Unprecedented Selective Oxidation of Styrene Derivatives using a Supported Iron Oxide Nanocatalyst in Aqueous Medium

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Abstract: Iron oxide nanoparticles supported on mesoporous silica-type materials have been successfully utilized in the aqueous selective oxidation of alkenes under mild conditions using hydrogen peroxide as green oxidant. The supported catalyst could be easily recovered after completion of the reaction and reused several times without any loss in activity (no metal leaching observed during the reaction), constituting a facile and straightforward example of aqueous oxidation chemistry promoted by iron-based heterogeneous systems.

Keywords: alkene oxidation; aqueous phase chemistry; heterogeneous catalysis; supported iron oxide nanoparticles

Aqueous phase reactions have attracted a great deal of attention in our quest to search for more environmentally friendly protocols including solvents and reaction conditions. However, conducting reactions in water has its challenges as they generally require a water-tolerant compatible catalyst which is hydrothermally stable under these conditions.^[1–4] Classical metal oxide supports are not particularly stable under these hydrothermal conditions (moderate temperatures and high water concentrations with respect to reactants and products) and upon strong interaction with water (e.g., alumina) undergo irreversible structural changes as well as loss of textural properties.^[1,2c,3] Consequently, the need for hydrothermally stable and water tolerant materials is a prerequisite to target future biorefinery concepts and the viability of a biobased economy is enhanced if the aqueous processing of platform chemicals in dilute solutions (e.g., fermentation-like) can be accomplished efficiently.

In our aim to develop sustainable methodologies for the preparation of designer materials for greener processes including biomass valorization, we have optimized two novel methodologies for the preparation of supported nanoparticles on mesoporous supports (SNPs). These include microwave-assisted irradiation^[5,6] and more recently mechanochemistry using a dry milling approach.^[7] Additionally, we have also been able to prepare supported nanoparticles in aminopropyl-functionalized SBA-15 materials.^[8] Thus a family of SNPs, ranging from metals (Cu, Pt, Pd, Au) to metal oxides (CuO, Fe₂O₃, Co₃O₄) nanoparticles on various supports including mesoporous aluminosilicates, silicas, zeolite-type materials and metal organic frameworks (MOFs) has been prepared which find extensive applications as heterogeneous catalysts in a wide range of processes such as oxidations,^[6-8] hydrogenations,^[9] C-C and carbon-heteroatom couprocesses.^[7,11] plings,^[5,10] acid-catalyzed among others.^[12] Supported iron oxide nanoparticles have been the major focus of our research endeavors in recent times, taking into account their benign nature in terms of cost, toxicity, availability and environmental compatibility. The versatility and usefulness of such nanomaterials have been also described in different areas of catalysis including environmental remediation,^[13] magnetic separation^[14,15] and biomedical applications.[15,16]

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Nonetheless, the versatile catalytic behavior of iron oxide nanoparticles^[17] and their particular water-tolerant properties^[8] make them highly attractive candidates for advanced aqueous catalytic processes. In view of these premises, we report here the unprecedent activity of supported iron oxide nanoparticles on mesoporous aluminosilicates in the aqueous phase selective oxidation of alkenes with hydrogen peroxide as a green oxidant. Although the selective oxidation of alkenes has been extensively carried out using aqueous hydrogen peroxide,^[18] to the best of our knowledge, it has never been previously reported under neat water conditions.

Results obtained in the selective aqueous oxidation of alkenes using the iron oxide nanoparticles as catalyst are summarized in Table 1. Styrene was initially selected as a starting material to optimize the reaction parameters and conditions. In principle the reaction progressed smoothly to afford benzaldehyde as the only product (no over-oxidation to benzoic acid was observed) in high yields of over 95% under reflux conditions for 3 h. The employed catalyst loading was initially 5 mol%, but this could be remarkably reduced to catalytic quantities of Fe-SNP (0.5 mol%) which were able to provide identical yields of benzaldehyde after 4 h reaction time. The poor solubility of styrene in water did not seem to be problematic for the successful development of the reaction, most probably related to the already demonstrated watertolerant properties of the catalyst in oxidation reactions.^[8] The hydrogen peroxide efficiency in the systems was very high (>95%), confirming the ability of Fe to activate this oxide and corroborating earlier observations.[6-8]

Upon optimization of the results for styrene, the scope of the reaction was subsequently examined by using substituted styrenes as well as related aromatic and linear alkenes and these results are summarized in Table 1. The optimized protocol was amenable to a wide range of electron-donating and electron-withdrawing substituents in all positions of the aromatic ring (ortho, meta and para). High yields of the ensuing aldehydes were obtained in all cases even for pyridine-type compounds (Table 1, entry 7). However, the scope of the methodology was found to be rather narrow in terms of the nature of the alkene, being unsuccessful for less activated linear alkenes (1-octene, Table 1, entry 11) or unconjugated aromatic substrates (Table 1, entry 12). The conjugation of the exo double bond in styrene with the aromatic ring seemed to have a significant effect on the activity of the systems, pointing out the importance of the electronic density in the double bond of the investigated substrates for the proposed aqueous selective oxidation of alkenes using supported iron oxide nanoparticles. Similar results have been previously reported in the literature for various Mn oxidation catalysts.^[22]

Table 1. Selective oxidation of styrene derivatives using supported iron oxide nanoparticles.

Entry	Substrate	Product	Yield [%] ^[a,b]	
1	5	СНО	95	
2	F	СНО	92	
3		СНО	90	
4	Br	CHO	90	
5		CHO	90	
6		СНО	92	
7	CI		95	
8	Ś	СНО	90	
9	OCH ₃		93	
10	CI	CHO	89	
11			-	
12		СНО +	-	

^[a] Isolated yields.

^[b] The reaction was conducted in the presence of 5 mmol alkene, 5 mmol H_2O_2 (30 wt%), 0.5 mol% Fe catalyst in water under reflux for 4 h.

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The most important feature of the proposed system is its hydrothermal stability under the investigated conditions. Reusability results are depicted in Figure 1 in which the reusable nature of the nanocatalyst is clearly demonstrated after several uses. Upon catalyst filtration, the filtrate was also checked for activity and quantities of Fe (which could have leached from the catalyst) providing virtually no additional conversion with fresh reagents after 12 h of reaction as well as no detectable Fe quantities in solution (<0.5 ppm as



Figure 1. Reusability of Fe-SNP catalyst in the aqueous oxidation of styrene with H_2O_2 . *Reaction conditions:* 5 mmol styrene, 5 mmol H_2O_2 , 0.5 mol% Fe-SNP, 2 mL water, 100 °C, 4 h reaction.

measured by ICP/MS). These findings indicate a truly heterogeneous protocol in which Fenton-type chemistries may take place. However, we do not have evidence for the presence of radicals in the reaction so that a plausible mechanism cannot be proposed since the reaction might take place *via* non-OH radical oxidizing mechanisms.^[23]

Further studies are ongoing to complete these results in an attempt to extend the scope of the protocol to related alkenes as well as to investigate the competitive effect of alcohol/double bonds in the selective oxidation of allylic alcohols. In any case, the proposed system possesses remarkably improved activities and selectivities compared to those of related heterogeneous systems reported in the literature (Table 2). These include the widely investigated TS-1 and related titanium materials, similar Fe-containing catalysts as well as V and Cu complexes.^[24-29]

A novel selective aqueous phase approach for the oxidation of styrene derivatives using water-compatible, supported iron oxide nanoparticles on mesoporous SBA-15 materials has been successfully demonstrated. High yields of aldehyde products (>90%) could be achieved in all cases using catalytic quantities (0.5 mol%) of the highly active iron catalyst. The salient features of the protocol are high hydrogen per-oxide efficiency (>95%), mild reaction conditions and an effective reusability of the catalyst that ameliorate its water-tolerant properties. At present, the

Table 2. Comparison of catalytic activities in the oxidation of styrene using heterogeneous catalysts.

Reference	Reaction conditions	Catalyst	Product(s)	Yield [mol%]	Benzaldehyde selectivity [mol%]
This work	5 mmol styrene, 5 mmol H ₂ O ₂ , 0.03 g Fe/ SBA-15, water, 373 K, 4 h	Fe/SBA-15	benzaldehyde	95	100 (isolated yield)
[24]	8.8 mmol styrene, 4.4. mL H_2O_2 (30	TS-1	benzaldehyde, styrene	21	26
	wt%), 20 mL acetonitrile, 0.1 g catalyst,	Ti-beta	oxide, benzoic acid,	20	57
	343 K, 5 h	Ti-MCM-41	etc.	26	52
[25]	10 mmol styrene, , 9.8 mmol H_2O_2 , 10 mL	TS-1	benzaldehyde, styrene	35	23
	DMF, 0.2 g catalyst, 376 K, 2 h	Fe-MCM-41	oxide, benzoic acid,	14	37
		Fe-ZSM-5	etc.	5	63
[26]	5 mmol styrene, 15 mmol H ₂ O ₂ (30 wt%), 10 mL acetonitrile, 0.015 g catalyst, 348 K, 6 h	V complex [VO ₂ (sal-ambmz)]/ Y zeolite	benzaldehyde, styrene oxide, benzoic acid, etc.	97	55
		Cu complex [Cu(sal- ambmz)Cl]/Y zeo- lite		57	51
[27]	10 mmol styrene, 10 mmol H_2O_2	2%Fe-SBA-1	benzaldehvde, styrene	66	73
	(30 wt%), 10 mL acetonitrile, 0.05 g cata- lyst, 80°C, 4 h	2%Ti-SBA-1	oxide, other	70	50
[28]	10 mmol styrene, 30 mmol H_2O_2	VO-salen-SBA-15	benzaldehyde, styrene	84	83
	(30 wt%), 10 mL acetonitrile, 80 °C, 8 h	Cu-Salen-SBA-15	oxide, other	97	45
[29]	5 mmol styrene, 15 mmol H_2O_2 (30 wt%),	Au-SBA-12	benzaldehyde, styrene	75	_
	0.1 g catalyst, microwaves, 300 W, 140 °C,	Ag-SBA-12	oxide, phenylacetalde-	90	_
	30 min	Pd-SBA-12	hyde	97	96

scope of the reaction is rather restricted to activated alkenes but further investigations are currently ongoing in our laboratories to improve the applicability of the nanocatalyst to less activated substrates and more challenging systems.

Experimental Section

Catalyst Synthesis

The preparation of supported iron oxide nanoparticles has been previously reported.^[8] Full details of the characterization of the materials have been given in the Supporting Information. Briefly, SBA-15 was functionalized with aminopropyl groups utilizing the protocol reported by Wang et al.^[19] to achieve NH₂ loadings of *ca*. 0.85–0.90 mmolg⁻¹ and then iron oxide nanoparticles were deposited on the materials using Fe(NO)₃·9H₂O as precursor.^[8] The final product was oven dried at 80°C overnight prior to its use in the catalytic reaction. Fe/SBA-15 materials had a surface area of 620 m²g⁻¹, a pore size of 4.8 nm, with nanoparticle sizes in the 5-7 nm range, homogeneously dispersed on the silica support (see the Supporting Information).

Catalytic Experiments

In a typical catalytic test, styrene (5 mmol), H₂O₂ (5 mmol, 50% v/v aqueous solution) and 0.5 mol% of Fe/SBA-15 materials in 2 mL water were refluxed (100 °C) for 4-6 h. Upon completion, as indicated by TLC, the final mixture was filtered off to recover the catalyst, which was washed with ethyl acetate and subsequently dried at 80°C prior to its reuse in the reaction. The combined filtrate and ethyl acetate washings were then washed with water and the organic layer separated and dried over magnesium sulfate. The product from the organic solution was obtained upon solvent removal. The conversion was determined by ¹H NMR (400 MHz) spectroscopic analysis and compounds were characterised by GC and GC/MS. In most cases, products could be isolated in their pure forms by simple filtration and evaporation of the solvent. Further purification required column chromatography in some cases. The isolated products all known compounds which have been previously identified and characterized in several literature reports.^[20,21]

Recyclability Experiments

Upon completion of the first reaction to afford a quantitative yield of the corresponding aldehyde (>95% yield), the catalyst was recovered by filtration, washed with acetone and ethanol and oven dried at 80 °C overnight. A new reaction was then performed with fresh solvent and reactants under identical conditions.

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