Supporting Information

Improved stability and activity of Fe-based catalyst through strong metal support interactions due to extrinsic oxygen vacancies in $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ for the efficient synthesis of ammonia

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Calculation of primary particle size by Scherrer's equation

From the obtained XRD results in Figure 1 (a) the primary particle size of $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ was estimated using Scherrer's equation given below.

$$\tau = \kappa\lambda/\beta cos\theta \qquad \text{(S1)}$$

Where τ is the mean size of the ordered particles, k is the shape factor which was taken to be a value of 0.9 rad, λ is the wavelength of the X-ray, β is the width of the maximum intensity at half height, and Θ is the Bragg angle. For the Cu K alpha 1 radiation a wave length of 0.15406 nm was used.

SEM/EDX analyses of the catalysts

Figure S1 shows the SEM images of the catalyst before and after reduction as well as after the 200 hour stability test. Pure Fe_2O_3 and $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ are also shown along with EDS element mapping showing particle size and distribution in the samples. It can be seen that Fe_2O_3 has a particle size of 20 nm to 40nm while the prepared $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ contains large clusters around 10 -15 μm in size of nano-flakes approximately 10 nm in diameter (Figure S1 b,c), which is in good agreement with the 13.6 nm obtained from Scherrer's equation. After mechanical mixing it can be seen that $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ nano-flakes adhere into spherical particles of approximately 1μm diameter. Unreduced Fe_2O_3 in this mechanical mixture maintains a small particles size and can be seen to adhere to the $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ surface or, the SDC surface is covered by small

Fe_2O_3 nano-particles (Figure S1d). This is the reason that SDC peaks are not obvious in the XRD pattern of the Fe_2O_3-SDC mixture (Figure 3a). After the reduction of the Fe_2O_3-SDC catalyst at 600 °C and the following ammonia synthesis activity test on cooling, the large grains can be seen to become smaller particle with a size of approximately 200 nm. EDS element mapping indicates iron is homogeneously distributed on the surface whilst there are some small areas where SDC is exposed (Figure S1e). This indicates that the reduced Fe and SDC is well mixed but partial sintering of the yielded iron particles takes place during the process.

Measurements on specific surface area of the catalysts by BET method

In order to verify this, the specific surface areas of the pure Fe_2O_3, SDC, the mixed Fe_2O_3-SDC and reduced Fe-SDC were measured by a BET method with the data shown in Table S1. The specific surface area of commercial nano-sized α-Fe_2O_3 was 36.54 m^2 g^{-1}. However, the specific surface area of as-prepared SDC was 101.41m^2 g^{-1}, which is roughly three times of that for commercial Fe_2O_3. This implies that the SDC flakes shown in Figure 1b,c are composed of smaller primary particles with a much smaller particle size. The specific surface area of the Fe_2O_3-SDC mixture was 39.73 m^2 g^{-1}, which is very close to that for Fe_2O_3. After the ammonia synthesis activity measurement, the specific surface area for the yielded Fe-SDC was only 8.04 m^2 g^{-1}, indicating partial sintering of the yielded iron particles during the reduction and ammonia synthesis process at high temperatures, leading to larger particle size, which has been confirmed by SEM observation (Figure S1e).

Table S1 The impurity composition of the BOC Zero grade H_2 and Zero grade N_2 used in the experiments.

Impurities	Impurity in Zero grade H_2 (ppm)	Impurity in Zero grade N_2 (ppm)
H_2O	5	5
O_2	5	5
CO_2	5	2
CO	10	/
N_2	20	/
total hydrocarbons	5	2
total oxygenates	25	12
total atomic oxygen	35	19

When the molar ratio of H_2 to N_2 is 3:1, the average oxygenate level is 21.75 ppm, the atomic oxygen level is 31 ppm.

Table S2: Comparison of specific surface area for the Fe-based catalyst promoted by CeO_2, SDC, ZrO_2 and YSZ before and after reduction and after stability test for the $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ promoted Fe catalyst.

Sample	Specific surface area ($m^2\ g^{-1}$)
Fe_2O_3	36.54
$Ce_{0.8}Sm_{0.2}O_{2-\delta}$	101.41
Fe_2O_3- $Ce_{0.8}Sm_{0.2}O_{2-\delta}$	39.73
Fe- $Ce_{0.8}Sm_{0.2}O_{2-\delta}$	8.04
Fe- $Ce_{0.8}Sm_{0.2}O_2$ after 200 hour stability test	20.00
CeO_2	46.71
Fe_2O_3- CeO_2	18.22
Fe- CeO_2	5.50
Sm_2O_3	0.36
Fe_2O_3-Sm_2O_3	24.14
Fe-Sm_2O_3	82.56
ZrO_2	2.80
Fe_2O_3- ZrO_2	22.52
Fe-ZrO_2	1.27
YSZ	3.70
Fe_2O_3- YSZ	24.83
Fe-YSZ	5.99

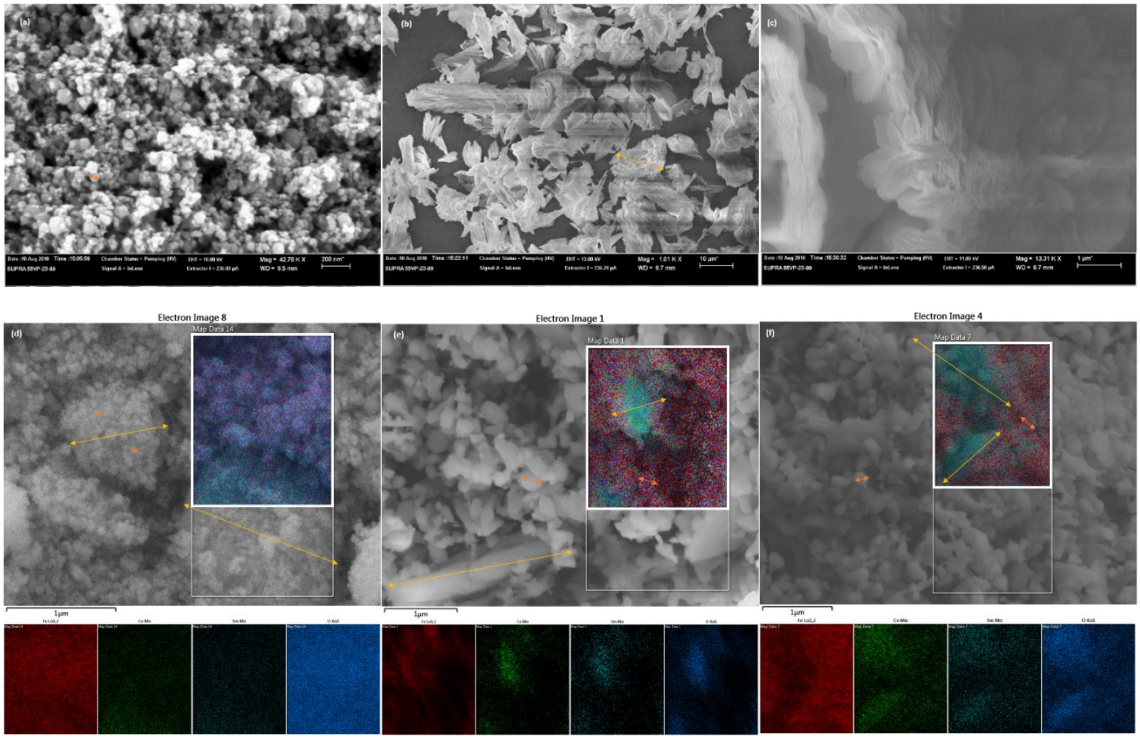

Figure S1. SEM with EDS layering for α-Fe_2O_3 (Alfa Aesar) (a), and $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ enlarged 1.01k (b) and 13.31k (c); unreduced Fe_2O_3-SDC catalyst (d), reduced Fe-SDC catalyst after activity test (e) and, reduced Fe-SDC catalyst after 200 hour stability test at 450 °C (f). Yellow arrows highlight the $Ce_{0.8}Sm_{0.2}O_{2-\delta}$ promotor while orange arrows highlight Fe_2O_3 and Fe in the unreduced and reduced catalysts respectively.