	 4a	2a	 5a	85
2	 4b	2a	 5b	93
3	 4c	2a	 5c	96
4	 4d	2a	 5d	80
5	 4e	2a	 5e	82
6	 4f	2a	 5f	82
7	 4g	2a	 5g	65
8	 4h	2a	 5h-1 &  5h-2	82 <sup>c</sup>
9	 4i	2a	 5i	62
10	 4j	2a	 5j	83

<sup>a</sup> Reaction condition: **4** (0.2 mmol), **2a** (0.5 mmol), AuNPs/SiO<sub>2</sub> (Au: 5 mol %), toluene (10 mL), O<sub>2</sub> bubbling, 110 °C, *t* = 21 h; unless otherwise stated. <sup>b</sup> Yield was determined by <sup>1</sup>H-NMR using Ph<sub>2</sub>C=CH<sub>2</sub> as the internal standard and calculated based on the amount of **4** added. <sup>c</sup> The ratio of **5h-1** and **5h-2** was 2:1.

FIG. 8

**SOLID SUPPORTED GOLD  
NANOPARTICLES, METHODS OF USE  
THEREOF, AND METHODS FOR MAKING  
SAME**

CROSS-REFERENCE TO RELATED  
APPLICATIONS

This application claims priority to provisional application Ser. No. 61/334,804 filed on May 14, 2010, the entire contents of which is incorporated herein by reference.

TECHNICAL FIELD

Described are improved catalysts of gold nanoparticles, methods for making such catalysts including silicon dioxide (silica) supported gold nanoparticles, methods for synthesizing quinolines using such nanoparticles, and methods for making silicon dioxide supported gold nanoparticles.

BACKGROUND

Quinolines are prevalent in natural product chemistry, and are important building blocks in organic synthesis, drug discovery and materials science. Owing to their importance, various named reactions are used, including Combes quinolines synthesis, Conrad-Limpach synthesis, Doebner-Miller reaction, Friedlander synthesis, Povarov reaction, Camps quinolines synthesis, Knorr quinolines synthesis and Gould-Jacobs reaction. However, most of these reactions involve strong acid, toxic chemicals (nitrobenzene and iodine) and high temperature reactions, even though they lead to low yields. Although the use of an iridium catalyst might circumvent this problem, this homogeneous catalyst is difficult to recover and recycle. The high cost of iridium metal might also detract from its use. Thus, there is an urgent need to develop a recyclable catalytic system, preferably that uses non-toxic reagents in the synthetic reactions.

U.S. Pat. No. 6,103,904 (Eva) discusses iodide and iodide salts (such as sodium and potassium iodide) to synthesize quinolones. These catalysts appear to require high pressure and temperature and use of toxic oxidizing agents including nitroaromatics and arsenic compounds. U.S. Pat. No. 5,700,942 (McAteer) discusses a process for preparing quinoline bases using non-metal catalysts including amorphous silica-alumina or zeolite. The reactions occur in vapor phase, and appear to require high temperature (400 to 550° C.). U.S. Pat. No. 4,617,395 (Dockner) relates to preparation of quinolines, but requires high boiling mineral oil (b.p. above 150° C.), and use a non-metal organic acid as a catalyst. The aldehydes useful in the method appear limited to  $\alpha$ ,  $\beta$ -monosaturated aldehyde, and require stoichiometric amounts of an oxidant which may be toxic, such as nitrobenzene, arsenic pentoxide, or iron (II) chloride.

Other more recent approaches to quinoline synthesis have included iridium complexes T. Igarishi, et al., *Chem. Lett.* 2005, 34, 106-07; T. Nakajima, et al., *Bull. Chem. Soc. Jan.* 2006, 79, 1941-49), or acid catalyzed synthesis of anilines with aldehydes to quinolines (S.-Y. Taualea, *J. Org. Chem.* 2006, 71, 800-03.). For general reviews on the synthesis of quinolines see Li, J. J. (ed.), *Name Reactions in Heterocyclic Chemistry*, Wiley-Interscience, Hoboken, N.J., 2005, pp. 35-494; J. A. Joule K. Mills *Heterocyclic Chemistry*, Wiley-Blackwell Oxford, 2010, pp. 188-198. The foregoing references are incorporated herein by reference. M. Sainsbury, *Heterocyclic Chemistry*, Royal Soc. Chem., Cambridge 2001, pp. 43-50; R. F. Manske, *Chem. Rev.* 1942, 30, 113-14.

The foregoing methods involve strenuous reaction conditions, toxic reactants, low yields, environmentally unfriendly methods, catalysts, or reactants, or a combination of the foregoing.

SUMMARY

The disadvantages of prior techniques are effectively addressed by the disclosure herein. This disclosure aims to develop an environmentally friendly catalytic system to synthesize quinolines using nanotechnology and an application of metal nanoparticles as catalysts for organic transformations. Because of its high surface area and high density of active sites, metal nanoparticles exhibit superior catalytic activities compared with the corresponding bulk materials. Among various gold catalysts examined, AuNPs/SiO<sub>2</sub> is the most effective catalyst for the synthesis of quinolines from aniline and aldehydes. The oxidant used for this reaction is oxygen, which is cheap and do not produce waste. In addition, AuNPs/SiO<sub>2</sub> can be easily recycled by centrifugation, and reused for seven times without significant deterioration of yields and selectivities. The same system can be used to synthesize nitrogen containing polyheterocyclic compounds.

Described herein are solid-supported gold nanoparticles for use as a catalyst for the synthesis of quinolines from anilines and aldehydes using oxygen as an oxidant. Also provided herein is a new method for the preparation of SiO<sub>2</sub>-supported gold nanoparticles by in situ deposition of gold nanoparticles to silica gel. Also provided herein is a method for synthesizing quinolines from anilines and aldehydes using oxygen as an oxidant.

Briefly, a composition of silica-supported gold nanoparticles as an efficient and recyclable catalyst for the synthesis of quinolines from anilines to aldehydes is provided. The catalyst composition can be easily prepared by the reaction of KAuCl<sub>4</sub> and 4-methoxybenzylamine in the presence of SiO<sub>2</sub> in a refluxing toluene solution. Recyclable silica-supported gold nanoparticles (27.9±3.0 nm) effectively catalyze the aerobic oxidation of anilines with aldehydes to quinolines with yields up to 96% (30 examples).

BRIEF DESCRIPTION OF THE FIGURES AND  
TABLES

FIG. 1 illustrates the proposed mechanism for the oxidative cyclization reaction catalyzed by AuNPs/SiO<sub>2</sub>.

FIG. 2 shows (a) powder XRD pattern and (b) TEM image of AuNPs/SiO<sub>2</sub>.

FIG. 3 shows the chemical structures of Au(NHC)Cl, [Au(Salen)]PF<sub>6</sub>, [Au(TPP)]Cl and Au(PPh<sub>3</sub>)Cl complexes.

FIG. 4 shows a typical TEM image of AuNPs/SiO<sub>2</sub> after the seventh recycling run.

FIG. 5 provides representative metal catalyst for the aerobic oxidative cyclization reaction.

FIG. 6 illustrates the recyclability of AuNPs/SiO<sub>2</sub> towards aerobic oxidative cyclization reaction.

FIG. 7 illustrates representative examples of quinolines by the used of "AuNPs/SiO<sub>2</sub>+O<sub>2</sub>" protocol.

FIG. 8 illustrates representative examples of nitrogen-containing polyheterocyclic compounds by the use of "AuNPs/SiO<sub>2</sub>+O<sub>2</sub>" protocol.

DETAILED DESCRIPTION

Commonly, gold nanoparticles (AuNPs) can be produced in a liquid by reduction of chloroauric acid (HAuCl<sub>4</sub>), although other methods exist. After dissolving chloroauric

acid, the solution is stirred while a reducing agent is added. This causes Au<sup>3+</sup> ions to be reduced to form neutral gold atoms. As more and more of these gold atoms form, the solution becomes supersaturated, and gold gradually starts to precipitate in the form of sub-nanometer particles. The rest of the gold atoms that form stick to the existing particles, and, with increased levels of stirring, the particles have a fairly uniform size, while decreased levels of stirring provide with a range in size.

To prevent the particles from aggregating, an optional stabilizing agent can be added. The AuNPs can be functionalized with various organic ligands to create organic-inorganic hybrids with desired functionality.

The AuNPs have a size that facilitates the synthesis of quinolines. In one embodiment, AuNPs have an average size from 1 nm to 100 nm. In another embodiment, AuNPs have an average size from 5 nm to 75 nm. In yet another embodiment, AuNPs have an average size from 10 nm to 50 nm.

The AuNPs have a monodispersity in the silica that facilitates the synthesis of quinolines. In one embodiment, the AuNPs have a monodispersity in the silica from 1% to 40%. In another embodiment, the AuNPs have a monodispersity in the silica from 2% to 30%. In yet another embodiment, the AuNPs have a monodispersity in the silica from 5% to 20%.

Quinoline is a heterocyclic aromatic organic compound having the chemical formula C<sub>9</sub>H<sub>7</sub>N. For purposes herein, however, quinoline encompasses not only quinoline but also substituted and non-substituted quinolines, hydrogenated quinolines, dehydrogenated quinolines, quinoline analogs, polyquinolines, and the like.

Generally speaking, aniline and an aldehyde are reacted in the presence of a AuNPs/SiO<sub>2</sub> catalyst to form a quinoline. In a manner similar to the interpretation of quinoline, both aniline and aldehyde encompass substituted and non-substituted anilines and substituted and non-substituted aldehydes. Substituents for any of quinolines, anilines and/or aldehydes include alkyl groups, alkenyl groups, aromatic groups, aryl groups, heteroatom containing groups such as hydroxyl groups, alkoxy groups, hydroxylalkyl groups, amino groups, aminoalkyl groups, alkylamino groups, phenyl groups, and the like.

The substituents, when containing carbon, can contain from 1 to 18 carbon atoms. Any of the substituted quinolines, anilines and/or aldehydes can have one or more (such as two or more, three or more) substituents thereon.

Examples of aldehydes include formaldehyde, acetaldehyde, propionaldehyde, and butyraldehyde, although many others exist. Examples of substituted anilines include 2-methylaniline and N,N-dialkylanilines such as N,N-dimethylaniline.

An oxidant such as oxygen (or oxygen generating species) is provided to the aniline-aldehyde reaction to facilitate formation of the quinoline. Oxygen can simply be bubbled through the reaction mixture. The reaction takes place in any suitable solvent, such as an organic solvent. The solvent is selected based on balancing the specific solubilities of the aniline, the aldehyde, and resultant quinoline. Examples of solvents include aromatic hydrocarbons such as benzene, toluene and xylene; halogenated hydrocarbons such as dichloromethane, chloroform, carbon tetrachloride, dichloroethane, chlorobenzene and dichlorobenzene; ethers such as diethyl ether, diisopropyl ether, tetrahydrofuran, dioxane, dimethoxyethane and diethyleneglycoldimethyl ether; amides such as formamide, N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidinone and hexamethylphosphorotriamide; or a solvent mixture of these can be mentioned.

The gold loading on SiO<sub>2</sub> is effective to facilitate the synthesis of quinolines. In one embodiment, the gold loading on silica is from 0.001 mmol/g to 100 mmol/g. In another embodiment, the gold loading on silica is from 0.01 mmol/g to 10 mmol/g. In another embodiment, the gold loading on silica is from 0.05 mmol/g to 1 mmol/g. Gold loading on silica can be determined by inductively coupled plasma-mass spectrometry (ICP-MS).

The AuNPs/SiO<sub>2</sub> catalyst has any size that facilitates the synthesis of quinolines. In one embodiment, the AuNPs/SiO<sub>2</sub> catalyst has an average particle size from 5 nm to 1 micron. In another embodiment, the AuNPs/SiO<sub>2</sub> catalyst has an average particle size from 10 nm to 0.5 micron. In yet another embodiment, the AuNPs/SiO<sub>2</sub> catalyst has an average particle size from 25 nm to 0.25 micron.

This disclosure relates to the use of SiO<sub>2</sub>-supported gold nanoparticles (AuNPs/SiO<sub>2</sub>) for the practical synthesis of quinolines. AuNPs/SiO<sub>2</sub> catalyst was prepared as follows: 4-methoxybenzylamine (1 mmol) was added into a refluxing toluene solution containing KAuCl<sub>4</sub> (0.1 mmol) and SiO<sub>2</sub> (1 g) and allowed to react for 6 h. The resulting solid was washed with piranha solution (30% H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>SO<sub>4</sub>=1/3 v/v) to remove residual organic substance capped onto the surface of AuNPs. After washing with water and centrifugation, AuNPs/SiO<sub>2</sub> particles were obtained as a brick red powder. The gold loading on SiO<sub>2</sub> was 0.1 mmol/g as revealed by inductively coupled plasma-mass spectrometry (ICP-MS). The presence of metallic gold on SiO<sub>2</sub> was confirmed by powder X-ray diffraction (XRD) (FIG. 1a), and the average diameter and monodispersity of the AuNPs were 27.7±2.9 nm and 11% respectively, as depicted from the transmission electron microscopy (TEM) image (FIG. 1b).

#### EXAMPLE 1

##### Catalytic Activity Screening

We screened the catalytic activities of various solid-supported AuNPs and gold salts towards the oxidative cyclization of 1a with 2a to give 3a using oxygen as an oxidant (Table 1). Among various gold catalysts, AuNPs/SiO<sub>2</sub> was the most active catalyst (entry 1). Similar product yield was found for AuNPs/SiO<sub>2</sub>-1 catalyst prepared according to Rossi's method (entry 2).<sup>3a</sup> Low product yields of 3a were obtained when other solid-supported AuNPs catalysts were used (entries 3-7). Notably, reference catalysts from World Gold Council AuNPs/Fe<sub>2</sub>O<sub>3</sub> (Sample No. 104C) and AuNPs/TiO<sub>2</sub> (Sample No. 168A) were inactive in this oxidative cyclization reaction (entries 5-6). Bulk gold powder (2-5 μm) was inactive under the employed reaction conditions (entry 8). KAuCl<sub>4</sub> and AuCl gave moderate yields of 3a (entries 9-10), but they could not be recycled. It should be noted that SiO<sub>2</sub> alone gave 3a in 38% yield accompanied with an equimolar amount of N-(3-phenylpropyl)benzenamine (formed by the reduction of imine) (entry 11), indicating that AuNPs plays a key role in catalyzing the aerobic oxidation. No product was found in the absence of gold catalyst (entry 12).

The organometallic gold complexes were also examined, but they showed no catalytic activities towards the oxidative cyclization reaction (entries 13-16). The chemical structures of these organometallic gold complexes are shown in FIG. 2. Other coinage group metal salts such as AgNO<sub>3</sub> and CuI were found to be catalytically inactive (entries 17-18).

#### EXAMPLE 2

##### Recycling Experiment

AuNPs/SiO<sub>2</sub> can be recovered by centrifugation and reused for seven consecutive runs without a significant loss of

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reactivity (Table 2). No significant change of the average particle size and monodispersity of the AuNPs were noted after each consecutive run. The average particle size and monodispersity of the AuNPs on SiO<sub>2</sub> after the seventh run were 27.9±3.0 nm and 10.8% respectively (FIG. 3). It is necessary to rinse the recovered AuNPs/SiO<sub>2</sub> catalyst with piranha solution before each recycling. Presumably, acid treatment can remove the organic impurity capped onto the surface of AuNPs and regenerate the active Au<sup>δ+</sup> sites. Indeed, X-ray photoelectron spectroscopy (XPS) analysis revealed that there was an increase of binding energy from 83.9 eV to 84.4 eV (Au 4f<sub>7/2</sub>) after the acid treatment, indicating a higher portion of Au<sup>δ+</sup> species on the surface of the AuNPs.

## EXAMPLE 3

## Synthesis of Substituted Quinolines

Next, we examined the substrate scope of the “AuNPs/SiO<sub>2</sub>+O<sub>2</sub>” protocol. As depicted in Table 3, this protocol could effectively catalyze the cyclization of a variety of substituted anilines 1a-n with 2a to give 3a-n with product yields up to 95% (entries 1-14). Good to excellent product yields were obtained when anilines with electron-donating substituent were used (entries 1-13). Cyclization of o-tolidine 1m, which contains two aniline groups, gave the corresponding di-quinoline 3m with moderate yield (entry 13). Anilines with electron-donating substituent (CH<sub>3</sub> or OCH<sub>3</sub>) at the meta-position gave better product yields than that of ortho- or para-substituted anilines (compare entries 4 and 10 with entries 3, 5 and 9). In containing an electron-deficient group gave poor product yield (entry 14). The oxidative cyclization of 1d or 1j with 2a both gave a mixture of 7- and 5-isomers in the ratios of 6:1 (3d-7:3d-5) and 9:1 (3j-7:3j-5) respectively, and similar selectivities have been reported in the related Ir-catalyzed reactions.<sup>13b</sup>

Apart from 2a, alkyl aldehydes 2b-d could also be used as the substrates (Table 3, entries 15-20). Relatively lower product yields of quinolines 3o-q are attributed to evaporation of the low boiling propanal 2b (46-50° C.) in the course of the reaction at 110° C. (entries 15-17). With high boiling aldehyde (2c-d), corresponding quinolines 3r-t were obtained in better yields (entry 18-20).

## EXAMPLE 4

## Synthesis of Nitrogen-Containing Polyheterocyclic Compounds

The “AuNPs/SiO<sub>2</sub>+O<sub>2</sub>” protocol is also applicable to the synthesis of nitrogen-containing polyheterocyclic compounds 5a-j using polycyclic anilines 4a-j with good to excellent product yields (Table 4). This protocol is effective even with bulky aniline 4j, resulting in polyheterocyclic compound 5j having five fused rings in 83% yield (entry 10). All of these results suggest that the “AuNPs/SiO<sub>2</sub>+O<sub>2</sub>” protocol is competent for preparing nitrogen-containing polyheterocyclic compounds, which can be used as chelating ligands for the design of cyclometalated transition metal complexes with novel materials and light emitting properties.

## EXAMPLE 5

## Mechanistic Studies

To get insight into the reaction mechanism, a radical trap experiment was performed. Addition of the radical scavenger

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2,6-di-tert-butyl-4-methylphenol (5 equiv. to aniline 1a) to the reaction mixture did not significantly affect the yield of 3a (73% yield). We propose that the mechanism of the oxidative cyclization is a Lewis acid-catalyzed reaction through initial imine condensation and Mannich reaction, similar to the previous reports by Shimizu,<sup>13b</sup> and Baba,<sup>13c</sup> using [IrCl<sub>2</sub>H(cod)]<sub>2</sub> and “HCl+DMSO” as catalyst (Scheme 1). The AuNPs/SiO<sub>2</sub> functions as a Lewis acid catalyst for the cyclization, while the AuNPs can catalyze the aerobic oxidation of 1,2-dihydroquinoline to 3.

## EXAMPLE 6

## Instrumental Analysis

In addition to electron microscopy and x-ray diffraction study, we have characterized the AuNPs/SiO<sub>2</sub> by x-ray photoelectron spectroscopy (XPS), selected area electron diffraction (SAED) and energy-dispersive X-ray microanalysis. Especially, XPS analysis of the AuNPs/SiO<sub>2</sub> catalyst showed a binding energy of 84.4 eV, revealing a higher portion of Au<sup>δ+</sup> species on the surface of the AuNPs. The binding energy of bulk gold metal is 84.0 eV [*Handbook of X-ray Photoelectron Spectroscopy* (Eds.: J. Chastain, R. C. King), Physical Electronic, Eden Prairie, Minn. (1995)]. Both XRD and SEAD analyses strongly indicated that metallic gold particles were grafted on the SiO<sub>2</sub> surface. The gold loading on SiO<sub>2</sub> was 0.1 mmol/g as determined by inductively coupled plasma-mass spectrometry (ICP-MS).

With respect to any figure or numerical range for a given characteristic, a figure or a parameter from one range may be combined with another figure or a parameter from a different range for the same characteristic to generate a numerical range.

Other than in the operating examples, or where otherwise indicated, all numbers, values and/or expressions referring to quantities of ingredients, reaction conditions, etc., used in the specification and claims are to be understood as modified in all instances by the term “about.”

The embodiments as disclosed and described in the application are intended to be illustrative and explanatory, and not limiting. Modifications and variations of the disclosed embodiments, for example, of the processes and apparatuses employed (or to be employed) as well as of the compositions and treatments used (or to be used), are possible; all such modifications and variations are intended to be within the scope of this application.

What is claimed is:

1. A catalyst composition, comprising: gold nanoparticles on a silica gel support, wherein gold loading on silica gel is from 0.001 mmol/g to 100 mmol/g; and the gold nanoparticles have a monodispersity in the silica gel from 1% to 40%.
2. A catalyst composition according to claim 1, wherein the gold nanoparticles have an average size from about 1 nm to 100 nm.
3. A catalyst composition according to claim 1, wherein the gold nanoparticles have an average size from about 5 nm to 75 nm.
4. A catalyst composition according to claim 1, wherein the gold loading on silica gel is from 0.01 mmol/g to 10 mmol/g.
5. A catalyst composition according to claim 1, wherein the gold nanoparticles have a monodispersity in the silica gel from 2% to 30%.

6. A catalyst composition according to claim 1, wherein the gold nanoparticles have a monodispersity in the silica gel from 5% to 20%.

7. A catalyst composition according to claim 1, further having an average particle size from 5 nm to 1 micron. 5

8. A catalyst composition according to claim 1, further having an average particle size from 10 nm to 0.5 micron.

\* \* \* \* \*