

Supplementary information

1. Catalyst preparation

The ordered mesoporous silica SBA-15 was synthesized according to the literature [1]. Bimetallic Ag–Ni/SBA-15 catalysts with a silver loading of 5 wt% were prepared using a co-impregnation method. In briefly, known amounts of AgNO₃ and Ni(NO₃)₂·6H₂O were dissolved in deionized water. SBA-15 was then added to the solution. The mixture was vigorously stirred and subjected to aging at room temperature for 12 h in the dark. The obtained powder was dried at 373 K overnight, calcined at 623 K for 4 h, and further reduced in 5%H₂-95%N₂ atmosphere at 693 K for 3 h to produce the final catalyst, which was denoted as 5Ag₁-Ni_x/SBA-15, where x represents the atomic ratio of Ni and Ag. The monometallic Ag/SBA-15 catalyst and Ni/SBA-15 catalyst were prepared using the procedure described above.

2. Catalyst characterizations

2.1 X-ray photoelectron spectroscopy (XPS)

XPS was performed using an Omicron Sphera II photoelectron spectrometer equipped with an Al-K_α X-ray radiation source ($h\nu = 1486.6$ eV). The sample was treated in an *in situ* chamber with 5% H₂-95% N₂ under 420 °C for 3 h before measurement. The binding energy (BE) was calibrated using the C 1s peak at 284.6 eV.

2.2 High sensitivity-low energy ion scattering (HS-LEIS)

The experiments were performed in a combined elevated-pressure reaction cell-ultrahigh vacuum (UHV) system. Sample preparation and characterization were conducted in the primary UHV chamber (base pressure, 2×10^{-9} Torr). HS-LEIS were measured by IONTOF Qtac100 using ²⁰Ne⁺ (5 keV) as ion source. The scattering angle was 145°.

2.3 Extended X-ray absorption fine structure (EXAFS)

EXAFS measurements at the Ag K-edge and Ni K-edge were conducted on B18 beamline at Diamond Light Source (Diamond, UK) to obtain information about the local structure of the Ag-Ni catalysts. Diamond installation comprises a 3GeV electron storage ring with typical currents of 200 mA, and B18 is a bending magnet beamline which has been designed to deliver monochromatic X-rays in the energy range of 2 to 35keV. A Si (311) double crystal monochromator was used for energy selection with a resolution of 1eV. Prior to the measurement, the samples were reduced in 5%H₂-95%Ar. The reduced monometallic Ag/SBA-15, Ni/SBA-15 samples and bimetallic Ag-Ni/SBA-15 samples were loaded in the capillary tubes with the diameter of 3mm. X-ray absorption spectroscopy data were collected at ambient temperature in transmission mode for the Ag K-edge measurements, while fluorescence spectra were acquired for the Ni K-edge measurements. Several scans were collected for each sample to get satisfactory data. The EXAFS data analysis was performed using IFEFFIT 1 with Horae packages 2 (Athena and Artemis). The spectra were calibrated with foils as a reference to avoid energy shifts of the samples. And the amplitude parameter was obtained from EXAFS data analysis of the foil, which was used as a fixed input parameter in the data fitting to allow the refinement in the coordination number of the absorption element. In this work, the first shell data analyses under the assumption of single scattering were performed with the errors estimated by R-factor.

3. Catalytic testing

The catalytic performance for vapor-phase DMO hydrogenation was evaluated using a stainless steel fixed-bed tubular reactor equipped with a computer-controlled auto-sampling system [2]. Typically, 150 mg of the catalyst precursor (40–60 mesh) was loaded into the centre of the reactor, with the top side of the catalyst bed packed with quartz powder (40–60 mesh). Prior to catalytic performance evaluation, the catalyst was activated under 5% H₂–95% N₂ flow at 693 K for 3 h. The catalyst bed was then cooled to the target reaction temperature, and pure H₂ was allowed to pass through the catalyst bed. A 10 wt.% DMO methanol solution was pumped into the reactor using a Series III digital HPLC pump (Scientific Systems, Inc.) with a system pressure of 3.0 MPa. The outlet stream was sampled using an automatic Valco 6-port valve system and then analysed using an online gas chromatograph (Agilent 7890A) equipped with flame ionization and a KB-Wax capillary column (30 m × 0.45 mm × 0.85 μm) at intervals of 30 min. In Ref. [3] lists the details of the product analysis and the calculation of the conversion, selectivity and turnover frequency.

The initial turnover frequency (TOF) of the reaction was measured at the DMO conversion below 25%. TOF was calculated based on the activity of the catalyst per surface Ag or Ni site (the average size of the particle was derived from either XRD or TEM analysis).

The value is calculated according to the following equation:

$$TOF = \frac{V \times C_{DMO} \times X_{DMO}}{D \times N_M}$$

Where V is the flow rate of the DMO methanol solution, C_{DMO} is the DMO concentration in the DMO methanol solution, X_{DMO} is the measured DMO conversion, D is the Ag or Ni dispersion, and N_M is the total amount of Ag or Ni. Thus, the TOF number equals to the number of mole of DMO converted per hour per mole of metal site on the catalyst surface ($\text{mol}_{DMO} \text{mol}_{\text{metal (surf)}}^{-1} \text{h}^{-1}$ or simply h^{-1}).

Table S1 TOF of Ag–Ni/SBA-15 catalysts for DMO hydrogenation at 473 K.^a

Catalyst	Conversion / %	WLHSV / h ⁻¹	TOF _{XRD} ^b / h ⁻¹	TOF _{TEM} ^c / h ⁻¹
5Ag/SBA-15	23.1	0.6	10.4	10.8
5Ag ₁ –Ni _{0.05} /SBA-15	22.9	3.0	50.8	51.4
5Ag ₁ –Ni _{0.10} /SBA-15	20.9	4.0	61.3	65.4
5Ag ₁ –Ni _{0.20} /SBA-15	23.1	6.0	96.9	106.0
5Ag ₁ –Ni _{0.40} /SBA-15	23.3	5.0	94.1	103.2
5Ni/SBA-15	10.5	1.0	23.5	– ^d

^a Reaction conditions: $P(\text{H}_2) = 3.0$ MPa, H_2/DMO molar ratio = 80.

^b TOF_{XRD} was calculated by metal dispersion based on the XRD data.

^c TOF_{TEM} was calculated by metal dispersion based on the TEM results.

^d Not measured.

Table S2 TOF of Ag–Ni/SBA-15 catalysts for DMO hydrogenation at 523 K.^a

Catalyst	Conversion / %	WLHSV / h ⁻¹	TOF _{XRD} ^b / h ⁻¹	TOF _{TEM} ^c / h ⁻¹
5Ag/SBA-15	18.5	4.0	55.5	57.6
5Ag ₁ –Ni _{0.05} /SBA-15	24.8	8.0	146.7	148.4
5Ag ₁ –Ni _{0.10} /SBA-15	29.7	12.0	261.3	278.8
5Ag ₁ –Ni _{0.20} /SBA-15	37.4	16.0	418.4	457.7
5Ag ₁ –Ni _{0.40} /SBA-15	31.1	12.0	301.4	330.6
5Ni/SBA-15	22.6	6.0	303.5	– ^d

^a Reaction conditions: $P(\text{H}_2) = 3.0$ MPa, H_2/DMO molar ratio = 80.

^b TOF_{XRD} was calculated by metal dispersion based on the XRD data.

^c TOF_{TEM} was calculated by metal dispersion based on the TEM results.

^d Not measured.

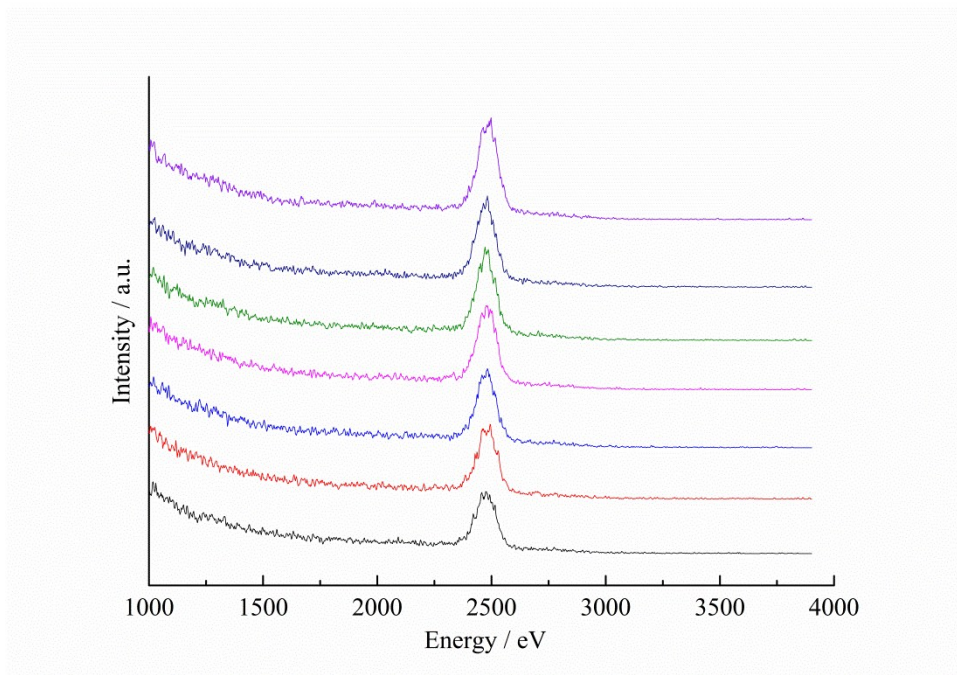


Fig. S1. HS-LEIS profiles of 5Ag₁-Ni_{0.20}/SBA-15 catalyst. The scanning range of 1000 μm × 1000 μm for 7 times (The depth is 0.7 nm.)

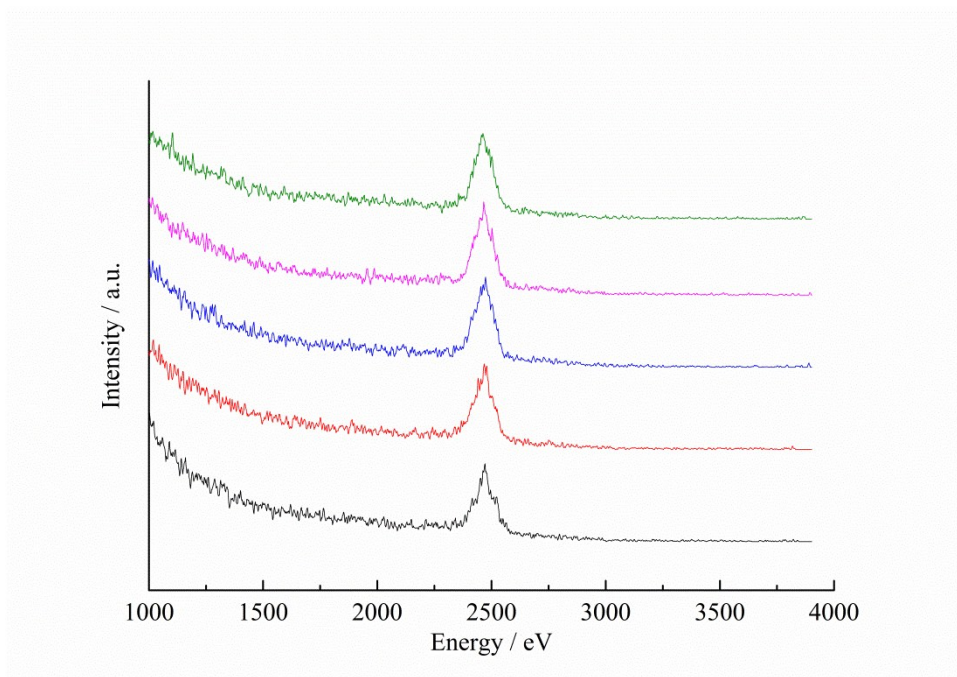


Fig. S2. The scanning range of 2000 μm × 2000 μm for 5 times (The depth is 0.1 nm.)

It is noted that NiAg nanoparticles are all placed in the SBA-15 channels, as shown in Fig 3A of the main manuscript. For the depth profiling of the HS-LEIS above, the Ag signal at around 2450 eV is increasing gradually from the surface to interior. It is because the external SBA-15 layer is first removed before a steady Ag signal of the enclosed particles is established.

Table S3 The Ni/Ag atomic ratio of Ag–Ni/SBA-15 catalysts by XRF and XPS measurements.

Catalyst	Ni/Ag atomic ratio	
	by XRF	by XPS
5Ag ₁ –Ni _{0.05} /SBA-15	0.06	0.01
5Ag ₁ –Ni _{0.10} /SBA-15	0.11	0.03
5Ag ₁ –Ni _{0.20} /SBA-15	0.21	0.09
5Ag ₁ –Ni _{0.40} /SBA-15	0.41	0.13

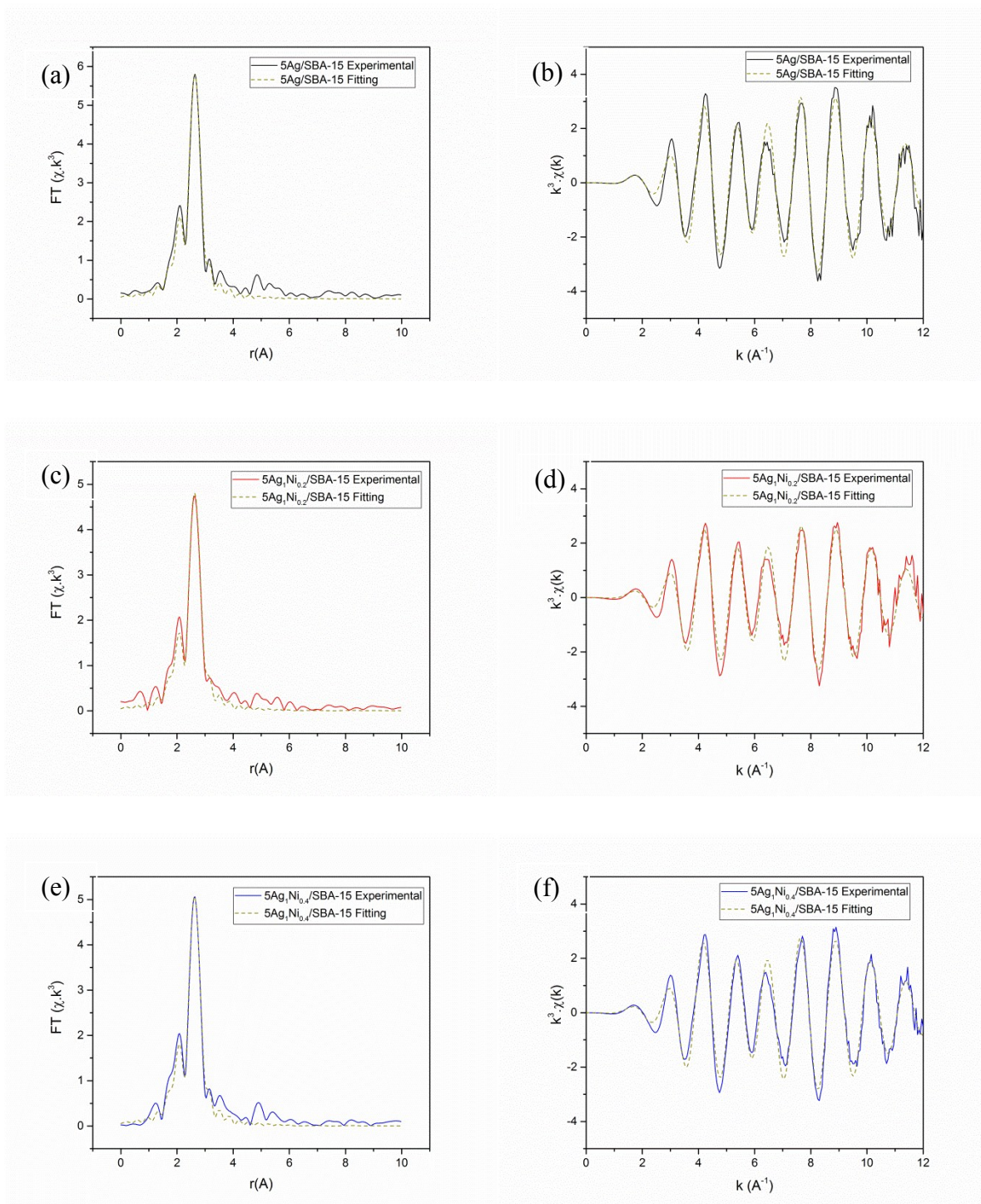


Fig. S3. Ag K-edge EXAFS plots of: **(A)** $k^3\chi$ phase corrected Fourier transform of experimental and fitted data for 5Ag/SBA-15; **(B)** $k^3\chi$ experimental and fitted data for 5Ag/SBA-15; **(C)** $k^3\chi$ phase corrected Fourier transform of experimental and fitted data for 5Ag₁Ni_{0.2}/SBA-15; **(D)** $k^3\chi$ experimental and fitted data for 5Ag₁Ni_{0.2}/SBA-15; **(E)** $k^3\chi$ phase corrected Fourier transform of experimental and fitted data for 5Ag₁Ni_{0.4}/SBA-15; **(F)** $k^3\chi$ experimental and fitted data for 5Ag₁Ni_{0.4}/SBA-15.

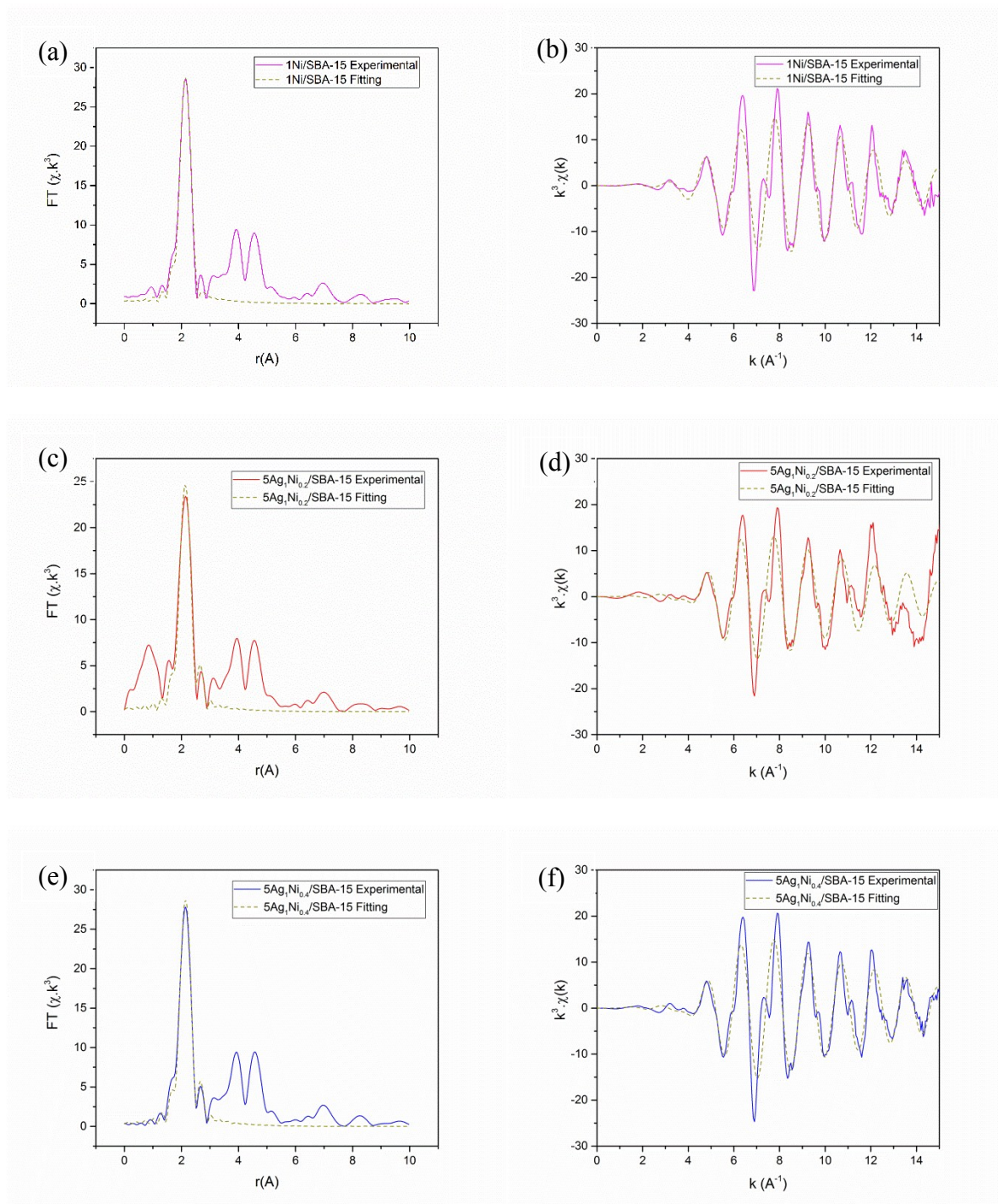


Fig. S4. Ni K-edge EXAFS plots of: **(A)** $k^3\chi$ phase corrected Fourier transform of experimental and fitted data for 1Ni/SBA-15; **(B)** $k^3\chi$ experimental and fitted data for 1Ni/SBA-15; **(C)** $k^3\chi$ phase corrected Fourier transform of experimental and fitted data for 5Ag₁Ni_{0.2}/SBA-15; **(D)** $k^3\chi$ experimental and fitted data for 5Ag₁Ni_{0.2}/SBA-15; **(E)** $k^3\chi$ phase corrected Fourier transform of experimental and fitted data for 5Ag₁Ni_{0.4}/SBA-15; **(F)** $k^3\chi$ experimental and fitted data for 5Ag₁Ni_{0.4}/SBA-15.

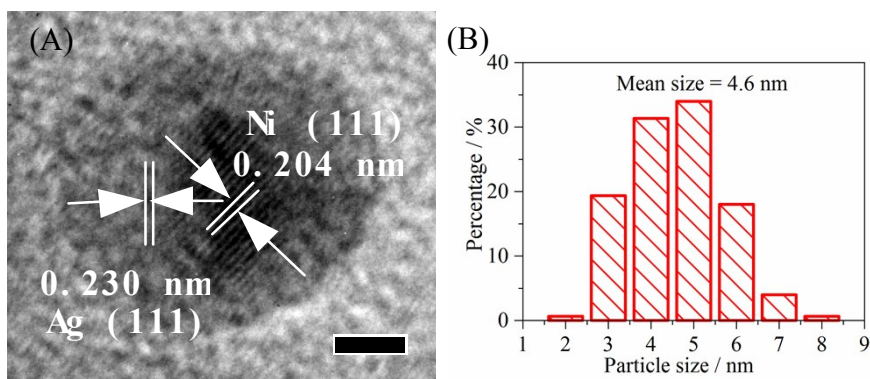


Fig. S5. (A) High-resolution TEM image of an isolated NiAg core-shell nanoparticle of a larger size for the benefit of a clearer lattice fringe identification (after removal of silica by NaOH); (B) Size distributions of $5\text{Ag}_1\text{-Ni}_{0.20}/\text{SBA-15}$ nanoparticles, following a typical pore size distribution of the mesoporous template).

It is noted that the typical size of Ag and Ni@Ag nanoparticles deposited in SBA-15 are around 4.5-5.0 nm, as shown in Fig. S5. It has been reported in the literature [4] that the Ag nanoparticles with the size range of 2 nm to 5 nm show the coordination numbers (CNs) of 6 to 8 (Ag-Ag), which is in agreement with our EXAFS result (Fig. S4 and Tables 3 and 4 in main text). Thus, the CNs derived from our EXAFS and the particle size statistics measured by TEM are comparable to the literature.

Active site for the hydrogenation:

Activation of H_2 molecule to surface hydrogenic species appears to be the key step in this catalytic hydrogenation reaction. From our experiments, the use of Ag_2O did not show high activity if the pre-reduction step was not carried out prior to the testing. Thus, Ag^+ does not seem to be as active as $\text{Ag}(0)$ for this reaction. On the other hand, Ag in form of metallic state promoted by Ni core appears to be active in this cooperative catalysis. However, one should be cautious that fast regeneration of $\text{Ag}(+)/\text{Ag}(0)$ in close proximity of Ni during catalysis may impose difficulties to identify the real active site for this reaction.

As a result, active site for DMO hydrogenation to methyl glycolate and ethylene glycol over core-shell particle is assumed to be the Ni core-modified Ag shell site (for the calculation of TOF). Since extensive Ni sites (pure Ni particles and high Ni/Ag particles) appear to catalyze the total hydrogenolytic cleavage of DMO molecules to produce methane. However, there is also a possibility the active site is not a single site but cooperative sites between Ag and Ni whereby isolated exposed Ni site may dissociate di-hydrogen and spill to adjacent Ag site for hydrogenation. Further research is currently underway on this point.

Reference

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2. Y. Huang, H. Ariga, X. L. Zheng, X. P. Duan, S. Takakusagi, K. Asakura and Y. Z. Yuan, *J. Catal.*, 2013, **307**, 74.
3. J. Zhou, X. Duan, L. Ye, J. Zheng, M. M. J. Li and S. C. E. Tsang, Y. Yuan, *Appl. Catal. A: Gen.*, 2015, 505, 344.
4. S. Ghosh et al., *Green Chem.*, 2015, 17, 1867–1876