Comparative investigation of simultaneous removal of NO and N_2O on supported Pt catalysts: effect of thermal ageing

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Introduction

The abatement of NO_x and N_2O is a great challenge for stationary source applications since no catalytic formulation active at moderate temperature around 300°C can remove both pollutants from exhaust gas simultaneously in a complex atmosphere. The replacement of ammonia by hydrogen as reducing agent has many potential applications as suggested by recent studies which show high efficiency for NO_x conversion at low temperature on $Pt/La_{0.7}Sr_{0.2}Ce_{0.1}FeO_3$ [1]. Noble metals are currently used for such applications but generally suffer from a poor selectivity in O_2 excess. It was also found that the perovskite structure is able to preserve a high degree of dispersion in severe temperature conditions [2]. Unfortunately, no relevant comparison with alumina based catalysts is available in the literature. Our work was focused on the comparison of Pt/Al_2O_3 and $Pt/LaFeO_3$ catalysts before and after several thermal treatments including ageing under reaction conditions. The influence of the support and metal loading was investigated and characterised with TPR, XPS, TEM and temperature-programmed reaction under the following mixture of $He+0.1\%NO+0.1\%N_2O+0.5\%H_2+0.5\%H_2O+3\%O_2$. Ageing thermal treatments were applied under reaction mixture at 500°C overnight.

Materials and Methods

$Pt/LaFeO_3$ (20 m^2g^{-1}) catalysts were prepared according to a so-called sol-gel method using a citrate route and a classical wet impregnation of the platinum precursor. Pt/Al_2O_3 catalysts were prepared using the same procedure as for the $Pt/LaFeO_3$ catalysts. Catalysts were finally calcined at 400°C and reduced at 300°C overnight.

Results and Discussion

The TPR experiments clearly show different metal-support interactions with a shift of the reduction temperature from 157 to 216°C for the $4\%Pt/Al_2O_3$ and $1\%Pt/Al_2O_3$ catalysts respectively and from 128 to 198°C for the $4\%Pt/LaFeO_3$ and $0.5\%Pt/LaFeO_3$ catalysts respectively. Additional information arose from XPS with the Binding Energy value of the Pt photopeak. On alumina after calcination, the BE value of 317 eV (Pt $4d_{5/2}$) corresponded to Pt^{2+} as a PtO phase whereas on the perovskite a mixture of PtO_2 (BE Pt 4f: 75 eV) and PtO (BE Pt 4f: 73 eV) was observed. After reduction, the platinum particles were observed with TEM. The average particle size and the distribution were then estimated for $4\%Pt/Al_2O_3$ and $4\%Pt/LaFeO_3$ catalysts (Figure 1). On the reduced samples, the average size was similar on both supports (1.2 nm on alumina and 1.5 nm on $LaFeO_3$) despite the lower specific surface area of the $LaFeO_3$ support.

The catalytic performances investigated in the simultaneous conversion of NO and N_2O are reported on Figure 2. In both cases, two distinct conversion ranges appeared for NO while the conversion of N_2O took place at higher temperature. The best catalytic performance was obtained on the freshly-prepared Pt/Al_2O_3 catalyst with 80% NO and N_2O conversion at 340°C. The thermal ageing under a reaction mixture at 500°C overnight had a detrimental effect on Pt/Al_2O_3 with a simultaneous conversion of approximately 8% at 450°C. Fresh $Pt/LaFeO_3$ was characterized by a lower conversion in comparison to the alumina one. However it is worthwhile to note that as opposed to Pt/Al_2O_3, a rate enhancement is observed for both the conversion of NO and N_2O. TEM images were recorded on $4\%Pt/Al_2O_3$ and $4\%Pt/LaFeO_3$ after successive thermal treatments. After ageing the apparition of large platinum particles was observed on alumina with a significant shift of the mean particle size from 1.2 nm on the fresh sample to 14.9 nm on the aged catalyst. For the $Pt/LaFeO_3$ catalyst after ageing, the average size is similar to that of the fresh catalyst (1.1 nm against 1.5 nm). TPR experiments reveal changes of the nature of platinum species. The chemical environment of Pt was then characterized with XPS for each thermal ageing. Such a behavior was related to the re-dispersion processes which took place on the pre-reduced catalyst. Stabilization of platinum on the perovskite would occur during thermal ageing instead of sintering of Pt particles which predominates on alumina. Such surface changes are accompanied by changes in catalytic properties both on the conversion of NO and N_2O in the former case.

Significance

The use of perovskite and/or noble metal in environmental catalysis applications develops and the characterisation of the catalyst especially after ageing under reaction conditions is an essential point for further developments and optimisations. This present study reports support effect on stabilisation of platinum particles.

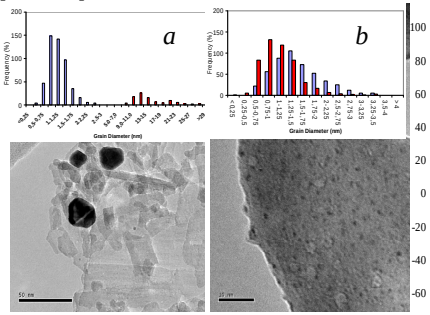

Figure 1. TEM images on aged $4\%Pt/Al_2O_3$ (*a*) and $4\%Pt/LaFeO_3$ (*b*); Particle size distribution (■: fresh sample; ■: aged sample)

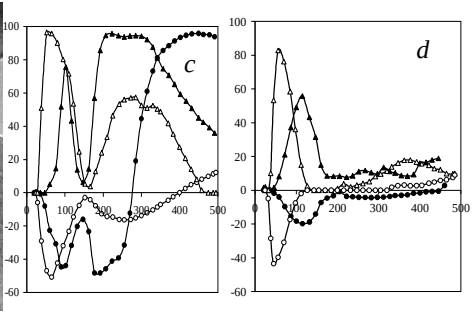

Figure 2. Conversion profiles v.s. temperature on $4\%Pt/Al_2O_3$ (***c***) on $4\%Pt/LaFeO_3$ (***d***) : NO (●) and N_2O (▲) on fresh – NO (○) and N_2O (△) on aged catalysts

References

1. C.N. Costa, V.N. Stathopoulos, V.C. Belessi, A.M. Efstathiou, J. Catal. 197 (2001) 350.
2. M. Uenishi, M. Tanigushi, H. Tanaka, M. Kimura, Y. Nishihata, J. Mizuki, T. Kobayashi, Appl. Catal. B 57 (2005) 267