Received: 26 February 2016

Revised: 7 April 2016

(wileyonlinelibrary.com) DOI 10.1002/aoc.3511

Accepted: 17 April 2016

Applied Organometallic

Chemistry

A green approach for the synthesis of 2oxazolidinones using gold(I) complex immobilized on KCC-1 as nanocatalyst at room temperature

Seyed Mohsen Sadeghzadeh*

A novel gold(I)-containing ionic liquid-based KCC-1 catalyst was applied for the cyclization of propargylic amines with CO_2 to provide 2-oxazolidinones. High catalytic activity and ease of recovery from the reaction mixture using an external magnet, and several recycle runs without significant loss in performance are additional eco-friendly attributes of this catalytic system. Copyright © 2016 John Wiley & Sons, Ltd.

Additional supporting information may be found in the online version of this article at the publisher's web site.

Keywords: KCC-1; nanocatalyst; one-pot synthesis; green chemistry; fibrous nanosilica

Introduction

Organic shell-inorganic core composite particles have received a lot of attention in a wide range of industrial fields due to their functional properties, high dispersibility and stability after a certain thickness of polymer coating. The core-shell nanostructure is an ideal composite system that combines the advantages of both the core and the shell to offer enhanced physical and chemical properties. In recent years, Fe₃O₄ magnetic nanoparticles (MNPs) have been extensively investigated as inorganic cores for the synthesis of organic-inorganic core-shell composite particles, due to their potential applications in many industrial and biological fields.^[1-13] Fe₃O₄ nanoparticles are naturally hydrophilic because of the existence of plentiful hydroxyl groups on the particle surface. Since they are prone to aggregate and their dispersion in organic media is difficult, the surface coating or modification of iron oxide nanoparticles is very important in many applications. Surfacefunctionalized mesoporous materials have emerged as one of the most important research areas in the field of advanced functional materials. Fibrous nanosilica (KCC-1), which features a high surface area and easy accessibility through its fibres (as opposed to the traditional use of pores), has been reported by Polshettiwar et al.^[14]

Development of green processes based on chemical stabilization of carbon dioxide has received a great deal of interest in recent years because CO₂ could be used as a safe, cheap and renewable C₁ building block to synthesize useful organic compounds. Various useful chemicals, such as dimethyl carbonate,^[15] urethanes,^[16] formic acid,^[17] methanol,^[18] cyclic carbonates,^[19] polycarbonates^[20] and others have been prepared by using CO₂ as a feedstock. One of the useful developments in which CO₂ has been utilized as a substrate is through the carboxylative cyclization of propargylic amines to provide 2-oxazolidinones.^[21] 2-Oxazolidinones are important heterocyclic chemicals playing an important role as chemical intermediates^[22] and chiral auxiliaries^[23] in organic synthesis, and as antibacterial drugs^[24] in pharmaceutical chemistry. One of the most promising examples of CO₂ fixation to access 2-oxazolidinones is the carboxylative cyclization of propargylic amines with CO₂, which represents an important clean and atom-economic reaction.

Gold catalysis has quickly become a hot topic in chemistry in the past decade.^[25] Gold species are equally impressive as heterogeneous or homogeneous catalysts,^[26,27] which show excellent results in diverse reactions.^[28,29] Gold complexes have been employed as highly efficient catalysts for the formation of C–O, C–C, C–S, C–N, C–P and C–F bonds starting from alkenes and alkynes.^[30–32] From the viewpoint of reactivity, gold complexes in-volving phosphorus ligands are one of the reactive classes of gold catalysts. Supporting these ligands on a recyclable support is one of the most important approaches for improving their applicability in organic reactions.^[33] In recent years, it has been revealed that the use of gold complexes grafted on solid supports plays an important role in preventing the aggregation of gold.^[34]

Herein, we report a simple and efficient synthesis of a nanoferrite-supported, magnetically recyclable and ionic liquid catalyst and a study of the effectiveness of KCC-1 for the performance of a new magnetic catalyst. The superior performance of the Fe₃O₄/KCC-1/tetrazolylidene/Au catalyst has been attributed to gold complex units incorporated into the fibres, which prevent the formation of agglomerated gold whilst maintaining

^{*} Correspondence to: Seyed Mohsen Sadeghzadeh, Department of Chemistry, College of Sciences, Sina Masihabadi Student Research, Neishabour, Iran. E-mail: seyedmohsen.sadeghzadeh@gmail.com

Department of Chemistry, College of Sciences, Sina Masihabadi Student Research, Neishabour, Iran

the catalytic activity of gold species. Considering the importance of the chemical stabilization of carbon dioxide as well as the remarkable properties of gold(I) complex-based nanomaterials in organic transformations, we prepared a novel bis (tetrazolylidene)-functionalized ordered mesofibre organosilica using 3-chloropropyltriethoxysilane material by and tetramethoxysilane as silica precursors on a magnetic core (Fe₃O₄/KCC-1/tetrazolylidene). The Fe₃O₄/KCC-1/tetrazolylidene material was then used as an efficient support for the immobilization of gold(I) (Fe₃O₄/KCC-1/tetrazolylidene/Au) as a catalyst for the synthesis of 2-oxazolidinone Scheme 1. The recyclability, reusability and stability of the catalyst were also investigated.

Results and discussion

We report the synthesis of a MNP-based solid gold(I) complex with a high density of gold(I) groups and discuss its performance as a novel strong and stable magnetic nanocatalyst.

The morphologies and structural features of Fe₃O₄, Fe₃O₄/SiO₂ and Fe₃O₄/KCC-1/tetrazolylidene/Au MNPs were evaluated using transmission electron microscopy (TEM) images (Fig. 1). The average size of Fe₃O₄ MNPs is about 10–20 nm (Fig. 1(a)). After being coated with a SiO₂ layer, the typical core–shell structure of the Fe₃O₄/SiO₂ MNPs can be observed. The dispersity of Fe₃O₄/SiO₂



Scheme 1. Synthesis of 2-oxazolidinone in the presence of Fe $_3O_4/KCC-1/$ tetrazolylidene/Au MNPs.

MNPs is also improved, and the average size increases to about 35–45 nm (Fig. 1(b)). As expected, uniform and monodisperse Fe₃O₄/KCC-1/tetrazolylidene/Au materials with radial-like channels, as shown in Fig. 1(c), were synthesized successfully. The length of the silica fibres coming out of the centre of Fe₃O₄/KCC-1/tetrazolylidene/Au and distributed in all directions is estimated to be 180–200 nm (Fig. 1(c)). The TEM image shown in Fig. 1(c) further clarifies that the distance between two fibres is about 10–15 nm. Comparison of TEM image of used catalyst (Fig. 1(d)) with that of fresh catalyst (Fig. 1(c)) shows that the morphology and structure of Fe₃O₄/KCC-1/tetrazolylidene/Au MNPs remain intact after ten recoveries. Agglomeration of Fe₃O₄/KCC-1/tetrazolylidene/Au MNPs can be seen.

The successful synthesis of the Fe₃O₄/KCC-1/tetrazolylidene/ Au MNPs was confirmed from Fourier transform infrared (FT-IR) spectra (Fig. 2). The peaks at 3415 and 590 cm⁻¹ appear in all FT-IR spectra, which are assigned to the –OH group and the Fe–O group, respectively (Fig. 2(a)). In the FT-IR spectrum of the Fe₃O₄/KCC-1 MNPs, the absorption intensity of Fe–O group decreases with the addition of silica portion and a strong absorption band of the Si–O–Si group appears at 1090 cm⁻¹ owing to the silica coat (Fig. 2(b)). The O–H stretching vibration at 3415 cm⁻¹, the Si–O stretching at 1110 cm⁻¹, the C=N stretching at 1635 cm⁻¹ and CH₂ stretching at 2905 cm⁻¹ are observed for the Fe₃O₄/KCC-1/tetrazolylidene/Au MNPs (Fig. 2(c)). These results indicate that the organic compound had been successfully introduced onto the surface of KCC-1.

The structural properties of synthesized $Fe_3O_4/KCC-1/$ tetrazolylidene/Au MNPs were analysed using powder X-ray diffraction (XRD). As shown in Fig. 3, XRD pattern of the synthesized $Fe_3O_4/KCC-1/tetrazolylidene/Au$ MNPs displays several relatively strong reflection peaks in the 2θ range 20–70°, which is quite similar to those of Fe_3O_4 nanoparticles reported by other groups. The six discernible diffraction peaks in Fig. 3(a) can be indexed to (220),



Figure 1. TEM images of Fe_3O_4 (a), Fe_3O_4/SiO_2 (b), $Fe_3O_4/KCC-1/$ tetrazolylidene/Au MNPs (c) and $Fe_3O_4/KCC-1/$ tetrazolylidene/Au MNPs after ten runs (d).



Figure 2. FT-IR spectra of Fe_3O_4 MNPs (a), Fe_3O_4/KCC-1 MNPs (b) and Fe_3O_4/KCC-1/tetrazolylidene/Au MNPs (c).



Figure 3. XRD analysis of Fe $_3O_4$ MNPs (a), Fe $_3O_4$ /KCC-1 MNPs (b) and Fe $_3O_4$ /KCC-1/tetrazolylidene/Au MNPs (c).

(311), (400), (422), (511) and (440) which match well with the database of magnetite in JCPDS (card no. 19–0629) file. Besides the peak of iron oxide, the XRD pattern of $Fe_3O_4/KCC-1$ core–shell nanoparticles presents a broad featureless peak at low diffraction angle, which corresponds to amorphous silica (Fig. 3(b)). Figure 3(c) shows a typical XRD pattern of the $Fe_3O_4/KCC-1/$ tetrazolylidene/Au MNPs indicating that there is no change in it.

The thermal behaviour of Fe₃O₄/KCC-1/tetrazolylidene/Au MNPs is shown in Fig. 4. A significant decrease in the weight percentage of the Fe₃O₄/KCC-1/tetrazolylidene/Au MNPs at about 130 °C is related to desorption of water molecules from the catalyst surface. This is evaluated to be 1–3% according to the thermogravimetric analysis (TGA). In addition, the analysis shows two other decreasing peaks. The first peak appears at around 250–280 °C due to the decomposition of gold. This is followed by a second peak at 420–620 °C, corresponding to the loss of the organic group derivatives.

The magnetic properties of the nanoparticles were characterized using a vibrating sample magnetometer. The magnetization curves of the obtained nanocomposite recorded at 300 K show nearly no residual magnetism (Fig. 5), which means that the nanocomposite exhibits paramagnetic characteristics. Magnetic measurement shows that pure Fe₃O₄, and Fe₃O₄/KCC-1/tetrazolylidene/Au MNPs have saturation magnetization values of 46.2 and 16.8 emu g⁻¹, respectively. These nanocomposites with paramagnetic characteristics and high magnetization values can quickly respond to an external magnetic field and quickly redisperse once the external magnetic field is removed. The result reveals that the



Figure 4. TGA diagram of Fe₃O₄/KCC-1/tetrazolylidene/Au MNPs.



Figure 5. Room-temperature magnetization curves of Fe_3O_4 and $Fe_3O_4/$ KCC-1/tetrazolylidene/Au MNPs.

nanocomposite exhibits good magnetic response, which suggests a potential application for targeting and separation.

First examined was the effect of solvent on the synthesis of 2-oxazolidinone from propargylic amine and CO₂ using the Fe₃O₄/KCC-1/tetrazolylidene/Au MNPs at 1.5 atm and heating under reflux (Table 1). Solvent does have an effect on catalyst performance. n-Hexane, a non-polar solvent, gives 2-oxazolidinone in a lower yield than that obtained under solvent-free conditions (Table 1, entries 9 and 15). CH₃CN, tetrahydrofuran (THF), CH₂Cl₂, dimethylformamide (DMF), toluene, dioxane, CHCl₃, EtOAc and dimethylsulfoxide (DMSO), aprotic polar solvents, also give 2oxazolidinone in low yields. These results suggest that the aprotic polar solvents cannot activate propargylic amine. The reaction was better in protic solvent. i-PrOH and ethanol give 2oxazolidinone in average yields (Table 1, entries 13 and 14). In contrast, the use of methanol results in an increased yield of 75%, and the yield is markedly increased up to 94% when H₂O is used as the solvent. The protic solvents can activate propargylic amine

Table 1. Synthesis of 2-oxazolidinone catalysed by Fe_3O_4/KCC-1/ tetrazolylidene/Au MNPs in various solvents $^{\rm a}$							
Entry	Solvent	Yield (%) ^b					
1	Dioxane	16					
2	H ₂ O	94					
3	CH ₃ CN						
4	THF	23					
5	CH ₂ Cl ₂	30					
6	EtOAc	41					
7	DMF	25					
8	Toluene	31					
9	<i>n</i> -Hexane	11					
10	CHCl₃	43					
11	DMSO	34					
12	MeOH	75					
13	EtOH	69					
14	i-PrOH	63					
15	Solvent-free	23					

^aReaction conditions: propargylic amine (1 mmol), Fe₃O₄/KCC-1/ tetrazolylidene/Au MNPs (0.2 mg) and CO₂ (1.5 MPa), under reflux of solvents after 48 h. ^bIsolated yield.

via hydrogen bonds formed between the hydroxyl and the acetylene groups. In this study, it is found that water is more efficient (Table 1, entry 2) compared to other organic solvents.

At this stage, the amount of catalyst necessary to promote the reaction efficiently was examined. It is observed that the variation of the amount of $Fe_3O_4/KCC-1/tetrazolylidene/Au$ MNPs has an effective influence. The best amount of $Fe_3O_4/KCC-1/tetrazolylidene/Au$ MNPs is 0.08 mg which affords the desired product in 94% yield (Fig. 6). Using this catalyst system, excellent yields of 2oxazolidinone can be achieved in 18 h and in the presence of 0.08 mg of $Fe_3O_4/KCC-1/tetrazolylidene/Au$ MNPs (Fig. 7).

Also investigated was the crucial role of temperature and pressure in the fixation of CO₂ with propargylic amine in the presence of Fe₃O₄/KCC-1/tetrazolylidene/Au MNPs as a catalyst. It is clear that the catalytic activity is not sensitive to reaction temperature. The best temperature for this reaction is room temperature. Temperatures greater than room temperature do not cause changes in the efficiency of the reaction. Pressure is a significant parameter with respect to safety concerns and connected costs, especially for industrial plants. Hence, conversion at low pressures is desirable. To investigate the effect of pressure, the conversion of propargylic amine was examined at 0-1.4 bar CO₂ pressure and under isobaric conditions (Fig. 8). In the pressure range 0.4–1.4 bar, there is no notable effect of pressure on the yield of 2-oxazolidinone in the presence of Fe₃O₄/KCC-1/tetrazolylidene/Au MNPs (blue line). These results indicate that the synthesis of 2-oxazolidinone in the presence of Fe₃O₄/SiO₂/tetrazolylidene/Au MNP (red line) had already been realized in excellent yields (94%) with a constant pressure (\geq 0.8 bar). However, by performing the reaction at extremely low pressures (≤0.5 bar), conversions and yields decrease significantly to 0%. This



Figure 6. Effect of increasing amount of $Fe_3O_4/KCC-1/tetrazolylidene/Au$ MNPs on yield of 2-oxazolidinone.



Figure 7. Effect of time on yield of 2-oxazolidinone.



Figure 8. Effect of pressure on yield of 2-oxazolidinone.

prominent catalytic performance of Fe₃O₄/KCC-1/tetrazolylidene/Au MNPs as compared with Fe₃O₄/SiO₂/tetrazolylidene/Au MNPs might be attributed to a great extent to the crucial promoting effect of confined KCC-1 in obtaining high catalytic activity possibly through suppressing catalyst deactivation and enabling easy CO₂ delivery via a phase transfer mechanism. It should be noted that the promoting effect of tetrazolylidene on the catalyst performance is, however, closely dependent on its content inside the fibrous catalyst.

To further evaluate the efficiency of the catalyst, various control experiments were performed and the obtained data are summarized in Table 2. Firstly, the reaction was examined in the presence of Fe₃O₄ MNPs. The result of this study shows that any amount of the desired product was not formed (Table 2, entry 1). When Fe₃O₄/KCC-1 or Fe₃O₄/KCC-1/tetrazolylidene is used as the catalyst, a reaction is still not observed (Table 2, entries 2 and 3). Based on these frustrating results, research was continued to improve the yield of the product by the optimization of the reaction conditions. To our delight, the reaction proceeds smoothly with the use of Fe₃O₄/KCC-1/tetrazolylidene/Au MNPs and bis (1-benzyl-4-methyl-4,5-dihydro-1H-1,2,3,4-tetrazol-5-ylidene)gold(I) chloride (compound 1; Scheme 2) as homogeneous catalyst, and their catalytic activities are identical (Table 2, entries 4 and 5). The nano-sized particles increase the exposed surface area of the active component of the catalyst, thereby enhancing markedly the contact between reactants and catalyst and mimicking homogeneous catalysts. Also, the activity and selectivity of the nanocatalyst can be manipulated by tailoring chemical and physical properties like size, shape, composition and morphology. As a result, Fe₃O₄/KCC-1/tetrazolylidene/Au MNPs were used in the subsequent investigations because of their high reactivity, high selectivity and easy separation.

Table 2. Influence of different catalysts in the synthesis of 2-oxazolidinone ^a						
Entry	Catalyst	Yield (%) ^b				
1	Fe ₃ O ₄	_				
2	Fe ₃ O ₄ /KCC-1	—				
3	Fe ₃ O ₄ /KCC-1/tetrazolylidene	_				
4	Fe ₃ O ₄ /KCC-1/tetrazolylidene/Au	94				
5	Compound 1	94				
2						

^aReaction conditions: propargylic amine (1 mmol), catalyst (0.1 mg) and CO₂ (1.5 MPa), in water at room temperature after 24 h. ^bIsolated yield.

$$\left[\begin{array}{c} CH_{3} H_{3}C\\ N^{-N} & N^{-N}\\ \cdots & N^{-N}\\ N^{-N} & N^{-N}\\ CH_{2} H_{2}C\\ Ph & Ph \end{array}\right] CI^{-1}$$

Scheme 2. Structure of bis(1-benzyl-4-methyl-4,5-dihydro-1*H*-1,2,3,4-tetrazol-5-ylidene)gold(I) chloride (compound 1).

To assess the exact impact of the presence of KCC-1 in the catalyst, the Fe₃O₄/KCC-1/tetrazolylidene/Au MNPs were compared with Fe₃O₄/SiO₂/tetrazolylidene/Au MNPs. The loading amount of gold(I) in Fe₃O₄/KCC-1/tetrazolylidene/Au and Fe₃O₄/SiO₂/tetrazolylidene/Au was determined using inductively coupled plasma mass spectrometry (ICP-MS). The amount of gold(I) in Fe₃O₄/KCC-1/tetrazolylidene/Au is more than double the amount of gold(I) in Fe₃O₄/SiO₂/ tetrazolylidene/Au (Table 3). But it is interesting that, after reuse for ten consecutive cycles of catalysts, still the amount of gold(I) in Fe₃O₄/KCC-1/tetrazolylidene/Au MNPs is more than about double that in Fe₃O₄/SiO₂/tetrazolylidene/Au MNPs. This remarkable ability of the Fe₃O₄/SiO₂/tetrazolylidene/Au MNP mesostructure may be attributed to KCC-1 units that effectively manage the reaction through preventing gold agglomeration and releasing and recapturing gold during the reaction process.

Since $Fe_3O_4/KCC-1/tetrazolylidene/Au$ MNPs were the most active of the one-component catalysts, they were tested in the conversion of other terminal propargylic amines (**1a**–**h**) into the corresponding 2-oxazolidinones (**2a**–**h**) Scheme 1, the results being summarized in Table 4. In each case, the 2-oxazolidinones are obtained with good to excellent isolated yield after 18 h using 0.08 mg of catalyst under solvent-free conditions at room temperature under a constant pressure of carbon dioxide. Notably, benzene ring of the terminal position increases the reactivity for the

 Table 3. Loading amount of nanometric gold in Fe₃O₄/KCC-1/ tetrazolylidene/Au and Fe₃O₄/SiO₂/tetrazolylidene/Au MNPs

 Entry
 Catalyst
 Amount (wt%)

 1
 Fe₃O₄/SiO₂/tetrazolylidene/Au
 2.9

Fe ₃ O ₄ /KCC-1/tetrazolylidene/Au	0.0
Fe ₃ O ₄ /SiO ₂ /tetrazolylidene/Au after ten runs	1.9
$Fe_3O_4/KCC-1/tetrazolylidene/Au$ after ten runs	6.4
	Fe ₃ O ₄ /ACC-1/tetrazolylidene/Au Fe ₃ O ₄ /SiO ₂ /tetrazolylidene/Au after ten runs Fe ₃ O ₄ /KCC-1/tetrazolylidene/Au after ten runs

Applied Organometallic Chemistry

We compared the catalytic performance of our catalyst with catalysts reported in the literature for the synthesis of 2-oxazolidinone (Table 5). Table 5 clearly demonstrates that the most favourable terms are required for the synthesis of 2-oxazolidinone, using Fe₃O₄/KCC-1/tetrazolylidene/Au MNPs, while an appropriate, highly perfect, performance of the present catalyst is observed for the reaction.

A plausible mechanism for the catalytic synthesis of 2oxazolidinone is shown in Scheme 3. Initially, the catalyst activates propargylic amine. Subsequent nucleophilic attack on CO_2 leads to the acetylene. Finally, ring closure gives the 2-oxazolidinone.

It is important to note that the heterogeneous nature of $Fe_3O_4/$ KCC-1/tetrazolylidene/Au facilitates its efficient recovery from the reaction mixture during work-up procedure. The activity of the recycled catalyst was also examined under the optimized conditions. After the completion of reaction, the catalyst was separated by magnetic filtration, washed with methanol and dried at a pump. The recovered catalyst was reused for ten consecutive cycles without any significant loss in catalytic activity (Fig. 9). For a poisoning test, we added higher than stoichiometric amount of mercury, Hg (0), to the catalytic reaction. The reaction shows weak activity in the presence of excess Hg(0) which confirms the existence of gold as soluble species in the reaction. No significant reduction in the activity of the catalyst is observed. To test if any gold is leached from the solid catalyst during the process, a hot filtration test was performed for the reaction of propargylic amine with CO₂ after ca 50% of the coupling reaction was completed. Interestingly, no gold species is detected in the filtrate using atomic absorption spectroscopy. Also, in order to know whether the reaction takes place at the surface of Fe₃O₄/KCC-1/tetrazolylidene/Au MNPs, ICP-MS analysis was conducted of the remaining mixture after catalyst and product separation upon reaction completion. The amount of gold after ten repeated recycles is 6.4% and the amount of gold leaching into the reaction mixture is very low (about 0.2 ppm). These observations indicate that the catalyst is stable and can tolerate the present reaction conditions.

Experimental

Materials and methods

Chemical materials were purchased from Fluka and Merck in high purity. Melting points were determined in open capillaries using

Table 4. Synthesis of 2-oxazolidinone derivatives Scheme 1 catalysed by Fe ₃ O ₄ /KCC-1/tetrazolylidene/Au MNPs ^a							
Entry	R ₁	R ₂	R ₃	Product	Yield (%) ^b	TON	M.p. (°C)
1	Н	Н	CH ₃ CH ₂ CH ₂ CH ₂	2a	95	11.9×10^{2}	Yellow oil
2	Н	Н	CH₃	2b	91	11.4×10^{2}	Yellow oil
3	CH₃	H	CH₃	2c	84	10×10^{2}	74–76
4	CH_3	Н	$C_6H_5CH_2$	2d	92	11.5×10^{2}	40-42
5	CH_3	Н	(CH ₃) ₂ CH	2e	91	11.4×10^{2}	Yellow oil
6	C_6H_5	Н	CH₃	2f	94	11.8×10^{2}	139–141
7	4-CH ₃ C ₆ H ₄	Н	CH ₃	2 g	96	12×10^{2}	134–136
8	C_6H_5	CH ₃ CH ₂	CH ₃ CH ₂ CH ₂ CH ₂	2 h	95	11.9×10^{2}	Yellow oil

^aReaction conditions: propargylic amine derivatives (1 mmol), catalyst (0.08 mg) and CO₂ (0.5 MPa), in water at room temperature after 18 h. ^bRefers to isolated product.

Table 5	Comparison of catalytic efficiency	of Fe ₃ O ₄ /KCC-1/tetra	zolylidene/Au M	NPs and various other	r catalysts		
Entry	Catalyst	CO ₂ (MPa)	Solvent	Temperature (°C)	Amount of catalyst	Time (h)	Yield (%)
1	$SiO_2-(CH_2)_3-NEt_2$	80	_	90	0.09 g	21	72 ^[35]
2	SiO ₂ –TBD	80	_	90	0.09 g	21	88 ^[35]
3	Hydrotalcite MG30	80	_	90	0.09 g	21	67 ^[35]
4	Hydrotalcite MG70	80	_	90	0.09 g	21	58 ^[35]
5	Al ₂ O ₃	80	—	90	0.09 g	21	85 ^[35]
6	PtCl ₂ /DBU	—	DMSO/H ₂ O	60	200 mol%	240	69 ^[36]
7	Cul/DBU	—	DMSO/H ₂ O	60	200 mol%	120	63 ^[36]
8	Cu(OAc) ₂ /DBU	—	DMSO/H ₂ O	60	200 mol%	114	78 ^[36]
9	AgOAc/DBU	—	DMSO/H ₂ O	60	200 mol%	24	86 ^[36]
10	AgOAc/DBU	—	DMSO	60	200 mol%	18	90 ^[36]
11	Ag ₂ O/DBU	—	DMSO	60	200 mol%	16	92 ^[36]
12	AgNO ₃ /DBU	—	DMSO	60	200 mol%	17	95 ^[36]
13	AgNO ₃ /DBU	—	DMSO	60	10 mol%	33	94 ^[36]
14	AgNO ₃ /DBU	—	DMSO	60	10 mol%	48	8 ^[36]
15	AgNO ₃ /DBU	—	DMSO	60	10 mol%	27	95 ^[36]
16	AgNO ₃ /DBU	—	DMSO	60	10 mol%	20	95 ^[36]
17	AuCl(IPr)	0.1	MeOH	40	2 mol%	48	76 ^[37]
18	(ⁿ C ₇ H ₁₅) ₄ NBr	99.999%, balloon	—	60	2.5 mol%	20	[38]
19	K ₈ [α-SiW ₁₁ O ₃₉]	99.999%, balloon	_	60	2.5 mol%	20	[38]
20	K ₆ [SiW ₁₁ O ₃₉ Cu]	99.999%, balloon	—	60	2.5 mol%	20	43 ^[38]
21	CuCl ₂	99.999%, balloon	—	60	2.5 mol%	20	67 ^[38]
22	$CuCl_2 + (^nC_7H_{15})_4NBr$	99.999%, balloon	—	60	2.5 mol%	20	68 ^[38]
23	[(ⁿ C ₇ H ₁₅) ₄ N] ₆ [α-SiW ₁₁ O ₃₉ Co]	99.999%, balloon	—	60	2.5 mol%	20	66 ^[38]
24	[(ⁿ C ₇ H ₁₅) ₄ N] ₆ [α-SiW ₁₁ O ₃₉ Fe]	99.999%, balloon	—	60	2.5 mol%	20	18 ^[38]
25	$[(^{n}C_{7}H_{15})_{4}N]_{6}[\alpha-SiW_{11}O_{39}Ni]$	99.999%, balloon	—	60	2.5 mol%	20	16 ^[38]
26	[(ⁿ C ₇ H ₁₅) ₄ N] ₆ [α-SiW ₁₁ O ₃₉ Zn]	99.999%, balloon	—	60	2.5 mol%	20	45 ^[38]
27	[(ⁿ C ₇ H ₁₅) ₄ N] ₆ [α-SiW ₁₁ O ₃₉ Mn]	99.999%, balloon	—	60	2.5 mol%	20	43 ^[38]
28	[(ⁿ C ₇ H ₁₅) ₄ N] ₆ [α-SiW ₁₁ O ₃₉ Cu]	99.999%, balloon	—	60	2.5 mol%	20	73 ^[38]
29	Fe ₃ O ₄ /KCC-1/tetrazolylidene/Au	0.5	H ₂ O	r.t.	0.08 mg	18	95

^aReaction conditions: propargylic amine (1 mmol) and CO₂ in various solvents and with various amounts of catalyst, temperature, and time.



Scheme 3. A plausible mechanism.



Figure 9. Recycling performance of the catalyst.

an Electrothermal 9100 apparatus and are uncorrected. FT-IR spectra were recorded with a VERTEX 70 spectrometer (Bruker) in transmission mode with spectroscopic grade KBr pellets for all powders. Morphology was analysed using high-resolution TEM with a JEOL transmission electron microscope operating at 200 kV. The content of phosphorus in the catalyst was determined using an OPTIMA 7300DV ICP analyser. Powder XRD data were obtained using a Bruker D8 Advance model with Cu K α radiation. TGA was carried out with a Netzsch STA449F3 at a heating rate of 10 °C min⁻¹ under

nitrogen. Magnetic measurements were carried out with a vibrating sample magnetometer (4 inch, Daghigh Meghnatis Kashan Co., Kashan, Iran) at room temperature. NMR spectra were recorded in CDCl₃ with a Bruker Avance DRX-400 instrument using tetramethylsilane as internal standard. Determination of purity of products and reaction monitoring were accomplished using TLC with silica gel polygram SILG/UV 254 plates.

General procedure for preparation of Fe₃O₄ MNPs

The synthesis procedure was as follows. (1) 0.01 mol FeCl₂·4H₂O and 0.03 mol FeCl₃·6H₂O were dissolved in 200 ml of distilled water, followed by the addition of poly(ethylene glycol) (1.0 g, MW 6000 g mol⁻¹). (2) Sodium hydroxide (NaOH) was added to the solution and the pH value was controlled in the range 12–13. (3) Various amounts of hydrazine hydrate (N₂H₄·H₂O, 80% concentration) were added to the suspension. The reaction was continued for about 24 h at room temperature. During this period, the pH value was adjusted using NaOH and kept in the range 12–13. The black Fe₃O₄ MNPs were then rinsed several times with deionized water.

General procedure for preparation of Fe₃O₄/SiO₂ MNPs

 Fe_3O_4 MNPs (0.02 mol) were dispersed in a mixture of 80 ml of ethanol, 20 ml of deionized water and 2.0 ml of 28 wt.% concentrated ammonia aqueous solution (NH₃·H₂O), followed by the addition of 0.20 g of tetraethyl orthosilicate (TEOS). After vigorous stirring for 24 h, the final suspension was repeatedly washed, filtered several times and dried at 60 °C in air.

General procedure for preparation of Fe₃O₄/SiO₂/KCC-1 MNPs

The Fe₃O₄/SiO₂/KCC-1 core–shell microspheres were synthesized according to a previously reported method.^[39] Fe₃O₄/SiO₂ (0.25 g) was dispersed in an aqueous solution (30 ml) containing urea (0.3 g) to form solution A under ultrasonication for 1 h. Cetylpyridinium bromide (0.5 g) was added to 0.75 ml of *n*-pentanol and 30 ml of cyclohexane to form solution B. Solution A was added to solution B under stirring at room temperature. Then 1.25 g of TEOS was added dropwise to the resulting solution. The resulting mixture was continually stirred for 1 h at room temperature and then placed into a 120 °C environment for 5 h, thus initiating the reaction. After the reaction was completed, the mixture was allowed to cool to room temperature, and the Fe₃O₄/SiO₂/KCC-1 core–shell microspheres were isolated by strong magnetic suction, washed with deionized water and acetone, and dried overnight in a drying oven at 40°°C. This material was then calcined at 550 °C for 5 h in air.

General procedure for preparation of $Fe_3O_4/SiO_2/KCC-1/3-$ chloropropylsilane MNPs

KCC-1 NPs (2 mmol) and THF (20 ml) were mixed together in a beaker, and then NaH (20 mmol) was dispersed into the mixture by ultrasonication. 3-Chloropropyltriethoxysilane (22 mmol) was added dropwise at room temperature and stirred for another 16 h at 60 °C. The resultant products were collected and washed sequentially with ethanol and deionized water, and then dried under vacuum at 60 °C for 2 h for further use.

General procedure for preparation of $Fe_3O_4/KCC\text{--}1/tetrazolylidene/Au MNPs$

Fe₃O₄/KCC-1/tetrazolylidene/Au core–shell microspheres were synthesized according to a previously reported method.^[40] A solution of 1-benzyltetrazole (1.5 mmol) in THF (15 ml) was treated with *n*-butyllithium in hexane (1.5 mmol) at -98 °C. After 30 min of stirring, [AuCl(tht)] (1.5 mmol) in THF (10 ml) was added to the orange-coloured solution. The reaction mixture was stirred for a further 1.5 h between -98 and -78 °C, during which time the solution became colourless. The product was treated with Fe₃O₄/SiO₂/KCC-

1/3-chloropropylsilane (0.5 mmol) at -78 °C, reacted for 1 h, and slowly allowed to reach room temperature. Then the Fe₃O₄/KCC-1/tetrazolylidene/Au MNPs were separated from the reaction mixture using an external magnet and washed several times with deionized water and acetone. Finally, Fe₃O₄/KCC-1/tetrazolylidene/Au MNPs were dried under vacuum at 50 °C.

General procedures for preparation of 2-Oxazolidinones

To a Schlenk tube were successively added Fe₃O₄/KCC-1/ tetrazolylidene/Au MNPs (0.08 mg), degassed water (1 ml) and a propargylic amine (1 mmol) under an argon atmosphere, and the inside of the Schlenk tube was replaced with CO₂ (0.5 MPa). The carboxylative cyclization of the propargylic amine with CO₂ proceeded by the stirring of the resulting mixture at room temperature. The progress of the reaction was monitored by TLC. When the reaction was completed, methanol and dichloromethane were added to the reaction mixture and the catalyst was separated using an external magnet under vacuum. Then the solvent was removed from solution under reduced pressure and the resulting product purified by recrystallization from methanol.

Conclusions

In summary, the design and preparation of a novel gold(I) complex containing KCC-1-based ordered mesofibre organosilica (Fe₃O₄/ KCC-1/tetrazolylidene/Au MNPs) and its catalytic application for the cyclization of propargylic amines with CO₂ to provide 2oxazolidinones have been described. Interestingly, it was found that while hot filtration tests and selective catalyst poisons showed the presence of soluble gold species during the reaction process, recovery studies illustrated that no significant decrease occurred in the activity and metal content of recovered Fe₃O₄/SiO₂/ tetrazolylidene/Au MNPs. In addition, the catalyst could be recovered and reused at least ten times with no decrease in its activity and selectivity. Based on these results, it is concluded that although the KCC-1 nanostructure acts as 'cobweb' for the soluble gold species, it can also operate as a nanoscaffold to re-uptake the gold(I) into the mesofibres, thereby avoiding agglomeration of gold(I) complex. This superior effectiveness of the Fe₃O₄/KCC-1/ tetrazolylidene/Au nanocatalyst may be ascribed to isolated KCC-1 units incorporated in the mesofibres which can control the reaction mechanism through preventing the formation of agglomerated gold(I) complex as well as stabilization of active catalytic gold species.

References

- A. Fihri, M. Bouhrara, B. Nekoueishahraki, J. Marie Basset, V. Polshettiwar, Chem. Soc. Rev. 2011, 40, 5181.
- [2] V. Polshettiwar, R. S. Varma, Green Chem. 2010, 12, 743.
- [3] C. W. Lim, I. S. Lee, Nano Today 2010, 5, 412.
- [4] V. Polshettiwar, R. Luque, A. Fihri, H. Zhu, M. Bouhrara, J. M. Basset, Chem. Rev. 2011, 111, 3036.
- [5] R. K. Sharma, S. Sharma, S. Dutta, R. Zborilb, M. B. Gawande, Green Chem. 2015, 17, 3207.
- [6] X. Du, S. Z. Qiao, Small 2015, 11, 392.
- [7] M. B. Gawande, P. S. Brancoa, R. S. Varma, Chem. Soc. Rev. 2013, 42, 3371.
- [8] R. Dalpozzo, Green Chem. 2015, 17, 3671.
- [9] Q. Yao, Z. H. Lu, Z. Zhang, X. Chen, Y. Lan, Sci. Rep. 2014, 4, 7597.
- [10] J. Cao, J. Z. Sun, J. Hong, H. Y. Li, H. Z. Chen, M. Wang, Adv. Mater. 2004, 16, 84.

- [11] R. B. Nasir Baig, R. S. Varma, Chem. Commun. 2013, 49, 752.
- [12] A. Mobinikhaledi, A. Khajeh-Amiri, *Reac. Kinet. Mech. Catal.* 2014, *112*, 131.
- [13] H. Naeimi, S. Mohamadabadi, Dalton Trans. 2014, 43, 12967.
- [14] V. Polshettiwar, D. Cha, X. Zhang, J. M. Basset, Angew. Chem. Int. Ed. 2010, 49, 9652.
- [15] a) M. He, Y. Sun, B. Han, Angew. Chem. Int. Ed. 2013, 52, 9620; b)
 P. Tundo, M. Selva, Acc. Chem. Res. 2002, 35, 706; c) M. Honda,
 M. Tamura, Y. Nakagawa, K. Tomishige, Catal. Sci. Technol.
 2014, 4, 2830; d) A.-H. Liu, Y.-N. Li, L.-N. He, Pure Appl. Chem.
 2012, 84, 581.
- [16] M. Yoshida, N. Hara, S. Okuyama, Chem. Commun. 2000, 36, 151.
- [17] R. Tanaka, M. Yamashita, K. Nozaki, J. Am. Chem. Soc. 2009, 131, 14168.
- [18] S. Wesselbaum, T. vomStein, J. Klankermayer, W. Leitner, Angew. Chem. Int. Ed 2012, 51–7499.
- [19] a) M. Honda, M. Tamura, K. Nakao, K. Suzuki, Y. Nakagawa, K. Tomishige, ACS Catal. 2014, 4, 1893; b) Q.-W. Song, W.-Q. Chen, R. Ma, A. Yu, Q.-Y. Li, Y. Chang, L.-N. He, ChemSusChem 2015, 8, 821; c) B. A. Vara, T. J. Struble, W. Wang, M. C. Dobish, J. N. Johnston, J. Am. Chem. Soc. 2015, 137, 7302.
- [20] D. J. Darensbourg, A. I. Moncada, W. Choi, J. H. Reibenspies, J. Am. Chem. Soc. 2008, 130, 6523.
- [21] a) S. Pulla, C. M. Felton, P. Ramidi, Y. Gartia, N. Ali, U. B. Nasini, A. Ghosh, J. CO2 Util 2013, 2–49; b) R. Maggi, C. Bertolotti, E. Orlandini, C. Oro, G. Sartori, M. Selva, Tetrahedron Lett. 2007, 48, 2131; c) Y. Kayaki, M. Yamamoto, T. Suzuki, T. Ikariya, Green Chem. 2006, 8, 1019; d) M. Feroci, M. Orsini, G. Sotgiu, L. Rossi, A. Inesi, J. Org. Chem. 2005, 70, 7795; e) K. Fujita, K. Inoue, J. Sato, T. Tsuchimoto, H. Yasuda, Tetrahedron 2016, 72, 1205; f) K. Fujita, J. Sato, K. Inoue, T. Tsuchimoto, H. Yasuda, Tetrahedron 2014, 55, 3013; g) S. Hase, Y. Kayaki, T. Ikariya, ACS Catal. 2015, 5, 5135; h) S. Hase, Y. Kayaki, T. Ikariya, Organometallics 2013, 32, 5285.
- [22] L. Aurelio, R. T. C. Brownlee, A. B. Hughes, Chem. Rev. 2004, 104, 5823.
- [23] C. W. Y. Chung, P. H. Toy, *Tetrahedron: Asymm.* 2004, 15, 387.

- [24] T. A. Mukhtar, G. D. Wright, Chem. Rev. 2005, 105, 529.
- [25] L. P. Liu, G. B. Hammond, Chem. Soc. Rev. 2012, 41, 3129.
- [26] A. S. K. Hashmi, L. Schwarz, J. H. Choi, T. M. Frost, Angew. Chem. Int. Ed. 2000, 39, 2285.
- [27] A. S. K. Hashmi, G. J. Hutchings, Angew. Chem. Int. Ed. 2006, 45, 7896.
- [28] W. B. Wang, G. B. Hammond, B. Xu, J. Am. Chem. Soc. 2012, 134, 5697.
- [29] L. Guczi, A. Beck, Z. Paszti, *Catal. Today* **2012**, *181*, 26.
- [30] A. S. K. Hashmi, A. M. Schuster, S. Litters, F. Rominger, M. Pernpointner, *Chem. Eur. J.* 2011, 17, 5661.
- [31] M. N. Hopkinson, A. D. Gee, V. Gouverneur, Chem. Eur. J. 2011, 17, 8248.
- [32] Y. Zhang, C. Zhu, Catal. Commun. 2012, 28, 134.
- [33] a) T. Yamamoto, T. Yamada, Y. Nagata, M. Suginome, J. Am. Chem. Soc. 2010, 132, 7899; b) X. Zhang, P. Li, Y. Ji, L. Zhang, L. Wang, Synthesis 2011, 2975.
- [34] M. S. Sadeghzadeh, RSC Adv. 2015, 5, 68947.
- [35] R. Maggi, C. Bertolotti, E. Orlandini, C. Oro, G. Sartori, M. Selva, *Tetrahedron Lett.* 2007, 48, 2131.
- [36] M. Yoshida, T. Mizuguchi, K. Shishido, Chem. Eur. J. 2012, 18, 15578.
- [37] K. Fujita, J. Sato, K. Inoue, T. Tsuchimoto, H. Yasuda, *Tetrahedron Lett.* 2014, 55, 3013.
- [38] M. Y. Wang, Q. W. Song, R. Ma, J. N. Xie, L. N. He, Green Chem. 2016, 18, 282.
- [39] K. Yu, X. Zhang, H. Tong, X. Yan, S. Liu, *Mater. Lett.* **2013**, *106*, 151.
- [40] W. F. Gabrielli, S. D. Nogai, J. M. McKenzie, S. Cronje, H. G. Raubenheimer, New J. Chem. 2009, 33, 2208.

Supporting information

Additional supporting information may be found in the online version of this article at the publisher's web-site.