Catalytic epoxidation of stilbene with FePt@Cu nanowires and molecular oxygen†

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A novel FePt@Cu nanowire catalyst was prepared by the reduction of Cu(acac)$_2$ on the surface of FePt nanowires, in oleylamine (OAm). This nanowire catalyst efficiently epoxidised stilbene in the presence of molecular oxygen, and the conversion and selectivity were maintained with repeated use of the catalyst, compared with recycled catalyst.

Alkene epoxidation is a key reaction in the fine chemical industry, and the resultant epoxides are essential precursors in the synthesis of various important plasticizers, perfumes and epoxy resins.[1] Traditional production of epoxides typically used chemical oxidants like PhIO, NaClO, and peracids.[2] These oxidants are often expensive and tend to be hazardous to handle. Some epoxidation reactions show nonselectivity for the epoxide formed, and also lead to undesirable products resulting in chemical waste. Since the 1980s, microporous titanium silicalite TS-1 has been used as a catalyst for alkene epoxidation. However, steric restriction imposed by the microporous structure on the reactant makes it unsuitable for the epoxidation of bulky alkenes. Novel metallic nanomaterials have more recently been found to be effective alkene epoxidation catalysts. Quek *et al.*[3] showed cobalt to be an efficient epoxidation catalyst, as Co-TUD-1 catalysing the *trans*-stilbene epoxidation produced an 87.7% yield of epoxide. The Valérie Caps[4] group suggested Au/TiO$_2$ was a useful catalyst for *trans*-stilbene epoxidation in methylcyclohexane, in the presence of TBHP. Christopher and Linic[5] concluded that Ag nanowire (NW) catalysts exhibited higher selectivity for ethylene oxide (EO) epoxidation than conventional particle catalysts. This was attributed to a higher concentration of Ag (100) surface facets in the NW catalysts.

Single-crystal studies[6] have demonstrated that oxygenated copper is better than oxygenated silver as an epoxidizing agent for lower alkenes like ethylene, styrene, and *trans*-methylstyrene (all analogues of stilbene). In the present work, we have deposited copper on FePt NW templates to form FePt@Cu NWs, and then used them as catalysts for the epoxidation of stilbene in *o*-xylene using molecular oxygen as the sole oxidant. The catalyst showed outstanding activity and stability.

The novel FePt@Cu NW catalyst was prepared as shown in Fig. 1. The precursor (FePt NWs) was prepared following the method reported by the Sun group,[7] in which 200 mg of Pt(acac)$_2$ was added to 20 ml of oleylamine with the reaction mixture degassed at 120 °C with Ar for 15 min. As the solution turned brown, Fe(CO)$_5$ ($\sim$0.15 ml) was injected. The temperature was raised to 160 °C and held there for 30 min. Cu(acac)$_2$ (50 mg in 10 mL OAm) was injected, and the temperature was then raised to 180 °C for 30 min before being reduced to room temperature. The black product was collected by repeated centrifugation from ethanol, and was easily dispersed in hexane or toluene.

The FePt and FePt@Cu NWs were characterized by transmission electron microscopy (TEM) and high-resolution TEM (HRTEM). The diameter of the FePt NWs was about 2 nm, and their length was over 200 nm (Fig. 1A and E). Cu was evenly distributed on the surface of the FePt NWs, causing the diameter to increase to about 4 nm (Fig. 1B and F). For FePt NWs, the visible lattice fringes corresponded to a spacing of 0.216 nm, and were in agreement with the expected *d*-spacing of the (111) plane of the FePt alloy (0.22 nm) (Fig. 1C).

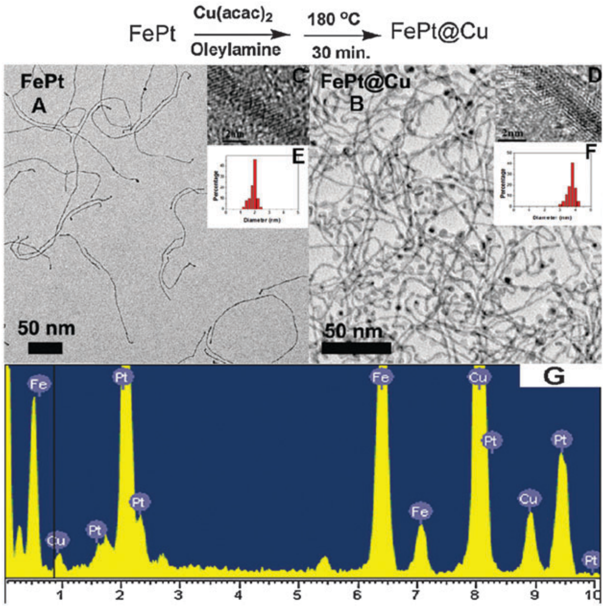

Fig. 1 The FePt@Cu NWs formation from FePt NWs. FePt NWs: (A) TEM; (C) HRTEM and (E) histograms of diameters. FePt@Cu NWs: (B) TEM; (D) HRTEM and (F) histograms of diameters. (G) EDS analysis of FePt@Cu NWs.

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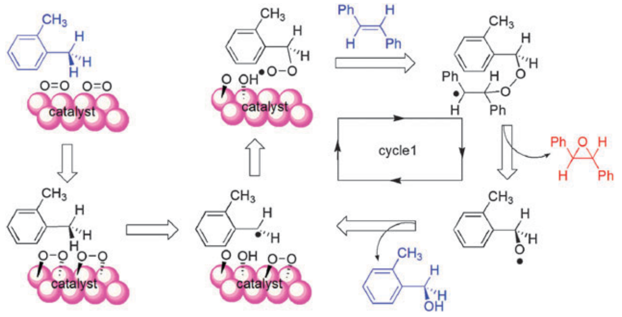
For FePt@Cu NWs, the interfringe distance was 0.220 nm, which was close to the lattice spacing of the (111) plane (0.218 nm) of the CuPt alloy.[8] The powder X-ray diffraction (XRD) pattern (Fig. S1) showed an fcc structure and (111) was the predominant plane.[9] An energy dispersive spectrum (EDS) (Fig. 1G) collected in different regions showed that the Cu content of the FePt@Cu NWs was about 47%. The oxidation states of Cu in the FePt@Cu NWs were examined by X-ray photoelectron spectroscopy (XPS). The results (Fig. S2 and respective discussion in the SI) suggest that the NWs consisted primarily of metallic Cu on the surface of FePt NWs.[10]

trans-Stilbene was selected for the investigation of the FePt@Cu NWs catalytic performance, as an activated and reusable heterogeneous catalyst. Table 1 shows the catalytic performance of the FePt@Cu NWs for *trans*-stilbene epoxidation in different solvents at the same temperature. NMR results showed that *trans*-stilbene oxide was the major product. The solvent efficiency (in terms of epoxide yield) was as follows: toluene, *m*-xylene < DMF < methylcyclohexane < dioxane < *p*-xylene < *o*-xylene. The trend did not appear to follow solvent polarity. Polar solvents (Table 1, entries 1 and 2) were expected to hinder oxidation because of the low catalyst and oxygen solubility. Aromatic hydrocarbons like *o*-xylene and *p*-xylene were efficient solvents for the *trans*-stilbene oxide formation (Table 1, entries 4 and 6).

When using *o*-xylene as solvent, 2-methylbenzaldehyde, *o*-tolylmethanol and 2-methylbenzoic acid were observed as byproducts from the oxidation of the solvent (Fig. S3). An aerobic epoxidation mechanism is proposed as follows: molecular oxygen was first adsorbed on the surface of the FePt@Cu NWs to form active oxygen. Both solvent and stilbene could react with this active oxygen, thus two pathways existed for the reaction: (1) if the solvent reacted with the active oxygen, an unstable free radical intermediate was formed, which could then form peroxide in the oxygenated environment. Peroxide acted as an oxidant in the stilbene oxidation with the epoxy compound as the major product; (2) if the solvent was more stable than stilbene, stilbene could react with the active oxygen and the epoxy compound was also the major product. The former can explain the solvent effects. When *o*-xylene was used as the solvent (Scheme 1, cycle 1), *o*-xylene reacted with the active oxygen to form the free radical intermediate. *trans*-Stilbene epoxidation by the free radical intermediate formed 2,3-diphenyloxirane, and *o*-xylene was oxidised to the corresponding alcohol, aldehyde or acid (cycles 1, 2 and 3). The alcohol or aldehyde could also react with the activated oxygen to form peroxy compounds (cycles 2 and 3) (Scheme S1). Table 1 shows neither toluene nor *m*-xylene was an efficient solvent, despite structural similarities. No oxidised products of toluene and *m*-xylene were detected by GC (Table S1), which resulted in the catalyst becoming inactive in the reaction for entries 3 and 5. Our observation was similar to that of Valérie Caps, who reported that epoxidation was accompanied by partial oxidation of the solvent, and attributed it to a free radical mechanism.[4] We used the same conditions (methylcyclohexane solvent and TBHP oxidant) as Valérie Caps, and their selectivity and conversion were 99.9% and 87.3%, respectively. When oxygen was used as the sole oxidant, the conversion was only 13.3% (Table 1, entries 7 and 8).



Scheme 1 Proposed mechanism for the FePt@Cu-catalyzed aerobic epoxidation of *trans*-stilbene in *o*-xylene (cycle 1).

Table 1 Oxidation of *trans*-stilbene in different solvents[a]

Entry	Solvent	Conv. (%)[b]	Select. (%)[b]	TON[c]
1	DMF	3.5	99	9
2	dioxane	36.7	99	90
3	toluene	Trace	—	—
4	*o*-xylene	87.0	97.8	215
5	*m*-xylene	Trace	—	—
6	*p*-xylene	49.2	76.8	121
7	methylcyclohexane	13.3	99	38
8	methylcyclohexane[d]	87.3	99	218

[a] All reactions were carried out with 0.9 mg FePt@Cu NWs, 0.2 mmol *trans*-stilbene and 2 ml solvent at 100 °C for 24 h under 1atm oxygen. [b] GC yield. [c] TON stands for turnover number, *i.e.* the number of mole of *trans*-stilbene converted per mole of copper in 24 h. [d] 1 equiv. of TBHP added.

Numerous studies have been reported on the epoxidation of alkenes using H_2O_2[11] or TBHP.[12] Several inherent problems were found with these two oxidants. Arends and Sheldon[13] showed that H_2O_2 resulted in the active sites being susceptible to leaching over several heterogeneous catalytic reactions. TBHP always needs to be used with oxygen or else at a lower temperature, and it needs a long reaction time as it quickly decomposes above 75 °C. It is vastly more favourable to employ molecular oxygen as a green environmentally friendly oxidant. In our study, the effect of conventional oxidant was tested and is summarized in Table 2. Our results show that molecular oxygen had a high activity (Table 2 entry 4). When TBHP was used exclusively, there was less epoxidation product detected (Table 2 entry 2), and TBHP quickly decomposed. Air also exhibited high activity with a yield of 70% epoxidation product (Table 2 entry 3). When no oxidant was used, no epoxidation products were detected (Table 2 entry 5).

Table 2 Oxidation of *trans*-stilbene with different oxidants[a]

Entry	Oxidant	Conv. (%)[b]	Select. (%)[b]
1[c]	H_2O_2[d]	15.5	99
2[c]	TBHP[d]	1.1	99
3	air	74.4	94.0
4	oxygen	87.0	97.8
5	none	—	—

[a] All reactions were carried out with 0.9 mg FePt@Cu NWs, 0.2 mmol *trans*-stilbene, and 2 ml *o*-xylene at 100 °C for 24 h. [b] GC yield. [c] All reactions had one equivalent of oxidant added. [d] The concentration of H_2O_2 was 30% and that of TBHP was 70% in water.

Table 3 Oxidation of *trans*-stilbene at different temperatures[a]

Entry	T/°C	Conv. (%)[b]	Select. (%)[b]
1	60	—	—
2	80	9.8	99
3	100	87.0	97.8
4	120	100	37.2

[a] All reactions were carried out with 0.9 mg FePt@Cu NWs, 0.2 mmol *trans*-stilbene, and 2 ml *o*-xylene for 24 h under oxygen (1 atm). [b] GC yield.

The activity of FePt@Cu NWs at different temperatures was investigated using *o*-xylene as the solvent. Temperature exerted a tremendous influence on the conversion and selectivity of both *o*-xylene (Table S2) and *trans*-stilbene (Table 3). At lower temperature (<60 °C), almost no reaction occurred for the FePt@Cu catalyst. When the temperature was elevated to 80 °C, the conversion efficiency increased to 9.8% with a high selectivity (99%) (Table 3 entry 2). The optimal temperature for this reaction was 100 °C (Table 3 entry 3), and the yield of the epoxidation product increased to 85%. When the temperature was increased to 120 °C, *trans*-stilbene was quantitatively converted, but the selectivity decreased to 37.2%. Most of the *trans*-stilbene was converted to benzaldehyde and benzoic acid.

FePt@Cu NWs could be recycled multiple times without obvious catalytic degradation (Fig. 2 and Table S3). For this, we selected *o*-xylene as the solvent and molecular oxygen as the oxidant, at 100 °C for 24 h. The FePt@Cu catalyst was collected by centrifugation and washed several times with ethanol. No significant loss of catalytic activity was observed, and the FePt@Cu NW structure was retained as confirmed by TEM (Fig. S4).

FePt NWs showed no catalytic activity for the epoxidation reaction at the same conditions, which indicated the activity arose from the copper on the surface of the catalyst. FePt@Cu NWs had a higher selectivity than that for Cu nanoparticles (Fig. S5). When *cis*-stilbene was used as the reactant, the yield and stereoselectivity of the oxide product were 80.2% and 60.6/39.4 (*cis*/*trans*), respectively.

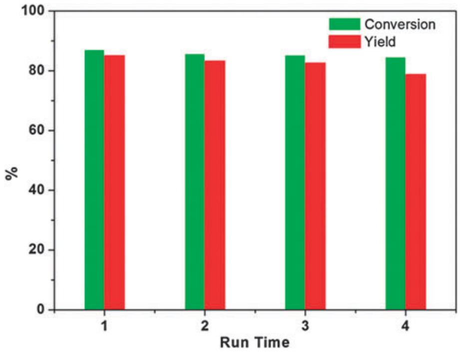


Fig. 2 Recovery and reuse of the FePt@Cu catalyst.

In conclusion, we have shown that FePt@Cu NWs are an effective catalyst for stilbene epoxidation in *o*-xylene with oxygen as the sole oxidant. This catalytic reaction underwent a free radical process, and the catalytic activity was comparable to that of a previously reported Au/TiO_2 catalyst. Our finding will broaden the application of nanomaterial catalysts in organic reactions.

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