A Pt–Rh synergism in Pt/Rh three-way catalysts

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A Pt/Rh catalyst, aged to mimic in-use catalyst performance, has HC/CO/NO activities significantly higher than Pt- or Rh-only catalysts, indicating that the high activity of the Pt/Rh three-way catalyst is due to a Pt–Rh synergism.

Pt/Rh three-way catalysts have been widely used to lower HC/CO/NO emissions from automobiles. It is generally recognized that Rh is the primary active component for NO reduction to nitrogen, and Pt contributes to HC/CO oxidations.[1,2] However, it has not been possible to ascribe entirely independent functions to the two noble metals, and many questions remain unanswered.

This study investigates catalyst performances of Pt, Rh and Pt/Rh catalysts after ageing in exhaust to mimic in-use catalyst operation. The activity of the Pt/Rh catalyst is about one order of magnitude higher than either a Pt or an Rh catalyst for HC/CO/NO three-way conversions.

Gamma alumina powders of BET surface area 150 m^2 g^{-1} were used as the catalyst support. Pt/alumina catalyst was prepared by impregnating amine-solubilized platinum hydroxide solution into the alumina powders *via* an incipient wetness procedure, then drying at 373 K for 12 h and calcining at 773 K for 2 h. Rhodium alumina catalyst powders were prepared using rhodium nitrate solution following the same procedure. Mixtures of Pt and Rh catalyst powders were then ball-milled to form an aqueous slurry. The slurry was then applied onto a ceramic honeycomb substrate, and excess slurry was blown off using a forced air flow to obtain the desired catalyst loading. The samples were dried at 373 K for 12 h and calcined at 773 K for 2 h.

A laboratory honeycomb reactor was used to evaluate catalyst activity in a simulated auto exhaust gas stream using catalyst cores (diameter 3.8 cm, length 7.6 cm). The average gas composition is 0.75% CO, 0.25% H_2, 0.6% O_2, 16.3% CO_2, 10% H_2O, 1600 ppm NO, 280 ppm C_3H_8, 280 ppm C_3H_6 and 40 ppm SO_2 with the balance nitrogen. The perturbation frequency is 1 Hz. Catalyst inlet and outlet gas compositions were determined using HC/CO/NO analysers while raising the temperature gradually from room temperature to 823 K at a space velocity of 50 000 VHSV.

Catalysts were aged to simulate in-use catalyst operation before activity measurements. The laboratory honeycomb reactor ageing was conducted in a simulated auto exhaust gas stream at 1173 K for 12 h.

The Pt/Al catalyst prepared in this study contains 1.18 g l^{-1} Pt and 122.0 g l^{-1} alumina. The Rh/Al catalyst contains 0.24 g l^{-1} Rh and 122.0 g l^{-1} alumina. The Pt/Rh/Al catalyst contains 1.18 g l^{-1} Pt, 0.24 g l^{-1} Rh and 122.0 g l^{-1} alumina, and the Pt/Rh ratio is 5 : 1 by mass. The above Pt and Rh loading and ratio are the same as that seen in typical commercial Pt/Rh three-way automotive catalysts.

These Pt/Al, Rh/Al and Pt/Rh/Al honeycomb catalysts were then aged in the simulated auto exhaust stream at 1173 K. Fig. 1 summarizes HC/CO/NO conversion as a function of reaction temperatures for the Pt/Al catalyst as shown in Fig. 1(*a*), the Rh/Al catalyst in Fig. 1(*b*) and the Pt/Rh/Al catalyst in Fig. 1(*c*). For the Pt/Al catalyst, HC/CO/NO conversions start to increase at temperatures around 620 K. HC/CO conversions increase to 50% around 640 K; however, NO conversion increases to a maximum of 35% at 700 K. On the Rh/Al catalyst, CO/NO conversions start to increase around 570 K, and HC conversion increases around 620 K. However, the HC/CO/NO conversions only increase slowly with increasing temperature. At about 670 K, CO and NO conversions increase to about 50%, and then remain almost constant at temperatures up to 700 K. HC conversion increases continuously with increasing temperature to a maximum of 30% around 700 K. For the Pt/Rh/Al catalyst, HC/CO/NO conversions start to pick up at temperatures between 520 and 550 K, and reach 50% conversion around 570 K. HC and CO conversions increase continually with increasing reaction

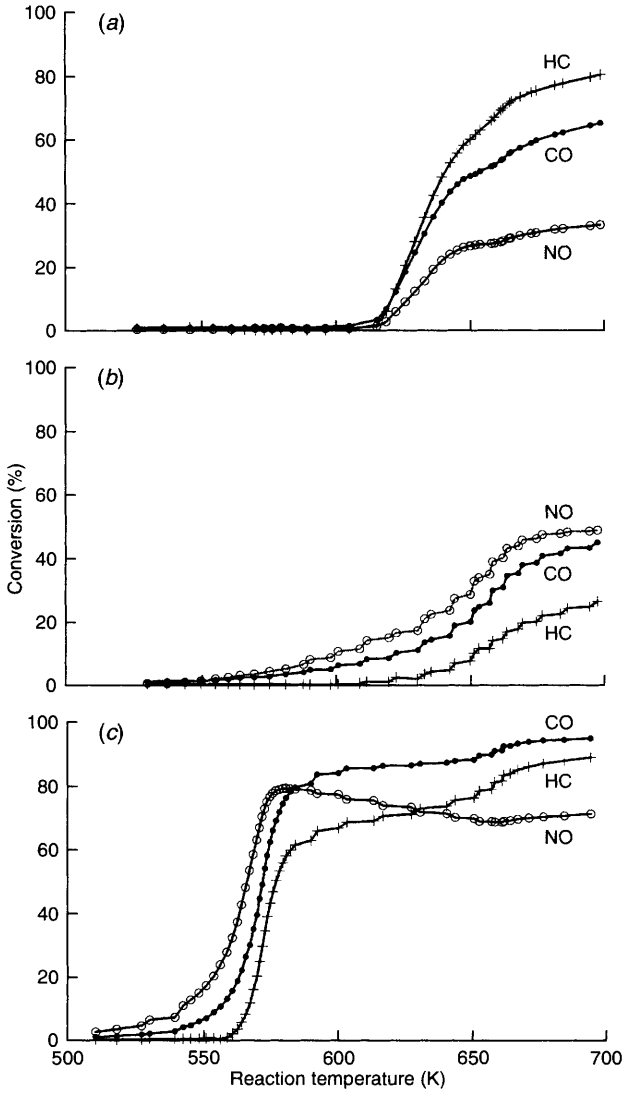

Fig. 1 HC/CO/NO conversions as a function of reaction temperatures for (*a*) Pt/Al (*b*) Rh/Al and (*c*) Pt/Rh/Al catalysts all aged in simulated exhaust at 1173 K

temperature, and reaches 90% around 700 K. NO conversion increases to a maximum of 80% around 590 K. Comparing HC/CO/NO conversions around 700 K, it is clear that both Pt-containing catalysts, *i.e.*, Pt/Al and Pt/Rh/Al, give high HC and CO conversions. Rh-containing catalysts, Rh/Al and Pt/Rh/Al, show relatively high NO conversion. These results suggest that Pt catalysts have HC/CO activities higher than Rh catalysts, but the reverse is true for NO reduction. It is also clear that the highest HC/CO/NO conversions are obtained on the Pt/Rh catalyst. In addition, the Pt/Rh/Al catalyst gives HC/CO conversions of 50% at temperatures lower than the Pt/Al catalyst by 70 K, and lower than the Rh/Al catalyst by 100 K. The NO conversion reaches 50% on the Pt/Rh/Al catalyst at 110 K lower than the Rh/Al catalyst, and never increases to 50% on the Pt/Al catalyst. It should be noted that around 570 K, the Pt/Rh/Al catalyst shows high HC/CO/NO conversions, while the Pt/Al and Rh/Al catalysts gave almost zero conversions.

These results indicate clearly that there is a Pt–Rh synergism operating in the aged Pt/Rh/Al catalyst which is responsible for the high HC/CO/NO activities. Further experimental investigation is needed to identify the origin of such a Pt–Rh synergism.

The Pt/Rh catalyst, aged to mimic in-use catalyst performance, has a significantly higher activity for HC/CO/NO three-way conversions in comparison with the Pt/Al and the Rh catalysts. This high activity is ascribed to a Pt–Rh synergism.

References

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Received, 5th January 1996; Com. 6/00126B