Electronic Supporting Information

Meso-macro-porous monolithic Pt-Ni/Al$_2$O$_3$ catalysts used for miniaturizing preferential carbon monoxide oxidation reactor

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Preparation of macroporous monolithic alumina. Macro-porous monolithic alumina was synthesized using a similar procedure that already reported by our team.[1] The macroporous polystyrene monolithic foams after imbibing the alumina hydrosols were calcined in a furnace in flowing air with a stepwise heating manner, in which the first step was at a heating rate of 1 °C min^{-1} to 600 °C and kept there for 4 h and the second step was at a heating rate of 10 °C min^{-1} to 1300 °C for 2h. The macro-porous polystyrene foams, the templates, were decomposed and oxidized completely in the calcination process. Thus the macro-porous alumina monoliths (denoted as M-α-Al$_2$O$_3$) were obtained. Translucent alumina hydrosols prepared from pseudo-boehmite were coated to improve the specific surface area of M-α-Al$_2$O$_3$. Alumina hydrosols were imbibed into M-α-Al$_2$O$_3$ under modest vacuum, which was similar to filling alumina hydrosols into polystyrene foams in making α-Al$_2$O$_3$ monoliths, and the thus coated samples were dried at 60 °C for 12 h. The coating and drying procedures were repeated for several times. After the last coating, samples were calcined in air at 600 °C for 2 h at a heating rate of 10 °C min^{-1} to obtain meso-macro-porous monolithic γ-Al$_2$O$_3$/α-Al$_2$O$_3$ (denoted as M-γ/α-Al$_2$O$_3$). The loading amount of γ-Al$_2$O$_3$ is 13% in weight.

Catalytic performance tests. PROX reactions were carried out in a fixed tubular reactor with a continuous-flow reaction system under atmospheric pressure. In each run, a piece of monolithic catalyst (4 mm length and 7 mm i.d.) was put into a high temperature resistant silicone tube, and the silicone tube was connected with two quartz tube at its both sides. The reaction temperature was monitored by a K-type thermocouple placed in the monolithic catalysts and controlled by a temperature controller. The effluent gases were analyzed using an on-line gas SP-3420 gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) and a column packed with 5A molecular sieve. As for detecting the CO concentration at ppm level, FID was used as the detector and equipped with a methanator, thus the CO detection limit is 1 ppm. The activities were evaluated on the basis of CO conversion, which can be calculated on the basis of CO in the reactant gas and the effluent gas. The selectivity of O$_2$ to CO oxidation is defined as the ratio of O$_2$ consumption for the CO oxidation to total O$_2$ consumption.

In each testing process, M-Pt-Ni/Al$_2$O$_3$ was pre-reduced at 300 °C for 1 h with 10 vol.% H$_2$ in N$_2$ at a heating rate of 10 °C min^{-1}. The total gas flow rate was kept constant at 40 mL min^{-1}, corresponding to the volume space velocity of 16,000 h^{-1}.

N$_2$ adsorption–desorption isotherms measurements. Nitrogen adsorption and desorption isotherms were determined on a Micromeritics apparatus of model ASAP-2020 system at -196 °C. The specific surface areas were calculated by the BET method and the pore size distributions were calculated from the desorption branch of the isotherm by BJH model.

Transmission electron microscopy (TEM). TEM analyses of catalysts were obtained on a Technai G^2 F20 microscope operated at 200 kV. Samples were pre-reduced at 300 °C in 10 vol.% H_2 in N_2 for 1 h, then finely grounded in a mortar to fine particles and dispersed ultrasonically in ethanol. The well dispersed samples were deposited on a Cu grid covered by a holey carbon film for measurements.

TPR measurements. The temperature programmed reduction (TPR) equipment is consisted of a thermal conductivity detector (TCD) connected to a flow-control system and a programmed heating unit. 40 mg sample placed in a quartz reactor was reduced in a stream of 5% H_2 in Ar at a flow rate of 20 mL min^{-1}.

Compressive strength measurement. The compressive strengths of the calcined samples were measured using a Shimadzu DSS-25T universal testing machine. The samples were fixed with flat steel plates closed with a circular head at a speed of 0.5 mm min^{-1}.
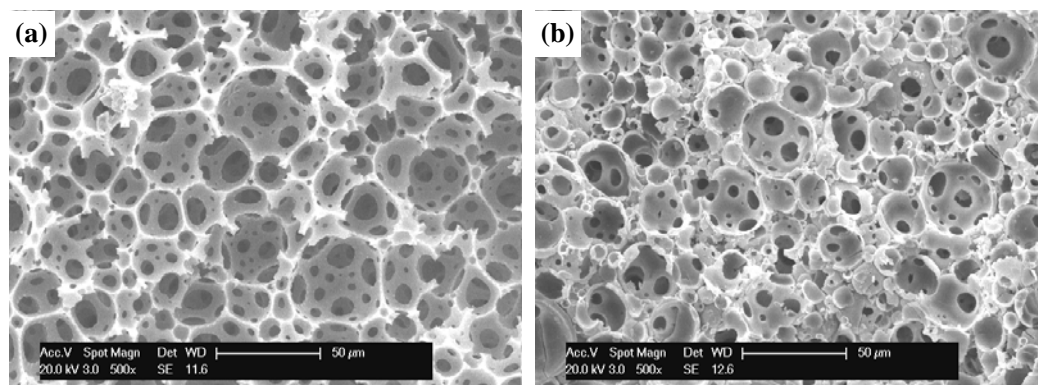
Supplementary Figures

Fig. S1-Supporting information

Fig. S1 SEM images of (a) polystyrene monolithic template and (b) M-γ/α-Al$_2$O$_3$. Scale bars: 50 μm for a and b.

Typical SEM images of polystyrene monolithic template and M-γ/α-Al$_2$O$_3$ are shown in Fig. S1. From Fig. S1-a, it can be seen that the macropores are in spherical shape and in diameter range of about 5 to 50 μm. The spherical macropores are interconnected via windows with the diameters approximately 1–15 μm. The microscopic appearance of M-γ/α-Al$_2$O$_3$ (Fig. S1-b) replicates the microstructure and morphology of the polystyrene monolithic template with shrinkage taken into account.
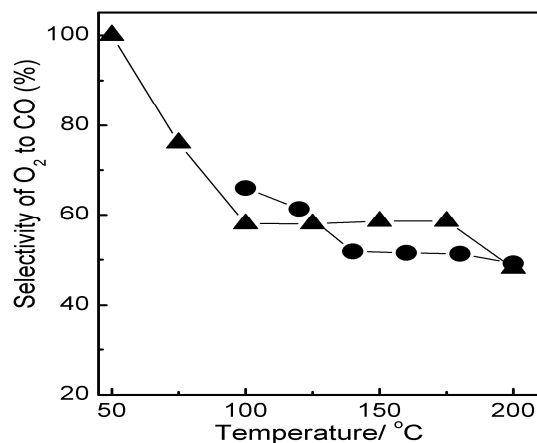
Fig. S2-Supporting information

Fig. S2 Reaction temperature dependence of selectivity of O$_2$ to CO oxidation in the CO-PROX reaction over M-Pt-Ni/Al$_2$O$_3$. Reaction conditions: 1 vol.% CO, 1 vol.% O$_2$, and 50 vol.% H$_2$ in N$_2$ balance ($\blacktriangle$); 1 vol.% CO, 1 vol.% O$_2$, 12.5 vol.% CO$_2$, 15 vol.% H$_2$O and 50 vol.% H$_2$ in N$_2$ balance ($\bullet$). The volume space velocity is 16,000 h^{-1}.

Fig. S3-Supporting information

High-resolution transmission electron microscopy (TEM) provides insight into the local structure of M-Pt-Ni/Al$_2$O$_3$. It can be seen that platinum and nickle nanoparticles have fairly uniform size, with an average diameter of about 2.5 nm.
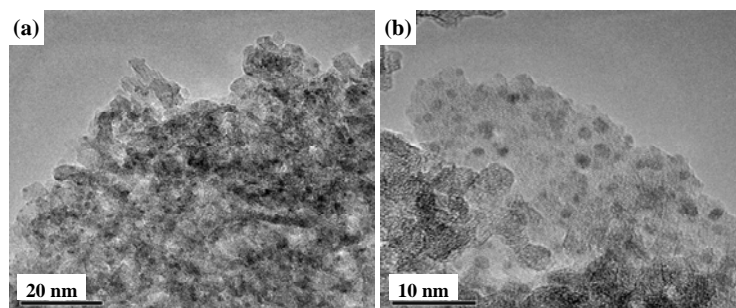
Fig. S3 TEM images of M-Pt-Ni/Al$_2$O$_3$ after reduction. Scale bars: 20 nm for (a) and 10 nm for (b).

Fig. S4-Supporting information

The H$_2$-TPR profiles of the different samples are given in Fig. S4. As can be seen, M-Ni/Al$_2$O$_3$ (Fig. S4-a) exhibits three reduction peaks centered at around 287 ^{o}C, 357 ^{o}C and 448 ^{o}C, which are attributed to the reduction of nickel oxide to metal nickel. The low-temperature reduction peaks at around 287 ^{o}C and 357 ^{o}C is related to the reduction of surface NiO species, and the high-temperature reduction peak at around 448 ^{o}C is assigned to the reduction of bulk NiO which is in interaction with the support.[2] There are two reduction peaks for M-Pt/Al$_2$O$_3$ (Fig. S4-b) at around 204 ^{o}C and 470 ^{o}C respectively. The peak at around 204 ^{o}C is attributed to the reduction of PtOx species on the support. The peak at around 470 ^{o}C is assigned to the reduction of PtOx species interacted with the alumina support.[3]

The reduction peaks of M-Pt-Ni/Al$_2$O$_3$ (Fig. S4-c) is consisted of a high-intensity, low-temperature peak at about 188 ^{o}C and a low-intensity peak at around 400 ^{o}C. The low temperature peak is attributed to the reduction of highly dispersed platinum species and NiO. Comparing to M-Ni/Al$_2$O$_3$ and M-Pt/Al$_2$O$_3$, the reduction peaks of nickel and platinum shift to lower temperatures, and this may be an indication of the formation of interaction between nickel and platinum species and the formation of Ni-Pt alloy as proposed by Ko et al..[4] The interaction between platinum and nickel is important for the high activity of CO-PROX.
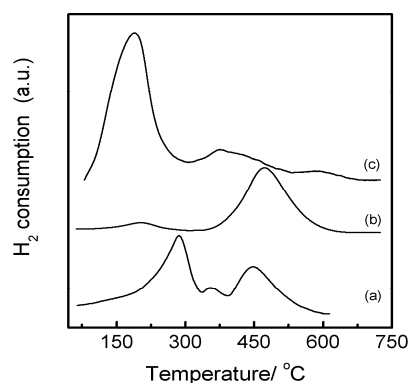

Fig. S4 TPR patterns of (**a**) M-Ni/Al$_2$O$_3$, (**b**) M-Pt /Al$_2$O$_3$ and (**c**) M-Pt-Ni/Al$_2$O$_3$.

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2   G. h. Li, L. J. Hu and J. M. Hill, *Appl. Catal. A*, 2006, **301**, 16.

3   J. W. Bae, J. S. Lee and K. H. Lee, *Appl. Catal. A*, 2008, **334**, 156.

4   E. Y. Ko, E. D. Park, K. W. Seo, H. C. Lee, D. Lee and S. Kim, *Catal. Today*, 2006, **116**, 377.