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Rh oxide reducibility and catalytic activity of model Pt–Rh catalysts

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Abstract

Pt and Rh were impregnated by different methods into the washcoat to investigate the differences in Rh oxidation state and catalytic activity of the samples. Both fresh and laboratory aged samples were studied. Clear differences in catalytic activity were noticed between the catalysts with different Pt and Rh addition methods. The best oxidation activity for fresh catalysts was achieved with the catalyst having both Pt and Rh deposited into the Ce–Zr mixed oxide. However, this state was observed to be unstable, and hence, this particular catalyst was dramatically deactivated in air ageing at high temperature. After ageing, the catalyst having both Pt and Rh impregnated lastly into the entire calcined washcoat matrix had the best activity in all three reactions, carbon monoxide and hydrocarbon oxidation and nitrogen oxide reduction. According to XPS studies, Rh was in easily reducible form in all the fresh samples. After ageing, the highest portion of reducible Rh was observed in the sample having also the best catalytic activity.

Keywords: Pt; Rh; XPS; Catalytic activity

1. Introduction

Ever tightening exhaust gas legislation is compelling catalyst manufacturers to seek more efficient ways to use costly precious metals. Many different strategies involve, for example, new thermally stable raw materials, various dopants and zone coating of the active material, to mention a few. Inserting the precious metal(s) on particular washcoat components is a prerequisite for modern exhaust catalysts. Tailoring metal–metal and metal–support interactions enables the optimum use of the small quantities of precious metals. Furthermore, synergism between certain elements or compounds can induce remarkable advantages in catalytic activity [1,2]. Pt and Rh are widely employed as active components in a typical automotive three-way catalyst (TWC). In general, Pt is associated with carbon monoxide and hydrocarbon oxidation, whereas nitrogen oxide reduction is mainly related to Rh. High surface area aluminum oxide is normally the basis of the washcoat and suitable for dispersing the small quantities of active components effectively. Cerium oxide or Ce–Zr mixed oxides act as an oxygen storage material to attenuate the air/fuel perturbation, i.e. the oxidative and reductive atmosphere fluctuation, in the exhaust gas [3–6]. Cerium oxide or Ce–Zr mixed oxides are also reported to promote catalytic activity of Pt in other ways than purely storing oxygen, and to keep Rh in easily reducible form after high temperature oxidative ageing [7–11].

In the present study, bimetallic Pt–Rh catalysts with different Pt and Rh addition methods were investigated. The precious metals were impregnated either into a particular washcoat component or into the entire calcined washcoat matrix. The purpose of this study was to find possible synergism in catalytic activity and to see whether it could be correlated with the Rh reducibility, as Rh is discovered to benefit from the incorporation of Pt [1,12].

2. Experimental

The washcoat composition in this study was the same for all the samples investigated, i.e. La-stabilized γ-alumina (50 wt.%) modified by $Ce_{0.18}Zr_{0.82}O_2$ mixed oxide

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(40 wt.%) and alumina sol (10 wt.%). In contrast, Pt and Rh were impregnated in different manner into each of the samples. The noble metals were either added by impregnation into Ce–Zr mixed oxide, after which, the slurry was formed or, alternatively, either one of the noble metals or both of them were impregnated into the coated catalyst afterward. The four samples are labelled in the following corresponding to their noble metal deposition, i.e. Pt + Rh/Ce-ZrO$_2$, Rh/Ce-ZrO$_2$ + Pt post-impregnation, Pt/Ce-ZrO$_2$ + Rh post-impregnation and Pt + Rh post-impregnation. The noble metal loadings of Pt and Rh in the washcoat were 0.5 wt.% and 0.2 wt.%, respectively. In the impregnation, $[Pt(NH_3)_4]\cdot 2HCO_3$ and $Rh(NO_3)_3\cdot 2H_2O$ were used as precious metal precursors. All the samples were coated onto a metal foil of 500 cells per square inch (cpsi). The sample was then dried overnight at 110 °C in normal atmosphere and finally calcined in air for 4 h at 550 °C. Thereafter, the precious metal was impregnated into the catalyst washcoat and the sample was again dried overnight at 110 °C in normal atmosphere and calcined in air for 4 h at 550 °C. Alternatively, in the pre-impregnation method, the precious metal was first impregnated into the Ce-ZrO$_2$ powder after which the precious metal-containing Ce-ZrO$_2$ powder was used as a washcoat constituent together with La-stabilized γ-alumina and alumina sol. Catalytic activity testing was performed with a stoichiometric synthetic gas mixture using a coated metallic foil test sample of 14 mm in diameter and 75 mm in length. A heating rate of 11.5 °C min^{-1} from room temperature to 400 °C, where the sample was held in order to reach stable conversion values, was used with a constant flow rate producing a space velocity (SV) of 50,000 h^{-1}. The gas composition was 1% CO, 375 ppm C_3H_6, 125 ppm C_3H_8, 1500 ppm NO, 0.65% O_2 (±0.22% perturbation at 1 Hz), 10% H_2O, 10% CO_2, balance N_2. To ensure stable results, the tests were performed twice. The results presented in Section 3 are for the second run. Catalyst ageing was performed in a muffle furnace in static air at normal atmospheric pressure for 3 h at 1000 °C or 900 °C. The reducibility of rhodium and platinum oxides formed in the ageing was investigated by annealing the catalysts in situ in 400 mbar of static H_2 at 300 °C for 30 min followed by the XPS measurements.

Noble metal dispersions were measured with CO adsorption at room temperature using a Carlo Erba Sorptomatic 1990. Pre-treatment consisted of reduction with hydrogen at 300 °C for 30 min and holding the sample in vacuum at 350 °C for 45 min. Active metal particle sizes and dispersions were calculated by assuming the stoichiometric factor between chemisorbed gas molecules and metal atoms being 1:1. XPS measurements were carried out with a Kratos XSAM 800 electron spectrometer with a base pressure less than 1×10^{-8} mbar. Non-monochromatic Mg Kα X-rays were used as a primary excitation and the hemispherical energy analyser was operated in a fixed analyser transmission (FAT) mode with a pass energy of 38 eV. The Al 2p line at 74.2 eV was used as a binding energy reference together with the C 1s line at 284.6 eV. All binding energies quoted in this work were measured within a precision of ±0.2 eV. The inelastic background was removed from the spectra using Shirley's method [13]. In the interpretation of the XPS results, it is assumed that the washcoat composition is homogeneous.

3. Results

3.1. Fresh samples

Fig. 1a shows the catalytic activity of the fresh samples for CO, THC and NO$_X$ at 400 °C, which corresponds to the end of the catalytic test. It can be seen that there are clear differences between the samples. The Rh + Pt post-impregnation sample has the best light-off (the temperature where the conversion reaches 50%) with every component, but has somewhat lower CO and hydrocarbon conversions than the best samples at 400 °C. The light-off, dispersion and binding energy values for the fresh and aged catalysts are presented in Table 1.

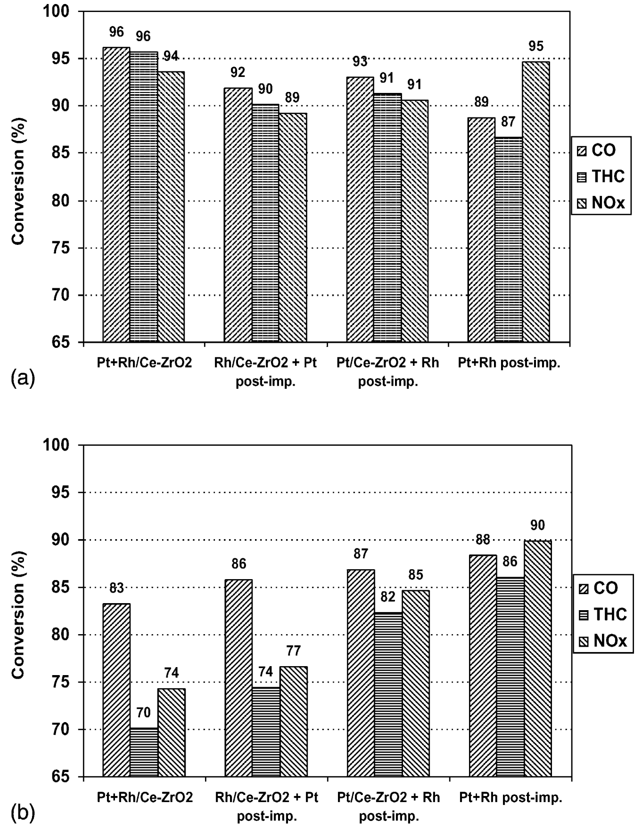

Fig. 1. (a) CO, THC and NO$_X$ conversions of fresh samples at 400 °C. Test gas composition: 1% CO, 375 ppm C_3H_6, 125 ppm C_3H_8, 1500 ppm NO, 0.65% O_2 (±0.22% perturbation at 1 Hz), 10% H_2O, 10% CO_2, balance N_2. (b) CO, THC and NO$_X$ conversions of high temperature (900 °C) air-aged samples at 400 °C. Test gas composition: 1% CO, 375 ppm C_3H_6, 125 ppm C_3H_8, 1500 ppm NO, 0.65% O_2 (±0.22% perturbation at 1 Hz), 10% H_2O, 10% CO_2, balance N_2.

Table 1
The Rh 3d binding energy values for the aged and aged + H_2-reduced catalysts and the dispersion and T_{50} values for the fresh and aged catalysts

	Rh $3d_{5/2}$ (eV) (met.)		Rh $3d_{5/2}$ (eV) (ox.)		Rh $3d_{5/2}$ (eV) (red.-res. ox.)		Dispersion (%)		T_{50} (°C)					
	Aged	Aged + H_2	Aged	Aged + H_2	Aged	Aged + H_2	Fresh	Aged	Fresh CO	Fresh THC	Fresh NO_X	Aged CO	Aged THC	Aged NO_X
Pt + Rh/Ce-ZrO_2	–	–	–	–	310.3	310.2	8.9	<2	222	247	236	311	340	327
Rh/Ce-ZrO_2 + Pt p-i	–	306.1	308.0	–	310.0	310.2	52	5.6	197	236	229	324	349	342
Pt/Ce-ZrO_2 + Rh p-i	–	305.9	307.7	–	309.9	310.0	79	2.8	229	242	235	271	300	278
Pt + Rh p-i	–	306.2	307.8	–	310.1	310.1	100	<2	188	207	194	265	298	275

red.-res. ox., Reduction-resistive oxide; p-i, post-impregnation.

According to the XPS results, Rh is reducible by in situ H_2-treatment in 400 mbar at 300 °C on the fresh Pt/Ce-ZrO_2 + Rh post-impregnation, Rh/Ce-ZrO_2 + Pt post-impregnation and Pt + Rh post-impregnation samples, as indicated by the Rh $3d_{5/2}$ peak shift from about 309 eV to about 307 eV in the H_2-treatment. On the fresh Pt+Rh/Ce-ZrO_2 sample, where both Pt and Rh have been pre-impregnated into the Ce-ZrO_2, the precious metals are undetectable by XPS.

3.2. Aged samples

After ageing in static air at 900 °C for 3 h, a considerable deterioration in the catalytic activity is observed, as shown in Fig. 1b. According to the activity results, activity is observed to be better with the samples where Rh has been post-impregnated.

The photoelectron spectra for 1000 °C air-aged samples (left) and for 1000 °C air-aged and H_2-reduced samples (right) are presented in Fig. 2. Rh is now detectable by XPS also from the Pt + Rh/Ce-ZrO_2 sample with the binding energy of 310 eV. The peak position is almost the same, 310 eV, also after H_2-treatment. This high binding energy value unaffected by the hydrogen treatment indicates the presence of reduction-resistive rhodium oxide phase [11,12]. In all the other aged catalysts, both Rh $3d_{5/2}$ and Pt $4d_{5/2}$ peaks are visible and rhodium appears to be in two different chemical states. The Rh $3d_{5/2}$ binding energy for the one state is about 310 eV and for another state, it is about 308 eV in all three catalysts. After the H_2-reduction of these aged catalysts, the reducible lower binding energy component of the Rh $3d_{5/2}$ peak shifts to about 306 and the other component remains at about the same binding energy of 310 eV. The measured binding energy values are presented in Table 1.

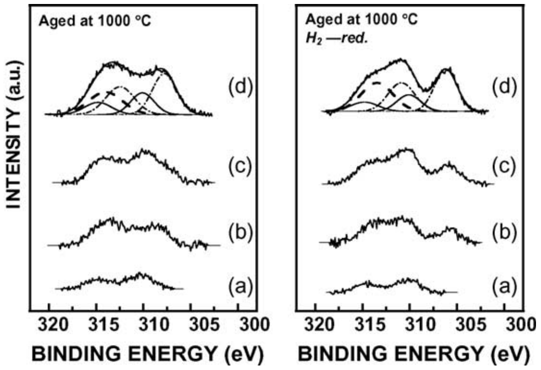

Fig. 2. The X-ray photoelectron spectra of the binding energy region containing Rh 3d and Pt $4d_{5/2}$ peaks for 1000 °C air-aged samples (left) and for 1000 °C air-aged and H_2-reduced samples (right). (a) Pt + Rh/Ce-ZrO_2; (b) Rh/Ce-ZrO_2 + Pt post-impregnation; (c) Pt/Ce-ZrO_2 + Rh post-impregnation; (d) Pt + Rh post-impregnation. An example of peak fitting with Rh 3d and Pt $4d_{5/2}$ synthetic components is shown for spectra (d).

4. Discussion

In the view of fresh catalytic activity versus chemisorption dispersion results, the best light-off corresponds to the best dispersion result as well (Pt + Rh post-impregnation). However, similar correspondence is not observed with the other samples, i.e. Pt + Rh/Ce-ZrO_2, Rh/Ce-ZrO_2 + Pt post-impregnation and Pt/Ce-ZrO_2 + Rh post-impregnation. The best and worst dispersions can be explained by the preparation method, i.e. by pre-impregnating both of the precious metals into the Ce-ZrO_2 or post-impregnating them into the whole washcoat matrix low and high dispersions are obtained, respectively. The other two results indicate higher dispersion for the sample with less precious metal on the surface (Pt/Ce-ZrO_2 + Rh post-impregnation). However, on Pt/CeO_2 CO is known to form carbonates on ceria, which could induce too high dispersion values [14]. On the other hand, CO spillover has also been observed on Rh/CeO_2 [15,16]. These observations show the complexity involved in measuring of the dispersion values in general.

According to the XPS results, rhodium is present as easily reducible rhodium oxide in the fresh catalysts. The only exception is the Pt + Rh/Ce-ZrO_2 catalyst, from which precious metals can not be detected by XPS. This is most probably related to the sample preparation, where the precious metals are incorporated into the slurry, and hence, encapsulated by the porous alumina [11]. After ageing, there is a substantial decrease in dispersion, catalytic activity and Rh reducibility. All the dispersion values are relatively small and close to each other, hence, it is difficult to make further assumptions based on them. Comparing XPS results with catalytic activity results at 400 °C, where all the catalysts have practically reached their stable values, the following results are obtained: XPS results indicate that the largest part of reducible Rh is found from the sample with the best catalytic activity, i.e. Pt + Rh post-impregnated. Some Rh reducibility is also found from the sample with almost an equal catalytic activity, i.e. Pt/Ce-ZrO$_2$ + Rh post-impregnated. The lowest catalytic activity is observed for the sample where no reducible Rh is noticed. Indeed, according to these values, a correlation between Rh reducibility and catalytic activity after ageing in air atmosphere at high temperature can be found. In addition, this is best observed for the NO$_X$ conversion, in which Rh has been found to be more active than for example Pt or Pd [17–19].

It seems that after an oxidative ageing at high temperature, Rh post-impregnation produces a better functioning catalyst compared to the pre-impregnation, if impregnation is used for the precious metal insertion. One reason for this could be the burying of the active material into the bulk of the washcoat, and hence, loss of active surface. Good conversion values were nevertheless observed for the fresh Pt + Rh/Ce-ZrO$_2$ sample despite of low dispersion values, which could possibly be an indication of having some synergism between the precious metals and/or the Ce-ZrO$_2$.

5. Conclusion

Considerable differences in both catalytic activity and Rh reducibility can be induced by simply modifying the precious metal surroundings in the washcoat, i.e. by modifying into which washcoat component(s) the precious metals are inserted. Following air ageing at high temperature, Rh reducibility after a hydrogen reduction at 300 °C and catalytic activity results were compared. Accordingly, a correlation was found, where the catalyst that had the most considerable part of reducible Rh likewise proved to have the best catalytic activity, and vice versa. The effects were especially observed for the NO$_X$ reduction that is a Rh-specific reaction.

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