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A Highly Efficient, Ligand-Free and Recyclable SBA-15 Supported Cu_2O Catalyzed Cyanation of Aryl Iodides with Potassium Hexacyanoferrate (Ⅱ)

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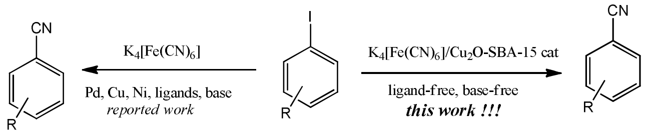
SBA-15 supported Cu2O nanoparticles (Cu2O/SBA-15) have been fabricated and characterized. The as-prepared Cu2O/SBA-15 is a highly effective catalyst for cyanation of aryl iodides using non-toxic $K_4[Fe(CN)_6]$ as a cyanide source in dimethylformamide (DMF). The approach achieves a high selectivity and an excellent yield without using any ligands and base additives. Moreover, the Cu2O/SBA-15 catalyst shows wide functional group tolerance and reusability with a slight loss of activity.

Introduction

Aryl nitriles are significant intermediates in a wide range of area including dyes, herbicides, agrochemicals, pharmaceuticals, and natural products.[1] As a sort of essential functional substituent in organic synthesis, the cyano-groups in aryl nitriles can be easily converted to amides, amines, aldehydes and heterocycles.[2] Based on these, many protocols have been developed for the synthesis of aryl nitriles. For example, Rosemund-von Braun[3] and Sandmeyer reactions[4] are two kinds of traditional method to access aryl nitriles. Drawback of Rosemund-von Braun reaction is the high reaction temperature (150–250 ℃), and Sandmeyer reaction needs multiple procedures. In addition, the two reactions use stoichiometric amounts of hypertoxic copper (I) cyanide as cyanide source. These lead to unavoidable environment and safety problems. To overcome these shortcomings, the transition-metal-catalyzed (Pd,[5] Ni,[6] and Cu[7]) elements for cyanation of aryl halides offer an efficient alternation for the synthesis of aryl nitriles in relatively mild reaction conditions and high yields.A general problem of metal catalyzed cyanations is the high affinity of cyanide towards Pd-, and Cu-catalysts. These led to equimolar amounts of heavy metal waste. There has been an increasing demand for the development of environmental friendly chemical processes for the syntheses of a variety of organic compounds on industrial and laboratory scales.[8] It is very desirable to explore reaction conditions with an easily available cyanide source and new catalytic systems that are economical, less toxic, and take less time. An attractive improvement had been made by Beller and co-workers in 2004.[9]The nontoxic cyanide source potassium hexacyanoferrate (II) ($K_4[Fe(CN)_6]$) was introduced into the cyanation reaction for the first time. Consequently, it provided us a nontoxic, inexpensive and easy handled cyanide source in synthetic chemistry. Motivated by these benefits, a large amount of work has been carried out by utilizing $K_4[Fe(CN)_6]$ as a cyanating agent.[10] The efficiency of these reactions was highly dependent on the involvement of suitable ligands and over-stoichiometic bases. Owing to the transition metals have high affinity with cyanide, stable cyanide complexes could be formed in catalytic system, which may interrupts the catalytic cycle.[11] Heterogenous catalysts have recently gained much importance because they are more selective, stable at high temperature, easily separated from the reaction mixture at theend of the process, and can be reused. These factors favour thecost effectiveness of what can be regarded as a “green reaction”.[12] In the past 20 years, ordered mesoporous silica (OMSs) based materials as well-defined catalyst support has aroused great interest for researchers due to their uniform pore distribution, large void volumes, high surface areas and high hydrothermal stability.[13]Compared with amorphous solids and organic polymers, the ordered mesoporous silica possibly provide a more comfortable environment for the interaction between catalysts and substrates. Considering these attractive properties, new organic–inorganic nanocomposites based on the mesoporous silica SBA-15 have been extensively investigated in the development of functional materials in various fields.[14] In recent years, Cu_2O (bulk or in NC form) was reported as an efficient catalyst for C-C, C-N, and C-O bond-formation cross-coupling reactions.[15] The significant difference of the nanostructured copper(I)oxide in comparison to bulk materials with respect to reactivity, stability in aqueous medium, environmental compatibility, non-toxicity and large surface-volume ratio, makes nano-copper (I) oxide more promising compared to expensive palladium catalysts systems.[16] In the present study, we report here the cyanation of aryl iodides with non-toxic$K_4Fe(CN)_6$ as cyanide source and SBA-15 supported copper (I) oxide as catalyst (Scheme 1). The reaction tolerated a variety of functional groups and heteroatoms with good to excellent yields of the corresponding aryl nitriles at 120 ℃ after 8 h. Moreover, the small and highly dispersed Cu_2O nanoparticles confined in the channels of mesoporous silica contribute to high reaction activity and the Cu_2O nanoparticles didn't agglomerate in the reaction process. Thus, the prepared Cu_2O/ SBA-15 with high stability provided the opportunity to explore the promising synthetic method for aryl nitriles.



Scheme 1. Cu_2O/SBA-15 catalyzed cyanation of aryl iodides

Results and discussion

X-ray diffraction

The small-angle XRD patterns of SBA-15 and Cu_2O/SBA-15 were given in Fig. 1. The fresh SBA-15 was ordered, showing two well defined peaks assignable to the 100 and 110 planes.[17] The reduction in the intensity of the (100) and (110) reflections for Cu_2O/SBA-15 was attributed to the change in the homogeneity and space correlation of pores caused by Cu_2O in pores. The nanoparticle ofCu_2O/SBA-15 was further investigated with wide angle X-ray diffraction (XRD). The Cu_2O/SBA-15 hardly displays any peak from 10° to 110°, which indicted Cu_2O with low crystallinity [Fig. 1b].

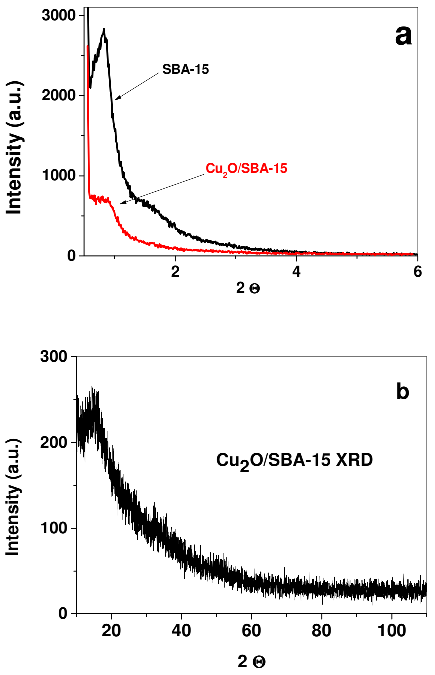


Fig. 1. The small-angle XRD patterns of SBA-15 and Cu_2O/SBA-15 (a); the wide angle XRD of Cu_2O/SBA-15 (b).

TEM

Complementary to the XRD data, the TEM images of the Cu_2O/SBA-15 exhibited arrays of silica pore channels with uniform diameter (about 7.6 ± 0.2 nm) and wall thickness (Fig. 2a). The shadowed areas in this image are attributed to Cu_2Onanoparticles.The Cu_2O nanoparticles (NPs) were highly dispersed and with uniform particle size (about 3–4 nm), and theCu_2O NPs were almost stayed inside the channels of SBA-15.Furthermore, it can be seen in Fig. 2b that the catalyst still kept the pore structure of SBA-15 even after 5 runs. The composites of Cu_2O/SBA-15 can be obtained via EDS (Fig. S1).The EDS spectrum with main peaks (C, Si, Ni, Cu and O) was achieved, indicating that the prepared catalysis was composed of Si, Cu and O elements (The C and Ni come from electron microscopicnickel grid).

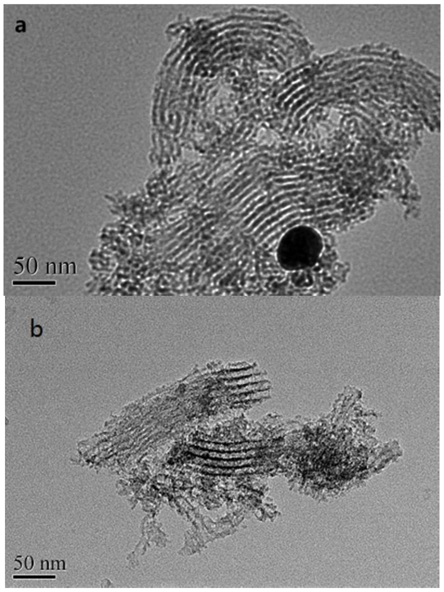


Fig. 2. TEM images of Cu_2O/SBA-15 (a) and catalyst recovered after five runs (b).

N_2 adsorption/desorption analysis

The N_2 isothermal adsorption-desorption curves of SBA-15 and Cu_2O/SBA-15 were shown in Fig. 3. The prepared SBA-15 present an obvious IV-type isotherm with H2 type of hysteresis loop, which demonstrate the ordered mesoporous structure ofSBA-15 (Fig. 3a). However,when Cu_2O nonparticles loaded on the SBA-15, it exhibited combination of H1 and H3 hysteresis loopcharacteristics (Fig. 3b). The upper closure point of the hysteresis loopappeared at a relatively higher value, than that of pureSBA-15. This was due to the presence of Cu_2O nanoparticls within the channels of SBA-15 which blocked the pores and caused partial strainand distortion in the pores and increased the pore diameter.[18]A considerable decrease in surface area, pore volume, and pore diameter was observed after Cu_2O modification. It showed that the BET surface area of Cu_2O/SBA-15 decreases to 281.26 m^2 g^{-1} compared with 520.27 m^2 g^{-1} of the original SBA-15. The pore volume of SBA-15 and Cu_2O/SBA-15 were 1.18 cm^3 g^{-1} and 0.50 cm^3 g^{-1} respectively from the N_2 adsorption is otherm and the Brunauer–Emmett–Teller (BET) method. The reduction in both surface areas and pore volumes of the Cu_2O/SBA-15 samples compared with that of the original SBA-15 is about 45%, indicating the scarcity of mesopore blockages by the loaded Cu_2O catalysts.The results suggested that the Cu_2O nonparticles blocked the pores of SBA-15 and led to disordered materials with a heterogeneous pore distribution. The pore size distributions were estimated from the desorption branch of the N_2 isotherms by the Barrett–Joyner–Halenda (BJH)method.Asshown in Fig.S2, the SBA-15 samples had narrow poresize distributions, centered at about 7.8 nm, which matched the results of TEM.

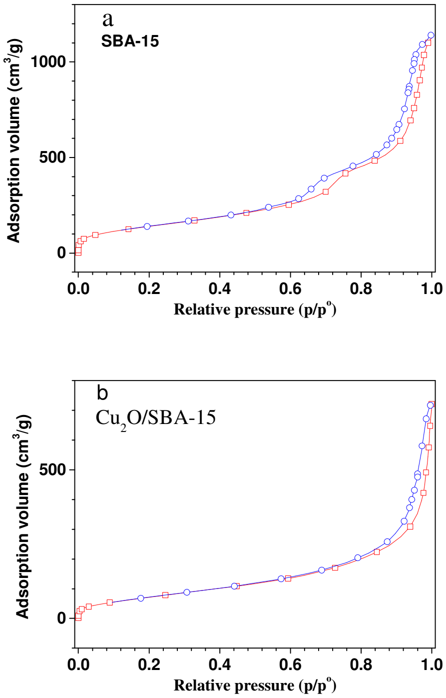


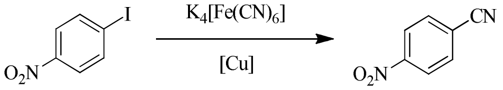
Fig. 3. N_2 adsorption/desorption isotherm plots for SBA-15 (a) and Cu_2O/SBA-15 (b)

The chemical state of the elements and the surface composition in the catalyst can be determined by the XPS spectrum. To further verity the form of Cu_2O, we carried out the XPS spectrum experiment (Fig. S3). The result shows the Cu $2p_{3/2}$ and Cu $2p_{1/2}$ peaks located at 932.2 and 952 eV, respectively, which are attributed to Cu_2O. No CuO signal is detected with Cu $2p_{3/2} \approx 933.6$.[19]

Catalytic activity for cyanation of aryl iodides reaction

Generally, cyanation of aryl iodides requires transition-metal-catalysts and ligand in base condition. In our initial studies, various copper catalysts in combination with different solvents were investigated using 1-iodo-4-nitrobenzene as a model substrate for the synthesis of 4-nitrobenzonitriles (see Table 1). In order to determine the optimal reaction conditions, we chose different copper salts or copper oxides as catalysts. Firstly, we chose $Cu(OAc)_2{\bullet}H_2O$ (10 mol%) as a catalyst candidate, NaOAc (2 mmol) as base, DMF (2 mL) as solvent and $K_4[Fe(CN)_6]$ (0.3 equiv) as a cyanide source, no product was afforded after heating to 120℃ for 8h (Table 1, entry 1). Then CuO, CuI, CuCl and Cu_2O were chosen as catalysts respectively. In the same reaction conditions, Cu_2O shows the best catalytic activity, with a 93% yield in the cyanation of 1-iodo-4-nitrobenzene (Table 1, entry 4). Meanwhile, CuCl gives a 37% yield (Table 1, entry 5) and CuO has no catalytic effect (Table 1, entry 2). Next, we tried to determine whether the base was essential for the reaction, the results showed that it is unnecessary. As shown in Table 1, no product was obtained in the absence of the copper (I) salt. While the catalyst was switched to Cu_2O, different reaction conditions were screened. The yields reduced when the reaction temperature decreases. These data clearly showed that the optimized temperature for this reaction was found to be 120℃. Then the optimized catalyst loading was considered as another parameter to be investigated. Using less than 10 mol% Cu_2O, the conversion drops significantly (Table 1, entry 12,13), but using more Cu_2O can't increase the yield (Table 1, entry 10, 11). However, when Cu_2O/SBA-15 was used as catalysts and the content of Cu_2O is only about 2 mol%, the yields reached to 95% (Table 1, entry 14). The results made it clear that Cu_2O/SBA-15 was the better catalyst for the system.

Table 1. Optimization of reaction conditions for the copper-catalyzed cyanation of 1-iodo-4-nitrobenzene using K4[Fe(CN)6] as a cyanide source [a]

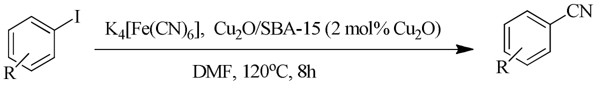


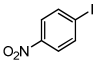
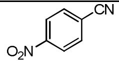
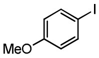
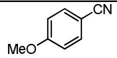
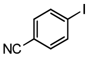
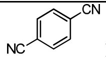
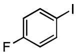
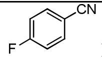
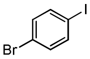
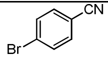
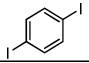
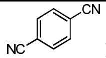
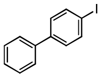
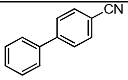
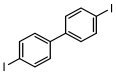
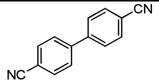
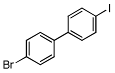
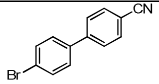
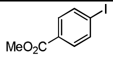
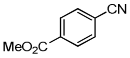
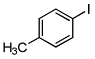
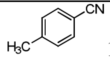
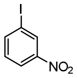
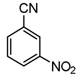
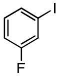
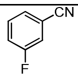
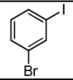
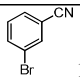
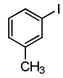
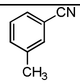
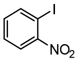
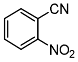
Entry	Cat.	Base	Temp (℃)	Yield[g] (%)
1	$Cu(OAc)_2\cdot H_2O$	NaOAc	120	0
2	CuO	NaOAc	120	0
3	CuI	NaOAc	120	53
4	Cu_2O	NaOAc	120	93
5	CuCl	NaOAc	120	37
6	Cu_2O	None	120	94
7	None	NaOAc	120	0
8	Cu_2O	None	100	76
9	Cu_2O	None	80	42
10[b]	Cu_2O	None	120	93
11[c]	Cu_2O	None	120	92
12[d]	Cu_2O	None	120	84
13[e]	Cu_2O	None	120	71
14[f]	Cu_2O/SBA-15	None	120	95

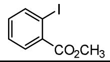
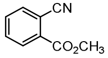
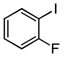
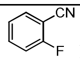
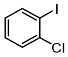
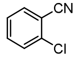
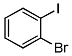
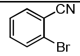
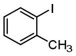
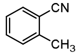
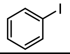
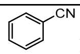
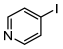
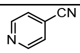
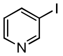
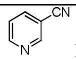
[a]Condition: 0.25 mmol 1-iodo-4-nitrobenzene, 0.075 mmol $K_4Fe(CN)_6$, cat. (10 mol%), 2 mLDMF, 8h. [b] Cat. (15 mol%), [c] Cat. (20 mol%), [d] Cat. (7 mol%), [e] Cat. (4 mol%), [f] 100 mg Cu_2O/SBA-15 (2mol% Cu_2O), [g] Isolated yield after flash chromatography on silica gel.

Because the Cu_2O catalyst is oxygen insensitive, all reactions were carried out under air atmosphere. Thus, the optimal conditions for this reaction are: aryl iodide (0.25 mmol), $K_4[Fe(CN)_6]$ (0.075 mmol), Cu_2O/SBA-15 (100 mg), heat to 120℃ for 8h. To explore the applied scope of this method, the optimized reaction conditions were applied to the cyanation of aryl iodides (Table 2). Thin layer chromatograph (TLC) and gas chromatograph (GC) results showed that the selectivity of cyanation is almost 100%. The aryl iodides could be converted to the corresponding aryl nitriles in excellent (Table 2, entries 1-7, 10, 12-13, 16-19 and 22-23) or good (8, 9, 11, 14, 15, 20, 21 and 24) yields. Generally, aryl iodides with strong electron-withdrawing groups gave the cyanated products in excellent yields. In addition, the nitro, halogen, and ester groups are well-tolerated under these reaction conditions.

Table 2. Substrate screening for the Cu_2O/SBA-15-catalyzed cyanation of aryl iodides using $K_4[Fe(CN)_6]$ as a cyanide source [a]



Entry	substrate	product	Yield (%)	Selectivity (%)
1		 1a	95	100
2		 1b	92	100
3		 1c	92	100
4		 1d	91	99
5		 1e	90	≥98
6[a]		 1c	91	100
7		 1f	94	100
8		 1g	86	99
9		 1h	83	99
10		 1i	91	99
11		 1j	87	99
12		 1k	94	100
13		 1l	92	99
14		 1m	85	98
15		 1n	87	99
16		 1o	92	100

Entry	substrate	product	Yield (%)	Selectivity (%)
17		 1p	91	100
18		 1q	92	99
19		 1r	93	≥98
20		 1s	88	99
21		 1t	83	100
22		 1u	95	100
23		 1v	95	100
24		 1w	87	100

Condition: 0.25 mmol 4-iodoaryl, 0.075 mmol $K_4Fe(CN)_6$, Cu_2O/SBA-15 (100 mg, 2 mol% Cu_2O), 2mL DMF, 120℃, 8h, [a]$K_4Fe(CN)_6$ (0.15 mmol). Isolated yield after flash chromatography on silica gel. The selectivity was determined by GC.

The successive experiment results prompted us to further investigate the reusability of Cu_2O/SBA-15 catalytic system for the cyanation of aryl iodides. 4-Nitro-1-iodobenzene was chosen as a model substrate in the optimized reaction conditions. It was found that Cu_2O/SBA-15 could be recycled at least five times with only a slight decrease in activity (from 95% to 92%)(Figure 4).In comparison with the results of the successive experiment, the slow gradual decrease of product yield in each recycle could be attributed to a loss of catalyst upon successive separation of the aqueous solution from the solid in each cycle.

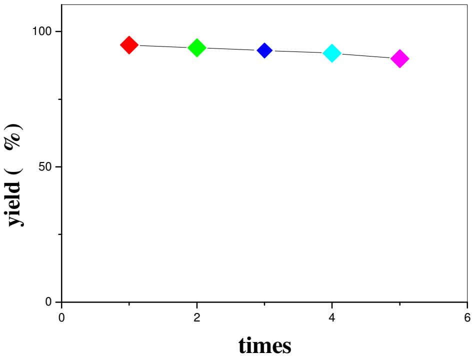
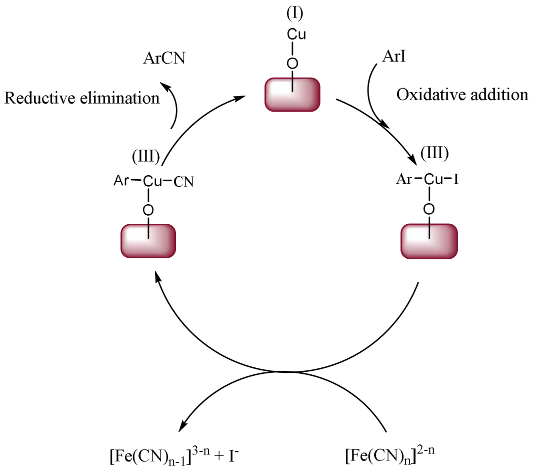


Fig. 4. Plot of Catalytic recyclability times of Cu_2O to yield

Based on the previous literatures,[20] a plausible three steps mechanism is proposed for Cu_2O/SBA-15 catalyzed cyanation of aryl iodides, as illustrated in Scheme 2. Firstly, oxidative addition of aryl iodide to Cu_2O leads to formation of Cu (III) complex (A), which undergoes transmetallation with $K_4[Fe(CN)_6]$ to provide a transient Cu (III) intermediate B. This gives aryl nitriles *via* reductive elimination of Cu (III) to Cu (I).



Scheme 2 Proposed mechanism

Experimental

General

All chemicals used were reagent grade and used as received without further purification. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded at in $CDCl_3$ or DMSO-d_6. The chemical shifts (δ) are reported in ppm units relative to TMS as an internal standard for NMR spectra. Coupling constants (J)are reported in hertz (Hz) and multiplicities are indicated as follows: s (singlet), bs (broad singlet), d (doublet), dd (doublet of doublet), t (triplet), m (multiplet). Column chromatography was carried out using silica gel (230-400 mesh). GCMS-QP 2010 was equipped with a DB-5MS capillary column. GC-MS method: initial temperature, 60℃; initial time, 2 min; ramp, 10℃ min^{-1}; final temperature, 280℃.

Catalyst preparation

SBA-15[21]was synthesized following literature approaches.In general, glucose is a common reducing regent for fabrication of Cu_2O from $Cu(OH)_2$.[22]The Cu_2O/SBA-15 was fabricated as following. In a typical synthesis, 0.35 g of $CuSO_4•5H_2O$ was first dissolved in 20 mL of distilled water, and then 1.0 g of freshly calcined SBA-15 was added. After stirring for 7 h, water was slowly evaporated under 100 ^{o}C. The dry powder was redispersed in 15 mL water, and then added 5 mL of glucose solution (0.1 g/mL,) and 5 mL of NaOH solution (0.25 M).The mixture was then maintained at a temperature of 100 ^{o}C for 10 h. Aftercooling down to room temperature naturally, the yellow or redproducts were collected and washed several times with deionized water and absolute ethanol, sequentially. The final products were dried at 50 ^{o}C for further characterization. The prepared SBA-15 supported Cu_2O nanoparticles contain 10% mass fraction of Cu_2O by calculating.

Catalyst characterization

The morphology of the prepared Cu_2O/SBA-15 nanoparticles was studied by transmission electron microscope (TEM, JEM-2100), X-Ray diffraction (XRD, Philips X'pert Pro X-ray diffractometer and Brunauer–Emmett–Teller (BET) N_2 adsorption–desorption isotherms (MIEROMERITICS ASAP 2020). Total pore volume was obtained from the volume of N_2 adsorbed at P/Po=0.95 and the pore size distributions were estimated from the desorption branch of the N_2 isotherms by the Barrett–Joyner–Halenda (BJH)method.X-ray photoelectron spectroscopy (XPS) measurements were carried out in a PHI5000 VersaProbe.

General Procedure for cyanation of aryl iodides with potassium hexacyanoferrate (II), $K_4[Fe(CN)_6]$

In a 25 mL glass tube was placed aryl iodides (0.25 mmol), $K_4[Fe(CN)_6]$ (27.6 mg, 0.075 mmol), Cu_2O/SBA-15 (100 mg, containing 0.005 mmol Cu_2O, 2 mol%) of DMF (2 mL), the mixture was heated to 120℃ and stirred for 8h. After allowing the mixture to cool to room temperature, the reaction mixture was treated via centrifugation， and the crude material was purified by column chromatography on silica gel (eluent: ethyl acetate/ petroleum ether,1:3 v/v).

Conclusions

In summary, we develop Cu_2O/SBA-15 nanoparticles as a kind of simple, efficient catalyst for cyanation of aryl iodides with non-toxic $K_4[Fe(CN)_6]$. The method at absence of ligand and base provides an environmental and economic perspective for industrial chemistry of aryl nitriles. Meanwhile, the catalyst can recycle five times with a few loss of activity. The significant practical advantages of this catalytic system meet the goals of green chemistry and make this synthetic method has potential application in industrial chemistry.

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Notes and references

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