Catalysis Letters 24 (1994) 107–112

NO decomposition over partially reduced metallized CeO_2–ZrO_2 solid solutions

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Received 20 July 1993; accepted 15 October 1993

Incorporation of ZrO_2 into a solid solution with CeO_2 strongly enhances the reducibility of the Ce^{4+} in the metallized samples and favours an effective NO decomposition over the reduced catalysts.

Keywords: Rh/CeO_2–ZrO_2 catalysts; NO decomposition

1. Introduction

Cerium oxide is added as an essential component to the automotive three-way catalytic converters. The suggested promoting roles of this component are the following: (i) stabilization of the metal dispersion and of the alumina support, (ii) promotion of the water–gas shift reaction and (iii) enhancement of the oxygen storage and release by interchanging between CeO_2 under oxidizing conditions and Ce_2O_3 under reducing conditions respectively [1,2]. Three-way catalysts are more active under reducing conditions, i.e. fuel-rich conditions, than in oxidizing conditions. Deactivation is attributed to oxidation of the noble metal. Oxygen storage capacities provided by Ce^{3+} may play a crucial role in enhancing the activity in the reducing conditions [3]. Further, oxygen vacancies associated with reduced ceria in the proximity of noble metal particles have been suggested recently as promoting sites for NO and CO conversions [4]. Therefore, stabilization of Ce^{3+} moieties in the reaction conditions would result in an enhanced activity of the metal catalyst as a large number of oxygen vacancies become available. This could also be achieved by incorporation of aliovalent metal ions, which creates oxygen vacancies in the CeO_2 lattice [5].

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We investigated CeO_2–ZrO_2 solid solutions as potential supports for three-way catalysts since, as shown in the patent literature [6], ZrO_2 effectively increases the thermal stability of the CeO_2 promoter under oxidizing conditions at high temperatures and, in addition, it inhibits undesirable interactions of rhodium with the support which are responsible for the deactivation of the catalyst. Here we report that the reduction of the support is strongly favoured in metallized CeO_2–ZrO_2 solid solutions as compared to metallized CeO_2. Furthermore, we show clear evidence for NO decomposition occurring over the reduced support, indicating a possible new role of the ceria promoter and of the rhodium in the three-way catalysts under transient conditions.

2. Experimental

The CeO_2–ZrO_2 solid solutions with CeO_2 contents ranging from 10 to 90% were prepared by firing a mixture of appropriate composition at 1873 K for 1 h. Powder X-ray diffraction analysis showed the presence of a pure fluorite type structure for CeO_2 molar contents greater than 60%. The supports were impregnated with $RhCl_3 \cdot 3H_2O$ or $Na_2PtCl_6 \cdot 6H_2O$ (metal loading 0.5 wt%) to incipient wetness, then dried at 393 K overnight and finally calcined at 723 K for 4 h. Temperature programmed reduction (TPR) was carried out in a conventional system equipped with a thermal conductivity detector in a flow of H_2 (5%) in Ar (20 ml min^{-1}). The amount of H_2 uptake in the TPR was estimated by using CuO as a standard. Catalytic experiments were carried out in a U-shaped glass microreactor. Reduction of the catalyst was routinely carried out at 473 or 673 K in H_2 (20 ml min^{-1}) for 2 h. The catalysts were then degassed at 473 K for 1 h in a flow of He before admitting the reaction mixture (NO (2%) in He, total flow 15 ml min^{-1} or NO (1%) and CO (3%) in He, total flow 30 ml min^{-1}, GHSV = 12500–50000 h^{-1}). The products were analysed on a gas chromatograph using Porapak Q and Haysep A columns. This allowed the detection of O_2, N_2, N_2O, NO, CO and CO_2. Magnetic susceptibility was measured with a Metronique MS02 SQUID magnetometer at 294 K with a static magnetic field 12.5 kOe. Weighted samples were treated in situ with H_2 or NO in a quartz sample holder and sealed under inert atmosphere. The susceptibility was corrected for the diamagnetic contribution of the sample holder.

3. Results and discussion

Fig. 1 shows the results of TPR experiments carried out on a CeO_2(60%)–ZrO_2(40%) support and on Rh or Pt/CeO_2(60%)–ZrO_2(40%) samples in comparison with those carried out on pure CeO_2 and Rh/CeO_2. Pure CeO_2 (trace 1) shows a strong reduction peak with a maximum at 1150 K which is assigned to bulk reduction [2]. The reduction peak is broadened and shifted to lower temperature in the

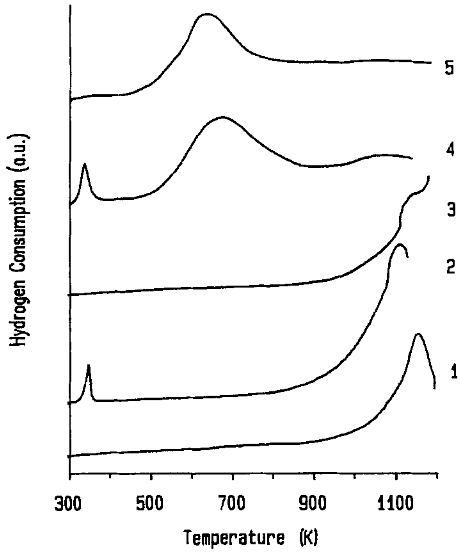

Fig. 1. The temperature programmed reduction profiles of (1) CeO_2, (2) 0.5% Rh/CeO_2, (3) CeO_2(60%)–ZrO_2(40%), (4) 0.5% Rh/CeO_2(60%)–ZrO_2(40%) and (5) 0.5% Pt/CeO_2(60%)–ZrO_2(40%).

presence of rhodium metal as seen in trace 2 of fig. 1. The sharp peak at 340 K is due to the reduction of supported Rh_2O_3 particles formed during the calcination. The low surface area ($1.4\ m^2\ g^{-1}$) of CeO_2 employed in our study accounts both for the missing peaks between 500 and 800 K in the TPR of Rh/CeO_2 (trace 2, fig. 1) due to surface reduction and for the lack of strong effects of the noble metal on the TPR profile. Strong enhancement of the CeO_2 reduction in the presence of supported metal, due to hydrogen spill-over, is generally observed on samples of high surface area [7]. The reduction of the CeO_2(60%)–ZrO_2(40%) solid solution occurs above 950 K (trace 3, fig. 1) and an overall H_2 uptake to 8.2 ml g^{-1} is estimated from the TPR profile which gives the final composition of $Ce_{0.6}Zr_{0.4}O_{1.94}$. A spectacular promotion of the reducibility of the CeO_2(60%)–ZrO_2(40%) solid solution is observed in the presence of noble metals (traces 4 and 5, fig. 1). The striking difference is the appearance of strong reduction features in the range 500–800 K in the TPR profiles of Rh (trace 4) and Pt/CeO_2(60%)–ZrO_2(40%) (trace 5) catalysts which are absent in the case of Rh/CeO_2. Notably, the magnitude of the peaks cannot account for the surface reduction only, hence partial bulk reduction of the support must occur as well. Consistently, for the rhodium catalyst, a composition of $Ce_{0.6}Zr_{0.4}O_{1.87}$ is estimated for the hydrogen consumption at the low temperature peak, while a final composition of $Ce_{0.6}Zr_{0.4}O_{1.77}$ is obtained taking also into account the peak at 1060 K. A TPR of a Rh/ZrO_2 catalyst showed no peak attributable to support reduction below 1000 K. This suggests that the reduction of the support should be associated with bulk Ce^{4+} which is reduced to Ce^{3+}. EXAFS studies are in progress to clarify this point.

Two processes are expected to facilitate the reduction of CeO_2 in the solid solutions at low temperatures. Firstly, surface oxygen vacancies are introduced on to the CeO_2 moieties by hydrogen spill-over from the noble metal to the solid solution. Secondly, these vacancies at the surface are subsequently filled up by the bulk oxygen being transported to the surface due to ionic conductivity [8].

As stated above, the presence of Ce^{3+} sites should promote the activity of the rhodium catalyst in the reduction of NO by CO. According to the TPR experiments, isothermal reduction at 673 K of the Rh/CeO_2(60%)–ZrO_2(40%) catalyst partially reduces the support while treatment at lower temperatures (473 K) reduces the metal only. This was confirmed in separate TPR experiments carried out on samples reduced in situ at 473 and 673 K; the TPR of the latter sample did not show any further reduction between 500 and 800 K. Formation of Ce^{3+} after reduction at 673 K of the Rh/CeO_2(60%)–ZrO_2(40%) sample is further confirmed by magnetic susceptibility measurements which showed a value of 3.5×10^{-6} emu g^{-1} at 294 K. Upon assumption that only Ce^{3+} is contributing to the magnetic moment [#1], we estimated, according to ref. [9], a composition of Rh/$Ce_{0.6}Zr_{0.4}O_{1.85}$ after the reduction at 673 K which is in a fairly good agreement with the TPR experiment.

We have therefore compared the activity of Rh/CeO_2(60%)–ZrO_2(40%) reduced at 473 and 673 K, in the CO + NO reaction in a flow reactor operating in differential conditions at 473 K using a mixture of NO (1%) and CO (3%) in He and GHSV = 41000 h^{-1}. The CO conversion slightly decreases with time on stream irrespectively of the catalyst pretreatment while the NO conversion over the catalyst reduced at 673 K slowly increases from an initial value of 0.3 to 1.4% after 80 min on stream and then it decreases slowly to a steady state value of 0.2%. Such a behaviour is quite unusual since, in this reaction, an initial deactivation is common for supported rhodium catalysts [10]. Notably, no such unusual NO conversion was observed over the catalyst reduced at 473 K.

A separate experiment (fig. 2, curve 1) using only NO as reactant showed that such unusual behaviour is best attributed to a NO decomposition process to give N_2 and N_2O. No O_2 evolution was detected, which indicates that the reduced support is reoxidized by the oxygen liberated in the decomposition of NO. Consistently, the O_2 uptake calculated from the NO conversion is, within 7% error, equivalent to the H_2 uptake for the TPR peak at 673 K in fig. 1, trace 4 ($O_2 = 1.6 \times 10^{-3}$ equiv. g^{-1}; $H_2 = 1.5 \times 10^{-3}$ equiv. g^{-1}). Besides this, no appreciable magnetic susceptibility could be measured on the Rh/CeO_2(60%)–ZrO_2(40%) sample which was prereduced at 673 K and then used in the decomposi-

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[#1] EXAFS measurements are in progress to further elucidate the role of zirconia in the reduction process. The degree of reduction was estimated by using a χ value of 1.06×10^{-5} emu g^{-1} for Ce_2O_3 at 294 K (ref. [9]).

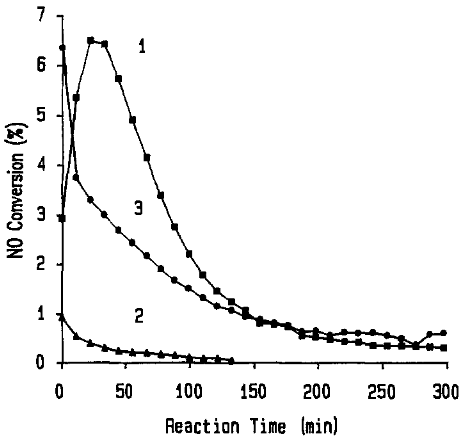

Fig. 2. NO decomposition at 473 K over Rh/CeO_2(60%)–ZrO_2(40%). (1) Fresh catalyst reduced in H_2 at 673 K for 2 h; (2) fresh catalyst reduced in H_2 at 473 K for 2 h; (3) catalyst recycled from run (1) and rereduced in H_2 at 673 K for 2 h.

tion of NO at 473 K. This result confirms that NO reoxidizes the support. The direct participation of the reduced support in the NO decomposition is also substantiated by the negligible NO conversion observed over the catalysts reduced at 473 K (fig. 2, curve 2). Remarkably, after re-reduction at 673 K of the catalyst employed in the experiment shown in fig. 2, curve 1, NO is promptly decomposed (fig. 2, curve 3). This observation reinforces the hypothesis of involvement of the bulk of the support in the reaction network, since repeated oxidation–reduction cycles enhance the oxygen mobility in CeO_2–ZrO_2 solid solutions due to the formation of structural defects [11]. In the light of these results we have reduced samples of pure CeO_2 and CeO_2(60%)–ZrO_2(40%) at 1073 K for 2 h. After this treatment both samples effectively decomposed NO. These experiments show unambiguously that NO dissociation can effectively occur at the reduced support sites re-filling the oxygen vacancies created by the high temperature reduction. The fact that NO is effectively decomposed on partially reduced CeO_2 reinforces the suggestion that the decomposition occurs at Ce^{3+} sites. This is consistent with the powerful oxygen abstraction capability of CeO_{2-x} suboxides which are easily reoxidized both by CO_2 and H_2O even at room temperature [12]. It appears that in general, splitting of a X–O bond (X = C, H, N) is strongly favoured over CeO_{2-x} except for CO which does not reoxidize surface Ce^{3+} sites [13].

In conclusion, the above observations appear to be strongly related to the behaviour of the commercial three-way catalysts since the presence of Ce^{3+} in catalytic conditions was repeatedly reported [3,4] and point out a new mechanism for the promoting effects of ceria in the reduction of nitrogen oxide attributable to the redox couple $Ce^{3+} \leftrightarrow Ce^{4+}$. Similarly, CO_2 dissociation is strongly enhanced in the presence of Ce^{3+} sites [7], but in this case only the surface boundary sites located at the border between the metal particles and the support appeared to be active. At variance, the present observations seem to be related also to the bulk properties of cerium containing materials.

Acknowledgement

Professor Renzo Rosei, University of Trieste is gratefully acknowledged for helpful discussions. We thank Dr. Roberta Sessoli, Dipartimento di Chimica, University of Florence for the magnetic susceptibility measurements. Ministero dell'Università e della Ricerca Scientifica (Rome) is acknowledged for financial support.

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