Experimental section

General remarks

Conversion and yields of the products were accomplished by GC-FID on a Shimadzu GC-16A instrument using a 25 m CBP1–M25 (0.32 mm ID, 0.5 mm coating) capillary column. IR spectra were recorded on a Perkin Elmer 780 instrument. UV-Vis spectra were recorded on a V670 JASCO spectrophotometer. NMR spectra were recorded with a Brucker Avance DPX FT-NMR 400 MHz instrument. TEM images were obtained by TEM instrumentation (Philips CM 10). X-ray diffraction (XRD, D8, Advance, Bruker, axs), TGA (Shimadzu 50) were employed for characterization of the heterogeneous catalyst. The Mn content of fresh and recycled catalyst were measured with ICP (Varian, visa-pro). The free Schiff base \(N,N'\)-bis(salicylidene)ethylenediamine: Salen and its manganese complex were synthesized as reported in the literature.\(^1\) The freshly prepared \(n\text{-Bu}_4\text{NHSO}_5\) (TBAOX),\(^2-4\) was a much stronger oxidant than commercially available samples.

**Synthesis of \(n\text{-Bu}_4\text{NHSO}_5\) (TBAOX),\(^2-4\)**

A sample of potassium monopersulfate (2.0 g, 6.5 mmol) in water (20 ml) was stirred with tetrabutylammonium hydrogen sulfate (2.0 g, 5.9 mmol) for 20 min. The solution was extracted with \(\text{CH}_2\text{Cl}_2\) (40 ml) and the organic phase was dried over sodium sulfate and filtered. After evaporation of the solvent, the remaining paste was washed with hexane (10 ml) and dried under vacuum. A white powder (1.5 g, 0.97 mmol) was obtained with a purity >90% (determined by iodometry). The freshly prepared TBAO showed much greater oxidizing ability than the commercially available samples, and remained quite active for at least two months.
Synthesis of silica-coated maghemite nanoparticles (SMNP)

The synthesized Fe$_2$O$_3$, suspended in 35 mL ethanol and 6 mL deionized water and sonicated for 15 min. 1.5 mL of tetraethylorthosilicate (TEOS) was added slowly to the mixture and sonicated for 10 min. Then aqueous ammonia (10%, 1.4 mL) was added slowly over 10 min under mechanical stirrer. The mixture was heated at 40 °C for 12 h. The iron oxide nanoparticles with a thin layer of silica (Fe$_2$O$_3$@SiO$_2$) were separated by an external magnet and washed three times with ethanol and dried under vacuum.

Silanation of silica-coated maghemite nanoparticles (ASMNP)

A 10g sample of dry SMNP powder was mixed by vigorous stirring with 200 ml of toluene. After the particles were well dispersed under sonication, 20 ml of (3-aminopropyl)triethoxysilane (APS) was added slowly to this mixture and the suspension was heated to refluxing temperature for 14 h while maintaining mechanical stirring. The final particles were separated by an external magnet and after washing twice with toluene, and once with acetonitrile were dried under vacuum. The dried sample was stored in refrigerator prior to use.

Fig. S1. The XRD patterns of MNP
Fig. S2. The XRD patterns of **ASMNP**

Fig. S3. The XRD patterns of **Mn-salen@ASMNP**
Fig. S4. TEM image of reused Mn-salen@ASMNP.

Fig. S5. The diffuse reflectance UV–Vis spectra of fresh (a) and used Mn-salen@ASMNP (b) after recovery from cyclooctene oxidation.
Fig. S6. EDS spectrum of the reused Mn-salen@ASMNP

Table S1. The recycling of catalytic system in the cyclooctene epoxidation\textsuperscript{a}

<table>
<thead>
<tr>
<th>Run</th>
<th>Cyclooctene conv.%\textsuperscript{b}</th>
<th>Mn Leached %\textsuperscript{c}</th>
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<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>0.87</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
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<td>0.0</td>
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<td>6</td>
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<tr>
<td>7</td>
<td>93</td>
<td>0.0</td>
</tr>
<tr>
<td>8</td>
<td>93</td>
<td>0.0</td>
</tr>
</tbody>
</table>

\textsuperscript{a}The reaction were run according to procedure mentioned in Table 2.
\textsuperscript{b}Determined by GC. \textsuperscript{c}Determined by ICP.
**GC conditions and retention times:**

GC (CPB1-M25 capillary column, 0.32 mm ID, 0.5 mm coating, GC-16A, Shimadzu Corporation)

» Cyclooctene oxide; Carrier gas (Ar, 1kg/cm$^2$), column temperature (100 °C), injection temperature (220 °C), detection temperature (250 °C), retention time (10.4 min).

» Cyclohexene oxide; Carrier gas (Ar, 1kg/cm$^2$), column temperature (80 °C), injection temperature (200 °C), detection temperature (250 °C), retention time (8.7 min).

» Norbornene oxide; Carrier gas (Ar, 1kg/cm$^2$), column temperature (100 °C), injection temperature (250 °C), detection temperature (250 °C), retention time (10.7 min).

» Indene oxide; Carrier gas (Ar, 1kg/cm$^2$), column temperature (110 °C), injection temperature (250 °C), detection temperature (250 °C), retention time (11.5 min).

» Pinene oxide

Carrier gas (Ar, 1kg/cm$^2$), column temperature (110 °C), injection temperature (220 °C), detection temperature (250 °C), retention time (10.5 min).

» 1-Octene oxide

Carrier gas (Ar, 1kg/cm$^2$), column temperature (100 °C), injection temperature (220 °C), detection temperature (250 °C), retention time (9.7 min).

» 2-(2-methyl-2-oxiranyl)ethanol; Carrier gas (Ar, 1kg/cm$^2$), column temperature (100 °C), injection temperature (200 °C), detection temperature (250 °C), retention time (8.1 min).

» (3,3-dimethyl-2-oxiranyl)methanol; Carrier gas (Ar, 1kg/cm$^2$), column temperature (100 °C), injection temperature (200 °C), detection temperature (250 °C), retention time (9.2 min).

» Acetophenone; Carrier gas (Ar, 1kg/cm$^2$), column temperature (120 °C), injection temperature (250 °C), detection temperature (250 °C), retention time (11.4 min).

» Benzaldehyde; Carrier gas (Ar, 1kg/cm$^2$), column temperature (120 °C), injection temperature (250 °C), detection temperature (250 °C), retention time (10.2 min).

» 4-chlorobenzaldehyde; Carrier gas (Ar, 1kg/cm$^2$), column temperature (120 °C), injection temperature (250 °C), detection temperature (250 °C), retention time (12.1 min).

» 4-Methylbenzaldehyde; Carrier gas (Ar, 1kg/cm$^2$), column temperature (120 °C), injection temperature (250 °C), detection temperature (250 °C), retention time (11 min).
1-Adamantanol; Carrier gas (Ar, 1kg /cm$^2$), column temperature, 120 °C, injection temperature (300 °C), detection temperature (300 °C), retention time (11.7 min).

Benzophenone; Carrier gas (Ar, 1kg /cm$^2$), column temperature program, 150 °C-5°C/min-250°C, injection temperature (300 °C), detection temperature (300 °C), retention time (10.6 min).

4-methoxybenzaldehyde; Carrier gas (Ar, 1kg /cm$^2$), column temperature program, 150 °C-5°C/min-250°C, injection temperature (300 °C), detection temperature (300 °C), retention time (8.3 min).

4-Nitrobenzaldehyde; Carrier gas (Ar, 1kg /cm$^2$), column temperature program, 150 °C-5°C/min-250°C, injection temperature (300 °C), detection temperature (300 °C), retention time (11 min).

4-t-Bu-benzaldehyde; Carrier gas (Ar, 1kg /cm$^2$), column temperature program, 150 °C-5°C/min-250°C, injection temperature (300 °C), detection temperature (300 °C), retention time (8.1 min).

Cyclohexanone; Carrier gas (Ar, 1kg /cm$^2$), column temperature, 100 °C, injection temperature (250 °C), detection temperature (250 °C), retention time (9.5 min).

2-Octanone; Carrier gas (Ar, 1kg /cm$^2$), column temperature, 100°C, injection temperature (250 °C), detection temperature (250 °C), retention time (10.1 min).

4-methoxyacetophenone; Carrier gas (Ar, 1kg /cm$^2$), column temperature program, 150 °C-5°C/min-250°C, injection temperature (300 °C), detection temperature (300 °C), retention time (9.7 min).

4-Nitroacetophenone; Carrier gas (Ar, 1kg /cm$^2$), column temperature program, 150 °C-5°C/min-250°C, injection temperature (300 °C), detection temperature (300 °C), retention time (9.2 min). 201°C

2-Hydroxy-1-phenylethanone; Carrier gas (Ar, 1kg /cm$^2$), column temperature program, 150 °C-5°C/min-250°C, injection temperature (300 °C), detection temperature (300 °C), retention time (8.5 min).

References:
