Electronic Supporting Information

Meso-macro-porous monolithic Pt-Ni/Al₂O₃ 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-Al₂O₃) were obtained. Translucent alumina hydrosols prepared from pseudo-boehmite were coated to improve the specific surface area of M-α-Al₂O₃. Alumina hydrosols were imbibed into M-α-Al₂O₃ under modest vacuum, which was similar to filling alumina hydrosols into polystyrene foams in making α-Al₂O₃ 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-Al₂O₃/α-Al₂O₃ (denoted as M-γ/α-Al₂O₃). The loading amount of γ-Al₂O₃ 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 O₂ to CO oxidation is defined as the ratio of O₂ consumption for the CO oxidation to total O₂ consumption.

In each testing process, M-Pt-Ni/Al₂O₃ was pre-reduced at 300 °C for 1 h with 10 vol.% H₂ in N₂ 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.

N₂ 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 G² F20 microscope operated at 200 kV. Samples were pre-reduced at 300 °C in 10 vol.% H₂ in N₂ 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% H₂ 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-Al₂O₃. Scale bars: 50 μm for a and b.](image)

Typical SEM images of polystyrene monolithic template and M-γ/α-Al₂O₃ 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-Al₂O₃ (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 O₂ to CO oxidation in the CO-PROX reaction over M-Pt-Ni/Al₂O₃.](image)

Reaction conditions: 1 vol.% CO, 1 vol.% O₂, and 50 vol.% H₂ in N₂ balance (▲); 1 vol.% CO, 1 vol.% O₂, 12.5 vol.% CO₂, 15 vol.% H₂O and 50 vol.% H₂ in N₂ balance (●). 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/Al₂O₃. 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/Al₂O₃ after reduction. Scale bars: 20 nm for (a) and 10 nm for (b).

Fig. S4-Supporting information

The H₂-TPR profiles of the different samples are given in Fig. S4. As can be seen, M-Ni/Al₂O₃ (Fig. S4-a) exhibits three reduction peaks centered at around 287 °C, 357 °C and 448 °C, which are attributed to the reduction of nickel oxide to metal nickel. The low-temperature reduction peaks at around 287 °C and 357 °C is related to the reduction of surface NiO species, and the high-temperature reduction peak at around 448 °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/Al₂O₃ (Fig. S4-b) at around 204 °C and 470 °C respectively. The peak at around 204 °C is attributed to the reduction of PtOₓ species on the support. The peak at around 470 °C is assigned to the reduction of PtOₓ species interacted with the alumina support.³

The reduction peaks of M-Pt-Ni/Al₂O₃ (Fig. S4-c) is consisted of a high-intensity, low-temperature peak at about 188 °C and a low-intensity peak at around 400 °C. The low temperature peak is attributed to the reduction of highly dispersed platinum species and NiO. Comparing to M-Ni/Al₂O₃ and M-Pt/Al₂O₃, 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/Al₂O₃, (b) M-Pt/Al₂O₃ and (c) M-Pt-Ni/Al₂O₃](image)