Mesoporous MnCeO$_x$ solid solutions for low temperature and selective oxidation of hydrocarbons

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The development of noble-metal-free heterogeneous catalysts that can realize the aerobic oxidation of C–H bonds at low temperature is a profound challenge in the catalysis community. Here we report the synthesis of a mesoporous Mn$_{0.5}$Ce$_{0.5}$O$_x$ solid solution that is highly active for the selective oxidation of hydrocarbons under mild conditions (100–120 °C). Notably, the catalytic performance achieved in the oxidation of cyclohexane to cyclohexanone/cyclohexanol (100 °C, conversion: 17.7%) is superior to those by the state-of-art commercial catalysts (140–160 °C, conversion: 3-5%). The high activity can be attributed to the formation of a Mn$_{0.5}$Ce$_{0.5}$O$_x$ solid solution with an ultrahigh manganese doping concentration in the CeO$_2$ cubic fluorite lattice, leading to maximum active surface oxygens for the activation of C–H bonds and highly reducible Mn$^{4+}$ ions for the rapid migration of oxygen vacancies from the bulk to the surface.
Aerobic oxidation has been considered as one of the most fundamental processes throughout organic synthesis and industrial chemistry. Nowadays, realizing the selective oxidation of sp³ C–H bonds at low temperatures represents a critical challenge in the petroleum industry, because the current methods for the activation of C–H bonds generally require high temperature (for example, ~600 °C for propane dehydrogenation) and excessive energy input, often resulting in uncontrolled product selectivity and undesirable cokes.

Among all C–H activation processes, the liquid-phase oxidation of cyclohexane to KA oil (K: cyclohexanone, A: cyclohexanol, production > 2 × 10⁸ ton per year) is widely deployed in Nylon-6 and Nylon-6,6 production. The industrial process proceeds with homogeneous Co/Mn carboxylate salts at 140–160 °C using 0.9–1.0 MPa air as an oxidant. To minimize the overoxidation of KA oil to by-products, cyclohexane conversion is preferentially limited to 50%. Figure 1a summarizes representative pathways to caprolactam (monomer for Nylon-6); the low cyclohexane conversion degree, ideally achieving a higher cyclohexane conversion.

Recently, MnₓOₓ–CeO₂ hybrid catalysts with multiple redox states and high oxygen storage capacity have exhibited superior performance in several types of catalytic oxidation, such as ammonia oxidation, combustion of volatile organic compounds (amines) and CO oxidation. Compared with either MnO₂ or CeO₂ (ceria), the significant decrease in reaction temperature enabled by the MnₓOₓ–CeO₂ composite is very appealing, which directly evidences the synergistic interaction of MnO₂ and CeO₂ with more active oxygen species. These ‘reactive’ oxygen species (for example, O₂⁻, O₂⁻ and O₂⁻) are generated exactly at the interface between the MnO₂ and ceria lattice, the so-called MnₓCe₁₋ₓOₓ solid solution. Since the formation of a Mn–O–Ce–bond would reduce the Coulomb interaction of Mn⁵⁺–O⁻ or Ce⁴⁺–O⁻, the formation energy of oxygen vacancies can be greatly lowered. Several approaches to MnₓOₓ–CeO₂ catalysts—such as the co-precipitation, sol-gel, combustion, surfactant-assisted precipitation and hydrothermal methods—have been developed. Unfortunately, traditional methods of preparing a MnₓOₓ–CeO₂ catalyst often lead to the formation of multiphases with limited MnₓCe₁₋ₓOₓ solid solution, which is only observed at the interfaces between MnO₂ and ceria nanocrystals. Recently, Yang and co-workers reported a general route to phase-pure transition-metal substituted ceria nanocrystals via solution-based pyrolysis of bimetallic Schiff base complexes, but the ratio of transition metal substitution (10 mol %) is somewhat low. Given that the solid solution phase of a MnₓOₓ–CeO₂ catalyst is responsible for the low-temperature redox activity, a MnₓOₓ–CeO₂ solid solution with 50% manganese atoms doping into a ceria lattice may be an ideal candidate for catalytic oxidation, because maximum active oxygen species are expected in such a structure. In the view of synthetic chemistry, the biggest challenge for constructing a MnₓOₓ–CeO₂ solid solution with as high as 50% cerium atoms substituted by manganese atoms but retaining the cubic fluorite structure lies in controlling the homogenization with Mn–O–Ce–bonds throughout the backbone (Fig. 1b).

In this contribution, we report an efficient, sustainable approach to a homogeneous Mn₀.₅Ce₀.₅Oₓ solid solution, whose ideal structure with Mn⁴⁺ ions in the ceria matrix is suggested by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron transmission microscopy–X-ray energy dispersive spectroscopy (STEM–XEDS) mapping analysis and H₂ temperature-programmed reduction (H₂–TPR). To the best of our knowledge, it is the first time for the ultrahigh concentration of Mn⁴⁺ ion to be stabilized in a ceria lattice. The essence of the current strategy for fabricating a uniform MnₓOₓ–CeO₂ solid solution is the slow hydrolysis of Mn/Ce precursors at the surfaces of ionic liquid ‘supermolecular’ networks. Surprisingly, a mesoporous structure with a high surface area is observed for the MnₓOₓ–CeO₂ solid solution after ionic liquids removal. This structure is highly advantageous in heterogeneous catalysis, since it can expose more surface oxygen species, and faster mass diffusion/transfer can be expected. This versatile soft-templating method for well-defined mesopores can cover various oxide solid solutions even transition metal perovskites such as CoₓSrₓTiO₃, CeₓSrₓTiO₃ and YMnO₃. We show the outstanding activity of a MnₓOₓ–CeO₂ solid solution catalyst in the low temperature, heterogeneous oxidation of cyclohexane (100 °C, conversion: 17.7%, selectivity for KA oils: 81%) with molecular oxygen as the oxidant. It is significantly superior to the results of current technology (140–160 °C, conversion: 3–5%); this process could be extended to the selective oxidation of various allylic or benzyl C–H bonds with the corresponding alcohols/ketones as products. This study provides a simple general strategy to obtain a mesoporous MnₓOₓ–CeO₂ solid solution catalyst that can make selective, O₂-based oxidation of sp³ C–H bonds at mild temperatures possible.

**Results**

Fabrication of MnₓOₓ–CeO₂ solid solutions. The detailed route to the MnₓOₓ–CeO₂ catalyst is shown in Fig. 1c. In the present model system, manganese (II) acetate, cerium (IV) methoxyethoxide, 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (BmimTf₂N) and ethanol were mixed at a ratio of 1.0:1.8:6.80 w/w/w, and stirred at room temperature for 2h. The dark red homogeneous solution was poured into a petri dish to evaporate solvents at 50 °C for 24 h, followed by solidification of the sample at 200 °C for 2 h with the formation of a primary metal oxo matrix around hydrophobic BmimTf₂N via electrostatic interaction; and a frizzy solid film formed (Supplementary Fig. 1). It should be emphasized that the initial treatment temperature (200 °C) was higher than values used during surfactants or block copolymers-induced processes (~95–120 °C). The good thermal stability of BmimTf₂N (decomposition temperature: >350 °C, Supplementary Fig. 2) results in its high tolerable temperature, which allows a higher condensation degree of Mn/Ce precursors for strong backbones, and therefore affords the possibility of recycling BmimTf₂N. In previous methods for forming mesoporous metal oxides, the surfactants or block copolymers used as soft templates usually cannot be removed and recycled before calcinations; otherwise, the porosity would collapse. However, the organic templates cannot survive during high-temperature treatment (for example, 500 °C) and this sacrificial behaviour obstructs their industrial application. In contrast, the structure-directing BmimTf₂N template can be easily extracted and recovered by refluxing in ethanol (Supplementary Figs 3–4), resulting in MnₓOₓ–CeO₂@200. The as-made sample was thermally treated at 500 °C for 2 h in air (MnₓOₓ–CeO₂@500).

Characterization of mesoporous metal oxides. Figure 1b illustrates the evolution of crystal structures upon doping of MnₓOₓ–CeO₂@200 into MnₓOₓ–CeO₂@500.
50% Mn⁴⁺ ions into a ceria lattice, and a density functional theory calculation of structural models showed the change in the optimized lattice parameter $a$. Compared with ceria ($a = 0.5464$ nm), an ideal Mn₀.₅Ce₀.₅Oₓ with a symmetrical Mn⁴⁺ substitution undergoes shrinkage along the $a$ axis ($a = 0.5181$ nm). This is reasonable because the ionic radii of manganese ions (Mn⁴⁺: 0.053 nm; Mn³⁺: 0.065 nm; Mn²⁺: 0.083 nm) are smaller in size than those of cerium ions (Ce⁴⁺: 0.097 nm; Ce³⁺: 0.114 nm). Indeed, the XRD pattern of the Mn₀.₅Ce₀.₅Oₓ sample showed a clear shift towards a higher Bragg angle compared with pure ceria and its corresponding lattice parameter $a$ calculated by a (111) peak at 29.795° ($a = 0.5194$ nm) was very close to the above theoretical result ($a = 0.5181$ nm), revealing the possible replacement of Ce⁴⁺ by Mn⁴⁺ in the cubic fluorite structure (Fig. 2a, Supplementary Fig. 5, Supplementary Table 1). Extremely broad diffraction peaks for (111), (220) and (311) reflections of the Mn₀.₅Ce₀.₅Oₓ sample were observed. The average crystalline size was 1.4 nm, calculated by the Scherrer equation. The small crystalline size can be attributed to the confined hydrolysis and condensation of Mn/Ce precursors templated by the heterogeneous BmimTf₂N structure [41]. In addition, a partially crystalline structure has already formed in the Mn₀.₅Ce₀.₅Oₓ sample.

**Figure 1 | Synthetic and catalytic strategies.** (a) A summary of state-of-art processes for caprolactam production (monomer for Nylon-6); (b) the evolution of doping 50% Mn⁴⁺ ions into a CeO₂ lattice; (c) a solvent evaporation-induced self-assembly between metal salts and hydrophobic ionic liquid, reaction conditions: manganese (II) acetate, cerium (IV) methoxyethoxide and 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (BmimTf₂N) in ethanol: (i) stirring at room temperature for 2 h, and pouring into a petri dish at 50 °C for 24 h and 200 °C for 2 h, (ii) removing and recycling the BmimTf₂N by Soxhlet extraction in ethanol (24 h), (iii) thermal treatment in air oven at 500 °C for 2 h.
To study the oxidation state of surface species, XPS spectra for the Mn 2p and O 1s core levels of the Mn0.5Ce0.5Ox@500 sample were recorded and are shown in Fig. 2b,c. The XPS curve of Mn 2p exhibited two peaks at 653.7 and 642.1 eV, which can be attributed to the Mn 2p3/2 and Mn 2p1/2 states, respectively. The spin orbit splitting is ΔE = 11.6 eV, close to the value of MnO2 (11.7 eV)\(^{42}\). In addition, the Mn 2p3/2 peak is fitted with a Shirley background and Gaussian-Lorenz model functions, and two peaks at 641.5 and 642.6 eV can be obtained, based on standard binding energies suggest the co-existence of Mn\(^{3+}\) and Mn\(^{4+}\) ions, but Mn\(^{1+}\) species with 87% content dominate the surface, in accordance with the structural model discussed above. Meanwhile, the O 1s spectrum with a shoulder peak is very broad, possibly owing to the overlapping contributions of various oxygen species. The curve was then resolved with the model discussed above and fitted into three peaks. The peaks at 529.4, 531.2 and 533.1 eV are ascribed to lattice oxygen atoms (O\(^2-\), denoted as O\(_{L}\)), surface oxygen species (for example, O\(^2-\), O\(^-\), O\(_{ads}\)), and chemisorbed water and/or carbonates (denoted as O\(_{ads}\)), respectively. It is well recognized in the literatures that the O\(_{ads}\) species from defective sites with an unsaturated structure are of great importance in the catalytic oxidation process\(^{32,37}\). The surface atomic concentration was then calculated by integrating the peak areas of different oxygen species. The atomic ratio of “reactive” oxygen species (O\(_{ads}\)) can reach 44.1%, arguing for the great potential of this solid solution in catalytic oxidations.

The porous nature of Mn\(_{0.5}\)Ce\(_{0.5}\)O\(_x\) samples was evaluated by nitrogen sorption measurements at 77 K. The Mn\(_{0.5}\)Ce\(_{0.5}\)O\(_x\)@200 sample was dominated by micropores with remarkable N\(_2\) uptake at low relative pressure and its specific surface area calculated by the Brunauer–Emmett–Teller (BET) method was 467 m\(^2\) g\(^{-1}\) (Supplementary Fig. 6). The rich porosity should be directed during the removal of BmimTf\(_2\)N. It also can be concluded that the backbone of the Mn\(_{0.5}\)Ce\(_{0.5}\)O\(_x\) sample formed at 200°C is strong enough to withstand the high pressure of molecular packing. Both XRD patterns and Fourier-transform infrared spectra of the Mn\(_{0.5}\)Ce\(_{0.5}\)O\(_x\)@200 sample suggest that it is an oxide precursor with acetate anions incorporated in the matrix (Fig. 2a, Supplementary Fig. 7). A weak coordination-induced network containing Mn(OAc)\(_2\) and partially dehydrated cerium hydroxide were proposed for the Mn\(_{0.5}\)Ce\(_{0.5}\)O\(_x\)@200 sample, wherein the close connection between manganese and cerium ions is the key to restructuring into a Mn\(_{0.5}\)Ce\(_{0.5}\)O\(_x\) solid solution during calcination. This confined restructuring can prevent the formation of separate bulk manganese or cerium oxide phases (Supplementary Fig. 8)\(^{38}\).

Thermal treatment of the Mn\(_{0.5}\)Ce\(_{0.5}\)O\(_x\)@200 sample led to pore expansion, as shown by the pore size distributions of samples at different temperatures (200, 400, 500 and 600°C); the pore expansion is possibly the result of the progressive growth of nanocrystals (Supplementary Fig. 9)\(^{43}\). It is interesting that the Mn\(_{0.5}\)Ce\(_{0.5}\)O\(_x\)@500 material possessed a characteristic type IV sorption isotherm with a H\(_2\) hysteresis loop, including a sharp capillary condensation step at p/p\(_0\) = 0.4–0.5. The pore diameter...
located in 3–6 nm with a narrow distribution, from the sorption branch of the isotherm by using Barrett–Joyner–Halenda model (Fig. 2d,e). The Mn$_{0.5}$Ce$_{0.5}$O$_x$@500 was a typically mesoporous material with a BET surface area of 89 m$^2$g$^{-1}$. A series of mixed oxide solutions with a different Mn/Ce atomic ratio (1:9, 2:8, 3:7, 7:3) were also prepared, and mesoporous structures with high surface areas were observed for those samples (Supplementary Table 2). The Mn$_{0.5}$Ce$_{0.5}$O$_x$@500 sample possessed a specific surface area of 125 m$^2$g$^{-1}$ with large mesopores around 10 nm. Moreover, the current solvent vaporization-induced assembly of binary Mn$_{0.5}$Ce$_{0.5}$O$_x$ around the BmimTf$_2$N template can easily be extended to more metal-oxide combinations with similar mesoporous structures, such as: Ce$_{0.8}$Mn$_{0.2}$O$_x$@500 (using another Period 4 transition metal: Si$^x$ = 52 m$^2$g$^{-1}$, pore size: ~3 nm; Supplementary Figs 10–11), YMnO$_x$@700 (transition metal perovskite: Si$^x$ = 36 m$^2$g$^{-1}$; pore size: ~7.5 nm; Supplementary Fig. 12), and Cu$_{0.2}$Mn$_{0.5}$Ce$_{0.5}$O$_x$@500 (ternary metal oxide: Si$^x$ = 78 m$^2$g$^{-1}$; pore size: ~4 nm; Supplementary Figs 13–14). In some cases, the pore size of the target material (for example, SiO$_2$) can be precisely tailored on a mesoporous scale (for example, 3–40 nm), via adjusting the mass ratio between precursor molecules and BmimTf$_2$N (Supplementary Fig. 15). Given that a large BmimTf$_2$N aggregation is responsible for generating distances/pores between the primary oxide particles, polymerized BmimTf$_2$N was then synthesized, which could lead to wider mesopores (Supplementary Figs 16–17).

The transmission electron microscopy (TEM) and STEM in high-angular dark field mode (STEM-HAADF) images directly witness the evolution of Mn$_{0.5}$Ce$_{0.5}$O$_x$ samples at different treatment temperatures. The Mn$_{0.5}$Ce$_{0.5}$O$_x$@200 sample was rich in porosity with apparent pores of around 1–3 nm, in agreement with the value by nitrogen sorption measurement (Fig. 3a,b,e,f). Actually, the ionothermal synthesis of carbon materials (200 °C) in BmimTf$_2$N solvent also resulted in a porosity within BmimTf$_2$N located in 3–6 nm with a narrow distribution, derived from the bulk to the surface to a large degree.44–46. With CuO as the standard material, the H$_2$ consumption of a Mn$_{0.5}$Ce$_{0.5}$O$_x$@500 sample can reach 4.22 mmol g$^{-1}$ and such a high value clearly suggests the large amount of the 'active' oxygen species. If the chemical composition of our catalyst is assumed to be Mn$^{3+}$Ce$^{4+}$O$_x$, the X value, based on the consumed H$_2$, is calculated to be 1.1, in turn evidencing the doping of Mn$^{4+}$ into the ceria lattice. Thus the H$_2$–TPR peak can be assigned to the highly reducible manganese species with direct reduction from Mn$^{4+}$ to Mn$^{2+}$, along with partial surface Ce$^{4+}$ reduction.47 It is interesting that the reduction peak starts at 75 °C, in other words, that the oxygen vacancy is forming at such a low temperature, allowing the possibility of low-temperature catalysis. To probe the reversibility of active oxygen at low temperature, multiple redoxes of the Mn$_{0.5}$Ce$_{0.5}$O$_x$@500 sample from 60 to 160 °C were carried out via a H$_2$ reduction–aerobic oxidation cycle (Fig. 4b). During three cycles, the H$_2$–TPR curves kept to the same trend and a similar amount of H$_2$ consumption. By combining the unique properties of the current solid solution (for example, abundant active oxygen species, redox activity at low temperature and good stability) and the characterstic features of mesoporous materials (large pore size and high surface area), Mn$_{0.5}$Ce$_{0.5}$O$_x$@500 contains most of the prerequisites for a noble metal-free heterogeneous catalyst to realize low-temperature selective oxidation of hydrocarbons by O$_2$.

**Aerobic oxidation of cyclohexene by Mn$_{0.5}$Ce$_{0.5}$O$_x$ Catalysts**

Initial attempts to optimize the aerobic oxidation of cyclohexene were performed at 100 °C in the presence of different catalysts. A blank run without catalysts did not give any products in 4 h, suggesting that the auto-oxidation of cyclohexene by molecular oxygen cannot proceed under such a condition (Table 1, Entry 1). When catalysed by Mn$_{0.5}$Ce$_{0.5}$O$_x$@500, the oxidation of cyclohexene occurred at 100 °C with a moderate conversion (6.5%) and a remarkable selectivity (95%) for Ka oil (Table 1, Entry 2). As a noble metal-free solid catalyst, Mn$_{0.5}$Ce$_{0.5}$O$_x$@500 indeed drives the aerobic oxidation of cyclohexene at a relatively low temperature. It should be emphasized that controlled oxidations of cyclohexane with CeO$_x$@500, MnO$_x$@500 or the physical mixture of CeO$_x$@500 and MnO$_x$@500 cannot proceed, confirming the synergistic action of manganese and cerium species in a Mn$_{0.5}$Ce$_{0.5}$O$_x$@500 solid solution (Table 1, Entries 3–5). The Mn$_{0.5}$Ce$_{0.5}$O$_x$@200 sample was also active for this process, which is reasonable since an initial crystalline structure has already formed at 200 °C (Table 1, Entry 6). The mixed oxides with various Mn/Ce atomic ratios (1:9, 2:8, 3:7 and 7:3) were also tested in the cyclohexene oxidation (Table 1, Entries 7–10). The optimal ratio was ~1:1, in accordance with the H$_2$–TPR results. The maximum –Mn–O–Ce– bonds throughout the matrix of the Mn$_{0.5}$Ce$_{0.5}$O$_x$@500 solid solution may be responsible for its high activity, because more oxygen vacancies can be expected at low temperature.

The reaction temperature had a strong effect on the oxidation of cyclohexene. The cyclohexene conversion increased as the
Figure 3 | Studies of the catalyst by electron microscopy. (a-c) TEM/HRTEM images of Mn$_{0.5}$Ce$_{0.5}$O$_x$@200 sample, the scale bar are 20, 10 and 5 nm, respectively. The inset in c is an electron microscopy pattern. (d) STEM-HAADF image of Mn$_{0.5}$Ce$_{0.5}$O$_x$@200, scale bar, 100 nm; the corresponding XEDS of the O–K, Mn–K, Mn–L, Ce–K, Ce–L signals and XEDS. (e,f) STEM-HAADF image of Mn$_{0.5}$Ce$_{0.5}$O$_x$@200 sample, scale bar, 20 nm and 10 nm, respectively. (g,h) TEM/HRTEM images of Mn$_{0.5}$Ce$_{0.5}$O$_x$@500 sample, scale bar, 20 and 5 nm, the inset in h is an electron microscopy pattern. (i) STEM-HAADF image of Mn$_{0.5}$Ce$_{0.5}$O$_x$@500 sample and the corresponding elemental mapping for Ce (j), Mn (k), O (m). Scale bar, 50 nm.
temperature increased from 80 to 150 °C; at the same time, a decreased selectivity for KA oil was observed (Table 1, Entries 11–13). It is interesting that oxidation can proceed at a temperature as low as 80 °C, which is in good agreement with the observation in H₂-TPR that the active oxygen species is available above 75 °C. With the development of processes for low-temperature cyclohexane oxidation in mind, we focused on catalytic oxidation at 100 °C. The optimization of reaction time suggested that the reaction time of 12 h seemed to be a suitable time, and a 17.7% cyclohexane conversion with 81% selectivity for KA oil was obtained (Table 1, Entries 14–16). To probe the reaction pathway, two controlled runs were then performed. When the catalytic oxidation was carried out in argon, no detectable products were observed, giving evidence that molecular

![Figure 4 | Redox property of the catalyst.](image)

(a) H₂-TPR curve of Mn₀.₅Ce₀.₅Oₓ@500 catalyst; (b) H₂-TPR curve of Mn₀.₅Ce₀.₅Oₓ@500 catalyst during H₂ reduction-aerobic oxidation cycles; (c) Catalytic CO oxidation at different temperature over Mn₀.₅Ce₀.₅Oₓ@500 catalyst; (d) Stability of Mn₀.₅Ce₀.₅Oₓ@500 catalyst under CO oxidation and its catalytic performance during varied temperatures.

| Table 1 | Selective oxidation of cyclohexane under different conditions*. |
|---|---|
| Entry | Catalyst | T (°C) | t (h) | Conv. (%) | Sel. (%) | K/A |
| 1 | Blank | 100 | 4 h | <0.1% | — | — |
| 2 | Ce₀.₅Mn₀.₅Oₓ@500 | 100 | 4 h | 6.5% | 95% | 4.8 |
| 3 | CeO₂@500 | 100 | 4 h | <0.1% | — | — |
| 4 | MnO₂@500 | 100 | 4 h | <0.1% | — | — |
| 5 | CeO₂@500 (50 wt%) MnO₂@500 (50 wt%) | 100 | 4 h | <0.1% | — | — |
| 6 | Ce₀.₅Mn₀.₅Oₓ@200 | 100 | 4 h | 5.1% | 92% | 4.2 |
| 7 | Ce₀.₅Mn₀.₅Oₓ@500 | 100 | 4 h | 0.4% | 98% | 7.5 |
| 8 | Ce₀.₅Mn₀.₅Oₓ@500 | 100 | 4 h | 2.3% | 96% | 5.8 |
| 9 | Ce₀.₅Mn₀.₅Oₓ@500 | 100 | 4 h | 2.6% | 97% | 6.1 |
| 10 | Ce₀.₅Mn₀.₅Oₓ@500 | 100 | 4 h | 4.8% | 98% | 5.2 |
| 11 | Ce₀.₅Mn₀.₅Oₓ@500 | 80 | 4 h | 1.0% | >99% | >99.0 |
| 12 | Ce₀.₅Mn₀.₅Oₓ@500 | 120 | 4 h | 10.5% | 84% | 3.5 |
| 13 | Ce₀.₅Mn₀.₅Oₓ@500 | 150 | 4 h | 18.8% | 52% | 5.4 |
| 14 | Ce₀.₅Mn₀.₅Oₓ@500 | 100 | 8 h | 13.5% | 90% | 3.3 |
| 15 | Ce₀.₅Mn₀.₅Oₓ@500 | 100 | 12 h | 17.7% | 81% | 3.6 |
| 16 | Ce₀.₅Mn₀.₅Oₓ@500 | 100 | 16 h | 21.8% | 63% | 6.5 |
| 17 | Ce₀.₅Mn₀.₅Oₓ@500; in argon | 100 | 4 h | <0.1% | — | — |
| 18 | Ce₀.₅Mn₀.₅Oₓ@500; hydroquinone 50 mg | 100 | 4 h | <0.1% | — | — |

Conv., conversion; Sel., selectivity.
*Reaction conditions: cyclohexane 10 mmol (842 mg), catalyst 30 mg, CH₃CN 3 ml, O₂ 10 bar. Selectivity = [cyclohexanol + cyclohexanone]/[consumed cyclohexane] × 100; conversion = [consumed cyclohexane]/initial cyclohexane × 100, respectively.
\[K/A = \text{the molar ratio between cyclohexanone and cyclohexanol.}\]
†In argon.
‡With hydroquinone 50 mg as additive.
Oxygen is the principal oxygen donor in the system (Table 1, Entry 17). In addition, the catalytic oxidation would be quenched, if hydroquinone, a free-radical scavenger, was added into the reaction system, which implied that the oxidation of cyclohexene may proceed through a radical chain mechanism (Table 1, Entry 18). The stability of the Mn$_{0.5}$Ce$_{0.5}$O$_x$@500 catalyst was then investigated by cyclohexane oxidation for 4 h. After each run, the catalyst was recovered by centrifugation, and then carefully transferred into a reactor by the reaction solvent. The Mn$_{0.5}$Ce$_{0.5}$O$_x$@500 worked well in at least 20 runs without significant activity loss, suggesting that the oxidation should run in a heterogeneous manner and it is a prerequisite for practical applications (Supplementary Figs 19–20). A possible reaction mechanism was then proposed, based on the results above, in situ diffuse reflectance infrared spectroscopy (DRIFTS) and in situ Raman spectra (Supplementary Fig. 21, Supplementary Note 1).

Aerobic oxidation of hydrocarbons and CO. To probe the potential of this Mn$_{0.5}$Ce$_{0.5}$O$_x$@500 solid solution, various hydrocarbons with sp$^3$ C–H bonds were oxygenated at 110–120 °C (Table 2). Cyclohexene was oxidized with a moderate conversion to the mixture of 2-cyclohexen-1-one and 2-cyclohexen-1-ol (Table 2, Entry 1). The oxidation of ethylbenzene proceeded with high selectivity to acetophenone, although the ethylbenzene conversion was somewhat low (Table 2, Entry 2). Catalysed by Mn$_{0.5}$Ce$_{0.5}$O$_x$@500 catalyst, the indane oxidation afforded a conversion of 75.4%, with 1-indanol and 1-indanone as the main products (Table 2, Entry 3). The catalyst also worked well in the oxidation of tetralin, a key step in the commercial production of α-naphthol (Table 2, Entry 4). Fluorene and diphenylmethane with a large molecular size could be transformed into fluorenone and diphenylmethanone, with high selectivity (Table 2, Entries 5–6). Therefore, it is probably fair to say that the Mn$_{0.5}$Ce$_{0.5}$O$_x$@500 solid solution is a general catalyst for aerobic oxidation of allylic- or benzyl sp$^3$ C–H bonds at relatively low temperature.

Actually, the same target for low temperature oxidation is also pursued in catalytic combustion, such as CO oxidation. Encouraged by the interesting activity of Mn$_{0.5}$Ce$_{0.5}$O$_x$@500 in O$_2$ activation, we undertook a study of CO oxidation over a Mn$_{0.5}$Ce$_{0.5}$O$_x$@500 catalyst. The profile for CO conversion as a function of reaction temperature is presented in Fig. 4c. The Mn$_{0.5}$Ce$_{0.5}$O$_x$@500 catalyst enables the 100% CO conversion at around 90 °C. It should be highlighted that the $T_{50}$ (Temperature at which the 50% CO conversion is achieved) by Mn$_{0.5}$Ce$_{0.5}$O$_x$@500 catalyst (60 °C) is lower than MnO$_x$–CeO$_2$ catalysts by other methods (co-precipitation method: 127 °C, surfactant-assisted method: 95 °C, hydrothermal method: 105 °C, citrate sol-gel method: 160 °C, Supplementary Table 3). The high activity of the Mn$_{0.5}$Ce$_{0.5}$O$_x$@500 catalyst enables the 100% CO conversion at around 90 °C. It should be highlighted that the $T_{50}$ (Temperature at which the 50% CO conversion is achieved) by Mn$_{0.5}$Ce$_{0.5}$O$_x$@500 catalyst (60 °C) is lower than MnO$_x$–CeO$_2$ catalysts by other methods (co-precipitation method: 127 °C, surfactant-assisted method: 95 °C, hydrothermal method: 105 °C, citrate sol-gel method: 160 °C, Supplementary Table 3). The high activity of the Mn$_{0.5}$Ce$_{0.5}$O$_x$@500 catalyst is attributed to the abundant superoxide species formed on the surface of the solid solution. The stability of Mn$_{0.5}$Ce$_{0.5}$O$_x$@500 catalyst was also investigated, and it was found that 100% CO conversion at 100 °C can be preserved for 240 min (Fig. 4d). Moreover, the catalytic

### Table 2 | Selective oxidation of different hydrocarbons by a Mn/Ce catalyst$^*$.  

| Entry | Substrate | $T$ (°C) | $t$ (h) | Conv. (%) | Product (sel. %) |
|-------|-----------|---------|--------|-----------|-----------------|
| 1     |           | 110     | 4      | 53.2      |                 |
| 2     |           | 120     | 6      | 20.3      |                 |
| 3     |           | 110     | 4      | 75.4      |                 |
| 4     |           | 120     | 4      | 44.8      |                 |
| 5     |           | 110     | 4      | 86.3      |                 |
| 6     |           | 120     | 6      | 36.2      |                 |

Conv., conversion; Sel., selectivity.

$^*$Reaction conditions: substrate 1 mmol, anisole 1 mmol (internal standard), Ce$_{0.5}$Mn$_{0.5}$O$_x$@500 catalyst 30 mg, O$_2$ 10 bar, CH$_3$CN 5 ml.
activity of the Mn$_{0.5}$Ce$_{0.5}$O$_{1.5}$@500 sample was stable at different temperatures, and showed a rapid response to the temperature change. Notably, the Mn$_{0.5}$Ce$_{0.5}$O$_{1.5}$@500 catalyst is active for CO oxidation even at room temperature (~19% CO conversion).

Discussion

In summary, we have shown the successful construction of mesoporous MnCeO$_x$ solid solutions via a simple, effective and sustainable self-assembly strategy, which has at the same time been recognized in the fabrication of other hybrid metal oxides with well-defined mesopores. Experimental results reported herein, illustrate that the aerobic oxidation of cyclohexane to KA oil by Mn$_{0.5}$Ce$_{0.5}$O$_{1.5}$@500 catalyst can proceed above 80°C without any noble metal catalysts or sacrificial additives, and under optimized reaction conditions (100°C, 17.7% cyclohexane conversion with 81% selectivity for KA oil was obtained. This finding could reinvigorate research into such a process for commercial exploitation, and thus make cyclohexane oxidation with 81% selectivity for KA oil was obtained.

Catalytic CO oxidation with outstanding proportion (44.1%) of active oxygen species on the surface to change. Notably, the Mn$_{0.5}$Ce$_{0.5}$O$_{1.5}$@500 catalyst was also witnessed in CO oxidation with outstanding activity at a relatively low temperature (100% conversion at 90°C).

Actually, the exceptional activity of the as-made catalyst can be the result of forming a Mn$_{0.5}$Ce$_{0.5}$O$_x$ solid solution—which has been confirmed by a structural model, an XRD pattern, XPS analysis, TEM images, STEM–XEDX mapping analysis and an H$_2$–TPR study—with several unique characteristics: (1) A high proportion (44.1%) of active oxygen species on the surface to promote O=O–C–H bond activation; (2) the introduction of 50 mol% Mn$_4^{3+}$ ions into ceria matrix for the formation of maximum solid solution phases that can lower the energy for oxygen vacancy formation and benefit the rapid migration of oxygen vacancies from the bulk to the surface, thus continuing the activation of gas oxygen molecules; (3) a mesoporous structure for fast mass transfer/diffusion, and rich porosity to expose any more active sites ready for interaction with cyclohexane/O2. We expect that the Mn$_{0.5}$Ce$_{0.5}$O$_x$ solid solution will provide a mild strategy for cyclohexane oxidation, and the manner of self-assembly with ionic liquids will inspire more designs of mesoporous oxide solid solutions for specific tasks in the near future.

Methods

Synthesis of Mn$_{0.5}$Ce$_{0.5}$O$_x$ solid solution. In a typical synthesis of mesoporous Mn$_{0.5}$Ce$_{0.5}$O$_x$ solid solution oxides, 6.16 g of cerium (IV) methoxyethoxide (18–20% in methoxyethoxide, Geela); 0.63 g Mn(OOCCH$_2$)$_3$·6H$_2$O (99%, Aldrich) and 1.0 g of ionic liquid (BmimTfN) were dissolved in 5.0 mol of ethanol. The solution was stirred at room temperature for 2 h until Mn(OOCCH$_2$)$_3$·6H$_2$O was completely dissolved. Subsequently, ethanol (5.0 mol) was added slowly with stirring. The mixed solution was gelled in an open petri dish at 50°C for 24 h and aged at 200°C for 2 h, and a solid film was obtained. The ionic liquid was extracted by refluxing the sample with ethanol in a Soxhlet extractor for 24 h. The as-made sample (Mn$_{0.5}$Ce$_{0.5}$O$_x$@200) was thermally treated at 500°C for 2 h with the heating rate of 1 K min$^{-1}$ in air, and the final sample denoted as Mn$_{0.5}$Ce$_{0.5}$O$_{1.5}$@500. Other metal oxides were prepared by the same process except with different metal precursors. The materials were characterized by N$_2$ adsorption (TriStar, Micromeritics) at 77 K, powder XRD (Panalytical Empyrean diffractometer with Cu Ka radiation k = 1.5418 Å operating at 45 kV and 40 mA), thermogravimetric analysis (TGA 2950, TA Instruments), Fourier-transform infrared spectrum (PerkinElmer Frontier FTIR spectrometer) and H$_2$–TPR (Auto chem II, Micromeritics).

Typical procedure for the catalytic oxidation of CO. Catalytic CO oxidation was carried out in a fixed-bed reactor (U-type quartz tube) with inner diameter of 4 mm at atmospheric pressure. A 30 mg catalyst supported by quartz wool was loaded in the reactor. The feed gas of 1% CO balanced with dry air passed through the catalyst bed at a flow rate of 10 ml min$^{-1}$, corresponding to a gas hourly space velocity of 20,000 ml (g cat)$^{-1}$.

Typical procedure for the catalytic oxidation of cyclohexane. Catalytic oxidations of cyclohexane under pressured O$_2$ were carried out in a Teflon-lined stainless steel batch reactor (PEEK internal USA). Typically, cyclohexane (10 mmol; calculated by weight), CH$_3$CN (3 ml) and catalysts used as described in the manuscript were loaded into the reactor (total volume: 100 ml). The reactor was sealed, and then purged with O$_2$ to replace the air for three times. The O$_2$ pressure was increased to 1 MPa, and then the reactor was heated to the desired temperature in 15 min. Then, the reaction was carried out for the desired time with stirring (stirring rate: 1,500 r.p.m.). After reaction, the reactor was placed in ice water to quench the reaction, and the products were analysed by gas chromatography (GC) with internal standard (2-butanol). The structure of products and by-products was identified using Perkin Elmer GC–MS (Clarus 680-Clarus SQ 8C) spectrometer by comparing retention times and fragmentation patterns with authentic samples.

Typical procedure for the catalytic oxidation of other hydrocarbons. In a typical oxidation, 1 mmol substrate, 1 mmol anisole (internal standard), 5 ml CH$_3$CN and 30 mg Mn$_{0.5}$Ce$_{0.5}$O$_{1.5}$@500 catalyst were added into a Teflon-lined stainless steel batch reactor. The reactor was sealed and purged with O$_2$ to replace the air for three times. After increasing the O$_2$ pressure to 1 MPa, the reactor was heated to the desired temperature in 20 min. Then, the reaction was carried out for the desired time with magnetic stirring (stirring rate: 1,500 r.p.m.). After the reaction, the reactor was placed in ice water to quench the reaction, and the products were analysed by GC and GC–MS.

Method for in situ DRIFTS. In situ DRIFTS measurement was performed on a Nicolet Nexus 670 spectrometer equipped with a MCT detector cooled by liquid nitrogen and an in situ chamber (HC-900, Pike Technologies) which allows the sample heated up to 900°C. The exiting stream was analysed by an online quadrupole mass spectrometer (Omnistar GSD-301 O$_x$ PF Pfeiffer Vacuum). Before measurement, the Mn$_{0.5}$Ce$_{0.5}$O$_{1.5}$@500 catalyst was completely dissolved in 500°C in 20% O$_2$/He (30 min) with a flow of 25 ml min$^{-1}$ to eliminate water traces. After cooling to room temperature in a He flow (20 ml min$^{-1}$), the background spectrum was collected for spectral correction, and background peaks were also collected at 100 and 150°C, respectively. Then, cyclohexane stream (bubbling with He 20 ml min$^{-1}$) was introduced to the in situ chamber for adsorption and reaction.

Method for raman spectroscopy. The procedure for Raman spectra collection: Raman spectra were excited with a 532 nm laser (LAS-NY532/50) and collected with Horiba JobinYvon HR800 (800mm optical length), with a diffraction grating of 600 grooves per mm, the scattered light was detected with a charge-coupled device cooled to 203 K for the reduction process. Raman spectra of the samples were collected from 25 to 150°C in the range of 100–4,000 cm$^{-1}$ with two accumulations for each spectrum.

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