Hollow Iron Oxide Nanoparticles are Selective Oxidation Catalysts of Styrene using Molecular Oxygen

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Equipment

High-resolution TEM and EDAX were performed using a Philips CM200 200 kV TEM. High-pressure experiments were performed employing a Parr Instruments 5000 Series Multiple Reactor System equipped with 100 mL reaction vessels. Gas chromatography (GC) was performed on an Agilent 7890A Gas Chromatograph equipped with an Agilent DB-WAX column.

Materials

Iron(0) pentacarbonyl, 1-octadecene, styrene, toluene, acetonitrile, benzyl ether, oleic acid, Fe(II/III) nanoparticles, Fe(III) nanoparticles were purchased from Sigma-Aldrich and used without further purification. Oleylamine was purchased from Sigma-Aldrich and vacuum distilled over CaH_2 prior to use. 400-mesh carbon supported TEM grids were obtained from Electron Microscopy Science.

Preparation of Fe/FeOC/S NP

In a 250mL Schlenk round bottom containing a stirrer, 20mL of 1-octadecene and 0.3mL of previously distilled oleylamine had argon bubbled through them at 120°C for 30min. The solution was then heated to 260°C. After the temperature was reached 0.7mL of $Fe(CO)_5$ was added. The solution was stirred at 260°C vigorously for 1h under argon. The solution was allowed to reach room temperature before the nanoparticles were separated using a supermagnet and then washed with four 10mL aliquots of hexanes. After each wash aliquot was delivered to the nanoparticles, the solution would be sonicated for 30 seconds prior to removal of liquid from nanoparticles that are held by a supermagnet. After the washes are complete, the nanoparticles are dried under vacuum and then weighed out as a powder for the use in catalysis.

Preparation of Fe_3O_4 NS

In a 250mL Schlenk round bottom containing a stirrer, 20mL of 1-octadecene and 0.3mL of previously distilled oleylamine had argon bubbled through them at 120C for 30min. The solution was then heated to 260C. After the temperature was reached 0.7mL of Fe(CO)5 was added. The solution was stirred at 260C vigorously for 1h under argon and then air was introduced through a syringe. The syringe was then inserted into the solution and air was bubbled through the solution at 260C for 1h. The solution was allowed to come to room temperature and nanoparticles were allowed to settle onto the stir bar with the aid of a supermagnet. The nanoparticles were washed with 10mL of hexanes four time and then dried under vacuum.
Their average diameter was measured to be 16.7+2.0nm based on the counting of over 100 NPs.

Preparation of eFe_3O_4 NS

In a 250mL Schlenk round bottom containing a stirrer, 20mL of 1-octadecene and 0.3mL of previously distilled oleylamine had argon bubbled through them at 120C for 30min. The solution was then heated to 260°C. After the temperature was reached 0.7mL of Fe(CO)5 was added. The solution was stirred at 260°C vigorously for 1h under argon and then air was introduced through a syringe. The syringe was then inserted into the solution and air was bubbled through the solution at 260°C for 1h. The solution was allowed to come to room temperature and nanoparticles were allowed to settle onto the stir bar with the aid of a supermagnet. The nanoparticles were washed with 10mL of hexanes four time and then dried under vacuum. These nanoparticles were then etched through a modified version of the process developed in Sun's lab (*J. Am. Chem. Soc.*, **2009**, *131* (30), pp 10637–10644) to give eFe_3O_4 NS. Briefly, a mixture was prepared in a 250mL schlenk round bottom flask was with 0.17mL oleylamine, 0.16mL oleic acid, 50mg of Fe_3O_4 NS, and 20mL of benzyl ether which was then degassed with argon at r.t. for 30min. The reaction was then heated to 260°C while being vigorously stirred and maintained at this temperature for 45 minutes. At the end of the reaction, the solution was allowed to cool and the etched nanoparticles were washed with four aliquots of 10mL hexanes before being dried under vacuum.
Their average diameter was measured to be 16.3+1.5nm based on the counting of over 100 NPs.

Catalysis experiments

Into a 25mL volumetric flask, 4.7g of styrene, 0.425g of dodecane and 0.2865g of octane were measured out and then the solution was diluted to a total of 25mL with solvent. The solution was then added to a glass liner containing 5mg of nanoparticle catalyst and sonicated to redisperse the nanoparticles. A stir bar was added and the whole apparatus was inserted into a high pressure reactor. The reactor was charged with O_2 pressure and heated for 24h while stirring. At the end of the reaction, the nanoparticles were allowed to settle onto the stir bar and the apparatus and nanoparticles were washed 3 times with solvent which was added to the reaction solution. The mixture was placed over a supermagnet and left for several minutes and then a sample was taken for GC-FID.

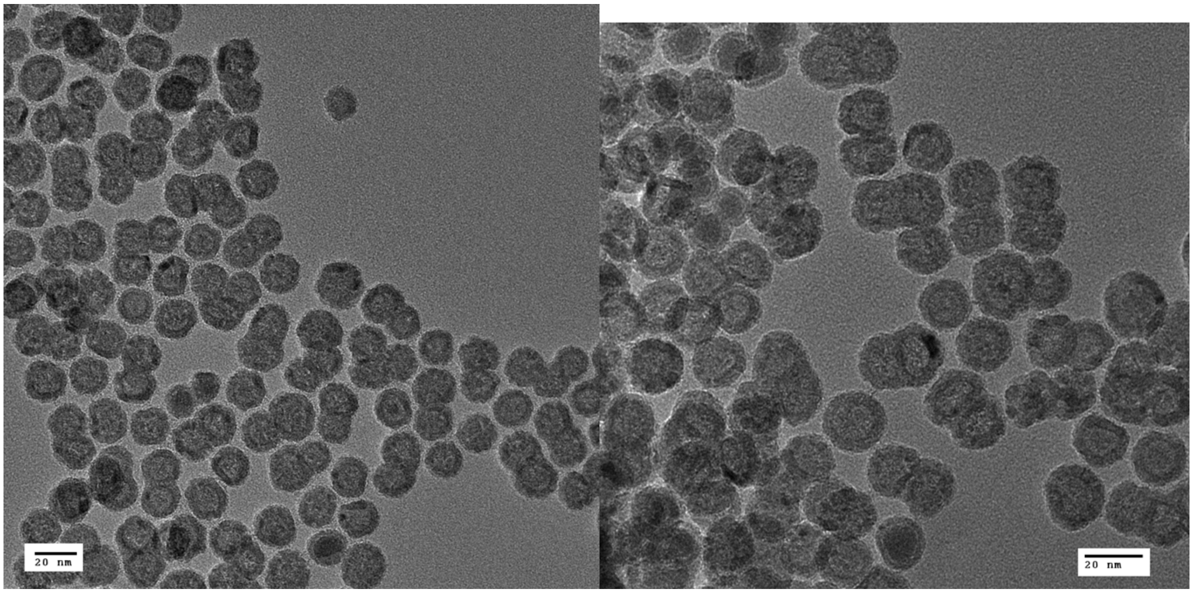

Figure S1: TEM micrographs of nanoparticle samples. Left: Fe_3O_4 NS, right: eFe_3O_4 NS (note that HR TEM images – see figure 1- are needed to visualize the etched structure)

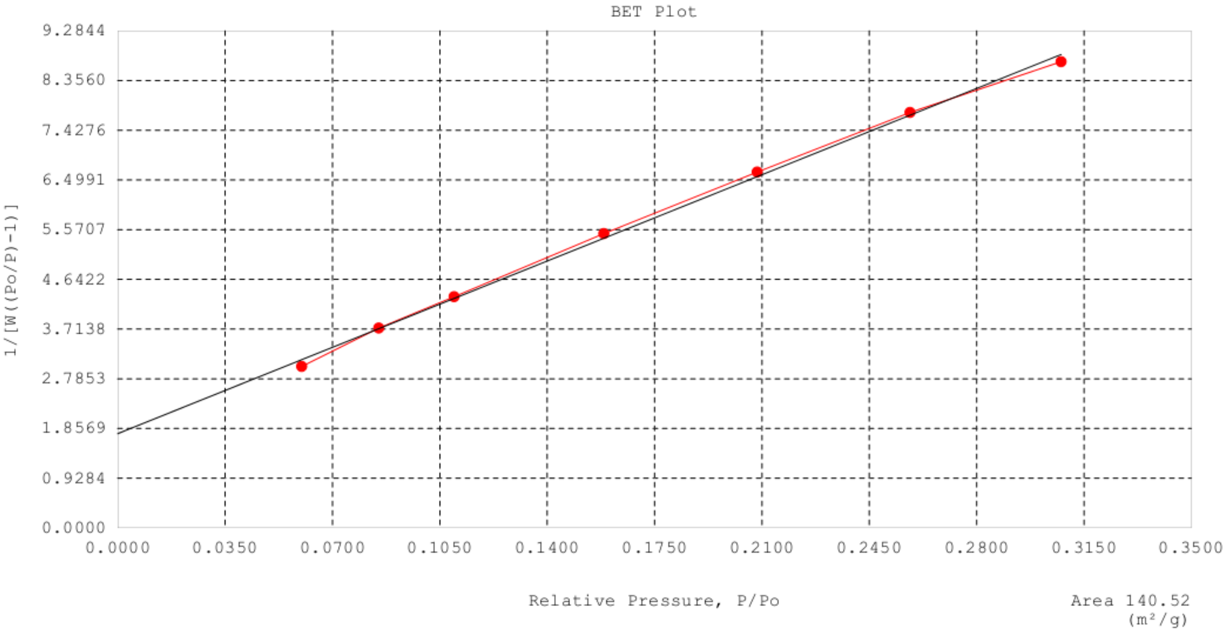

Figure S2: A7-point BET surface area plot of Fe_3O_4 NS. *W* is the quantity of adsorbed gas; *P* and *P*0 are the equilibrium and the saturation pressure of the N_2 adsorbate molecule.

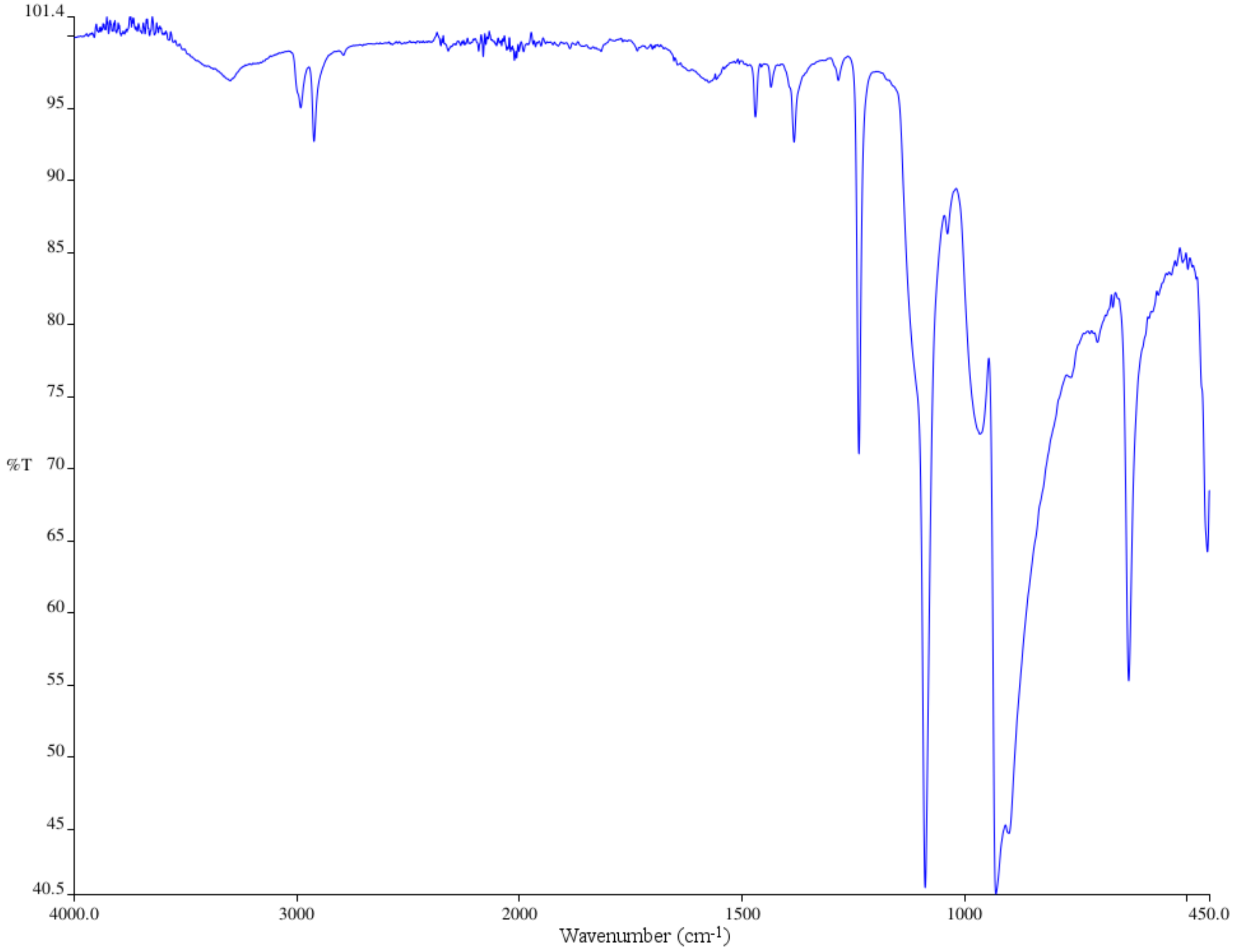

Figure S3: FTIR of polyacetal formed during catalytic reaction.

Table S1: Catalyst screening in toluene[a]

Catalyst	Conv.%	Benzaldehyde	Benzoic Acid	Other[b]
Fe_2O_3 NP	33	72	13	15
Fe_3O_4 NP	26	76	12	12
FeFeOCS	40	76	0	24
Fe_3O_4 NS	59	65	20	15
eFe_3O_4_NS	48	49	25	26

[a] Reaction conditions: 0.5 mol % catalyst, 4bar O_2, 24h, 90°C, 1.8M toluene. [b] Sum of acetophenone, styrene oxide, and oligomers.

Table S2: Temperature optimization at 4bar in toluene using Fe_3O_4 NS [a]

Catalyst	Conv.%	Selectivity %		
		Benzaldehyde	Benzoic Acid	Other [b]
80	29	100	0	0
90	66	56	17	27
95	76	56	17	27
100	78	44	16	40

[a] Reaction conditions: 0.5 mol % Fe_3O_4 NS, 4bar O_2, 24h, 90°C, 1.8M toluene. [b] Sum of acetophenone, styrene oxide, and oligomers.

Table S3: Temperature optimization at 30bar in toluene using Fe_3O_4 NS [a]

Catalyst	Conv.%	Selectivity %		
		Benzaldehyde	Benzoic Acid	Other [b]
80	15	100	0	0
90	93	41	49	10
95	94	42	49	9
100	97	38	48	14

[a] Reaction conditions: 0.5 mol % Fe_3O_4 NS, 4bar O_2, 24h, 90°C, 1.8M toluene. [b] Sum of acetophenone, styrene oxide, and oligomers.

Table S4: Temperature optimization at 4bar in acetonitrile using Fe_3O_4 NS [a]

Catalyst	Conv.%	Selectivity %		
		Benzaldehyde	Benzoic Acid	Other [b]
80	31	76	14	10
90	77	64	21	15
95	85	58	13	29
100	87	55	18	27

[a] Reaction conditions: 0.5 mol % Fe_3O_4 NS, 4bar O_2, 24h, 90°C, 1.8M acetonitrile. [b] Sum of acetophenone, styrene oxide, and oligomers

Table S5: Temperature optimization at 4bar in acetonitrile using eFe_3O_4 NS [a]

Catalyst	Conv.%	Selectivity %		
		Benzaldehyde	Benzoic Acid	Other [b]
80	11	79	15	6
90	90	73	13	14
95	91	60	19	21
100	97	57	17	26

[a] Reaction conditions: 0.5 mol % eFe_3O_4 NS, 4bar O_2, 24h, 90°C, 1.8M acetonitrile. [b] Sum of acetophenone, styrene oxide, and oligomers

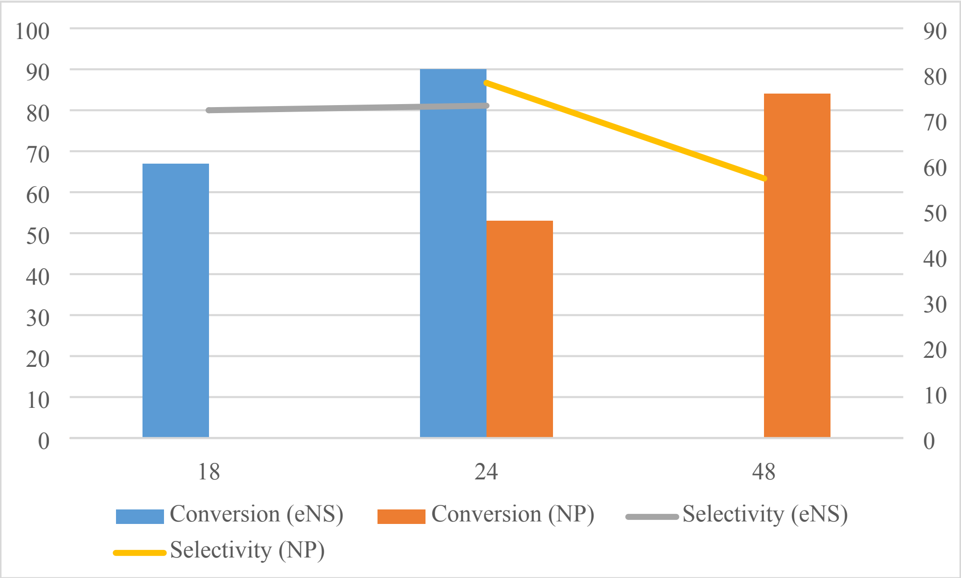

Figure S4: Comparison of the conversion and selectivity for commercial Fe_3O_4 NP (NP) and synthesized eFe_3O_4 NS (eNS) at various times. Three salient points to note: 1) eNS are faster catalysts than NP 2) Conversions can be enhanced with longer reaction times 3) eNS is a unique catalyst as it sustains high selectivity as the reaction evolves.

Table S6: Comparison between the conversions and selectivity to benzaldehyde obtained in the articles most related to this work (same oxidant: O_2, same reagent: styrene and otherwise comparable conditions, Refs. 9, 10 and 11) and this work (in bold).

Reference	Catalyst	Conversion (%)	Selectivity to benzaldehyde (%)	Reaction time (h)
9	Au_{55} clusters onto silica. Loading: 0.67wt%	25.8	82.1	15
10	$Pt@Fe_2O_3$ nanowires at 80°C	76.8	43.9	24

	Pt@Fe_2O_3 nanowires at 50°C	4.5	93.8	24
11	Gold wires in 1,4-dioxane as solvent	81.7	38.5	20
	Gold wires in toluene as solvent	17	87.2	20
This work	**eFe_3O_4 NS (Hollow etched)**	**90**	**73**	**24**

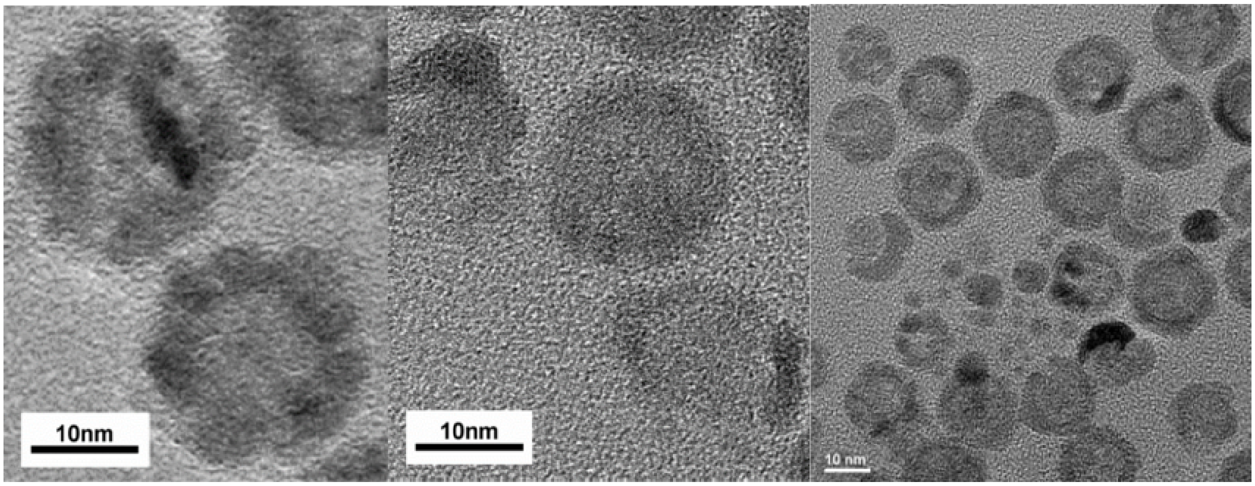

Figure S5: TEM micrographs of nanoparticle samples. Left: eFe_3O_4 NS, middle: eFe_3O_4 NS after 1 recycle, right: eFe_3O_4 NS after 2 recycles.

Table S7: Catalytic tests to probe the role of oleylamine in conversion and selectivity

Entry		Styrene conversion	Benzaldehyde selectivity	Benzoic acid	other
1	eFe_3O_4 NS recycle 1 + oleylamine	88%	67%	9%	24%
2	Fe_3O_4 NPs + oleylamine	68%	67%	10%	23%
3	Fe/FeOC/S	56%	81%	7%	12%

Conditions: 90°C, 4bar, 1.8M in acetonitrile

It was important to probe the role of oleylamine in the catalysts presented. One possibility is that the drop in selectivity for eFe_3O_4 NS after recycling was due to loss of oleylamine. In entry 1 is presented a catalytic run done after one catalytic cycle, washing and reloading of the catalyst with 1mL of oleylamine. In this experiment, conversion was conserved and selectivity dropped (from 73% to 67%), but by less than in absence of oleylamine (from 73% to 41%). This shows that oleylamine does play a role in selectivity in these system upon recycling. The presence of oleyamine however is not sufficient to explain the reactivity, as seen through analysis of entries 2 and 3. In entry 2 is presented a test where fresh Fe_3O_4 NPs + 1mL of oleylamine were used as catalyst. In this case, comverstion was improved (from 53 to 68%) while selectivity dropped (from 78% to 67%). Also, in entry 3 is presented the results obtained with Fe/FeOC/S, the precursor to Fe_3O_4 NS and a material that also has a ferrite surface and oleylamine as surfactant (from table 1). So oleylamine alone can not explain the unique results observed in the article.