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Comparison of catalytic activity and selectivity of Pd/(OSC + Al_2O_3) and (Pd + OSC)/Al_2O_3 catalysts

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Abstract

The effect of the Pd addition method into the fresh Pd/(OSC + Al_2O_3) and (Pd + OSC)/Al_2O_3 catalysts (OSC material = $Ce_xZr_{1-x}O_2$ mixed oxides) was investigated in this study. The CO + NO and CO + NO + O_2 model reactions were studied over fresh and aged catalysts. The differences in the fresh catalysts were insignificant compared to the aged catalysts. During the CO + NO reaction, only small differences were observed in the behaviour of the fresh catalysts. The light-off temperature of CO was about 20 °C lower for the fresh Pd/(OSC + Al_2O_3) catalyst than for the fresh (Pd + OSC)/Al_2O_3 catalyst during the CO + NO + O_2 reaction. For the aged catalysts lower NO reduction and CO oxidation activities were observed, as expected. Pd on OSC-containing alumina was more active than Pd on OSC material after the agings. The activity decline is due to a decrease in the number of active sites on the surface, which was observed as a larger Pd particle size for aged catalysts than for fresh catalysts. In addition, the oxygen storage capacity of the aged Pd/(OSC + Al_2O_3) catalyst was higher than that of the (Pd + OSC)/Al_2O_3 catalyst.

Keywords: Al_2O_3; Ceria–zirconia mixed oxides; $DeNO_x$; Nitrogen oxides; Palladium; Three-way catalysts

1. Introduction

The CO + NO reaction is one of the most important reactions in automobile exhaust gas catalysis, in which the most used noble metals to catalyse this reaction are rhodium (Rh), platinum (Pt), and palladium (Pd). On the basis of economical aspects (the high cost and limited supply of Rh and Pt), considerable attention has been paid to Pd as a single active metal component in three-way catalysts (TWCs). Other components of these systems are usually zirconia–ceria (Zr–Ce) as promoters especially for noble metal dispersion [1] and alumina as a high surface area thermally stable promoter [2].

The study aims to improve the understanding of which one of these metal-oxide interactions, Pd-promoter, Pd–alumina or both is the most favourable in promoting NO reduction reactions. Cordatos and Gorte [3] found that Pd–Ce interactions have an influence on the adsorption of NO but have a negligible effect on CO adsorption. A similar result was also presented by Ciuparu et al. [4], who also reported that the Pd–Ce interaction has an effect on the chemical state of palladium, and therefore the adsorption properties on palladium. For instance, Pd oxide is much less effective for NO decomposition than reduced Pd in the presence of CeO_2. However, Pd–Ce interaction has a negligible effect on the adsorption properties of CO [4]. Hu et al. [5] have shown in their XPS studies that ceria retards the reduction of Pd oxide through a Pd–Ce interaction, and furthermore, according to Holles et al. [6] ceria affects the NO + CO reaction by facilitating the dissociation of NO at the metal/promoter interface. Martínez-Arias et al. [7] proposed that NO conversion is enhanced during the light-off due to oxygen vacancies created after the reduction of the promoter in the proximity of palladium, which can act as promoting sites for NO reduction. In addition, they have

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reported that Pd dispersion as well as Pd–alumina interaction have a greater influence on the NO reduction reaction than on the CO oxidation reaction [8]. In our previous study [9] based on light-off temperatures, NO reduction and CO oxidation reactions were enhanced more over the preoxidised Pd/(OSC + Al_2O_3) catalyst than over the preoxidised Pd/Al_2O_3 catalyst. We concluded that the OSC material provides oxygen to Pd for the oxidation reactions, while reduced sites provide adsorption sites for NO.

The goal of this work was to study the Pd–OSC–Al_2O_3-based catalysts, in order to understand the effect of the Pd addition method on the alumina or on the OSC material ($Ce_xZr_{1-x}O_2$ mixed oxides) in NO reduction and CO oxidation reactions. In addition, the effect of aging on the light-off performance of preoxidised Pd/(OSC + Al_2O_3) and (Pd + OSC)/Al_2O_3 catalysts during the CO + NO and CO + NO + O_2 reactions is determined.

2. Experimental

Metallic monoliths, Pd/(OSC + Al_2O_3) and (Pd + OSC)/Al_2O_3, were used to study NO reduction and CO oxidation in CO + NO and CO + NO + O_2 mixtures. The main difference between the catalysts was that in the case of (Pd + OSC)/Al_2O_3 catalyst Pd was preimpregnated to the OSC material. The powder was dried overnight at 100 °C and calcined in air at 550 °C for 3 h. After that the Pd/OSC-powder was mixed together with an Al_2O_3-slurry. Finally, the catalyst was calcined at 550 °C for 4 h. In the case of Pd/(OSC + Al_2O_3) catalyst, Pd was added to the washcoat slurry in the final stage and the catalyst was calcined as previously.

Two different catalyst types, fresh and aged, were employed. Aging of the catalyst sample was performed by treating the fresh sample under cyclic rich and lean conditions simultaneously with the temperature changes from 925 to 1040 °C [10]. For the determination of the palladium metal dispersion, CO chemisorption measurements were carried out at room temperature by the volumetric adsorption method using a sorptometer (Carlo Erba Sorptomatic 1990). Specific surface areas were determined by physical adsorption of N_2 at the liquid nitrogen temperature using a Coulter Omnisorp 360 CX. The chemical composition, BET surface area, and CO chemisorption results of the fresh and aged catalysts are given in Table 1. A dynamic OSC technique was used to study the oxygen storage capacity by changing CO and O_2 from 2 to 5 s at 400 °C. FT-IR (Gasmet™ FT-IR Gas Analyser) was used to analyse reaction gas compounds: CO, CO_2, NO, N_2O, and NO_2. The nitrogen balance, $N_{bal} = NO_{inlet} - NO_{outlet} - NO_{2\ outlet} - 2N_2O_{outlet}$, was calculated [11]. A paramagnetic oxygen analyser (ABB Advanced Optima) was used to determine the oxygen content.

Prior to each experiment the catalyst was pretreated with oxygen. The catalyst chamber was heated in a nitrogen flow from room temperature to 500 °C with a heating rate of 10 °C/min. The catalyst was oxidised at 500 °C (50 ml/min air) for 20 min. Then, the catalyst was cooled down to room temperature under an air flow. The reaction chamber was rinsed with a nitrogen flow for a few minutes [9].

Table 1
Chemical composition, BET surface areas, and CO chemisorption results of the fresh and aged Pd/(OSC + Al_2O_3) and (Pd + OSC)/Al_2O_3 catalysts

	Pd/ (OSC + Al_2O_3)		(Pd + OSC)/ Al_2O_3[a]	
	Fresh	Aged	Fresh	Aged
Pd content (%)	1	1	1	1
OSC[b] content (%)	20	20	20	20
BET surface area (m^2/g)	154	61	128	50
Particle size of Pd (nm)	3	>100	5	>125
Dispersion value (%)	35[c]	<2	25[c]	<2

[a] In the case of (Pd + OSC)/Al_2O_3 catalyst, Pd and OSC material were mixed and added together.

[b] $Ce_xZr_{1-x}O_2$ mixed oxides were used as OSC.

[c] The CO dispersion values for the fresh studied catalysts are probably too high, because CO can also adsorb on ceria.

The redox characteristics of the gas mixture were identified by the stoichiometric number, S (oxidising–reducing components ratio), calculated from Eq. (1) [12]:

$$S = \frac{2[O_2] + [NO]}{[CO]} \tag{1}$$

The reaction chamber was rinsed with the reaction gas mixture for 5 min at room temperature before increasing temperature up to 500 °C with the linear heating rate of 10 °C/min [9]. In the feed gas mixture, the following constant concentrations were used: 1 vol.% CO, 0.09 vol.% NO, and 0.86 vol.% O_2. Nitrogen was used as an inert carrier gas, balancing the total flowrate at 1 dm^3/min corresponding to GHSV of 43 000 h^{-1}.

3. Results

3.1. $CO + NO \rightarrow CO + N_2O + N_2$

Based on Eq. (1), the CO + NO reaction occurred in rich conditions ($S = 0.09$). The main results of the light-off tests for the CO + NO reaction for both fresh and aged catalysts can be seen in Fig. 1, where the conversion curves of NO and CO as well as the concentration curves of N_2O and N_2 are presented. For fresh catalysts, the Pd addition method has only a slight effect on the light-off temperature of NO (see Table 2). As can be seen in Fig. 1, the formation of N_2O increases up to a maximum, roughly following the initial NO conversion profile, and then decreases, while the fresh catalysts become fully selective to N_2 formation. For both fresh catalysts, N_2 selectivity was 100% at 500 °C. Over the fresh (Pd + OSC)/Al_2O_3 catalyst the maximum amount of N_2O formed was higher than over the Pd/(OSC + Al_2O_3) catalyst. The CO conversion curve decreased for the fresh

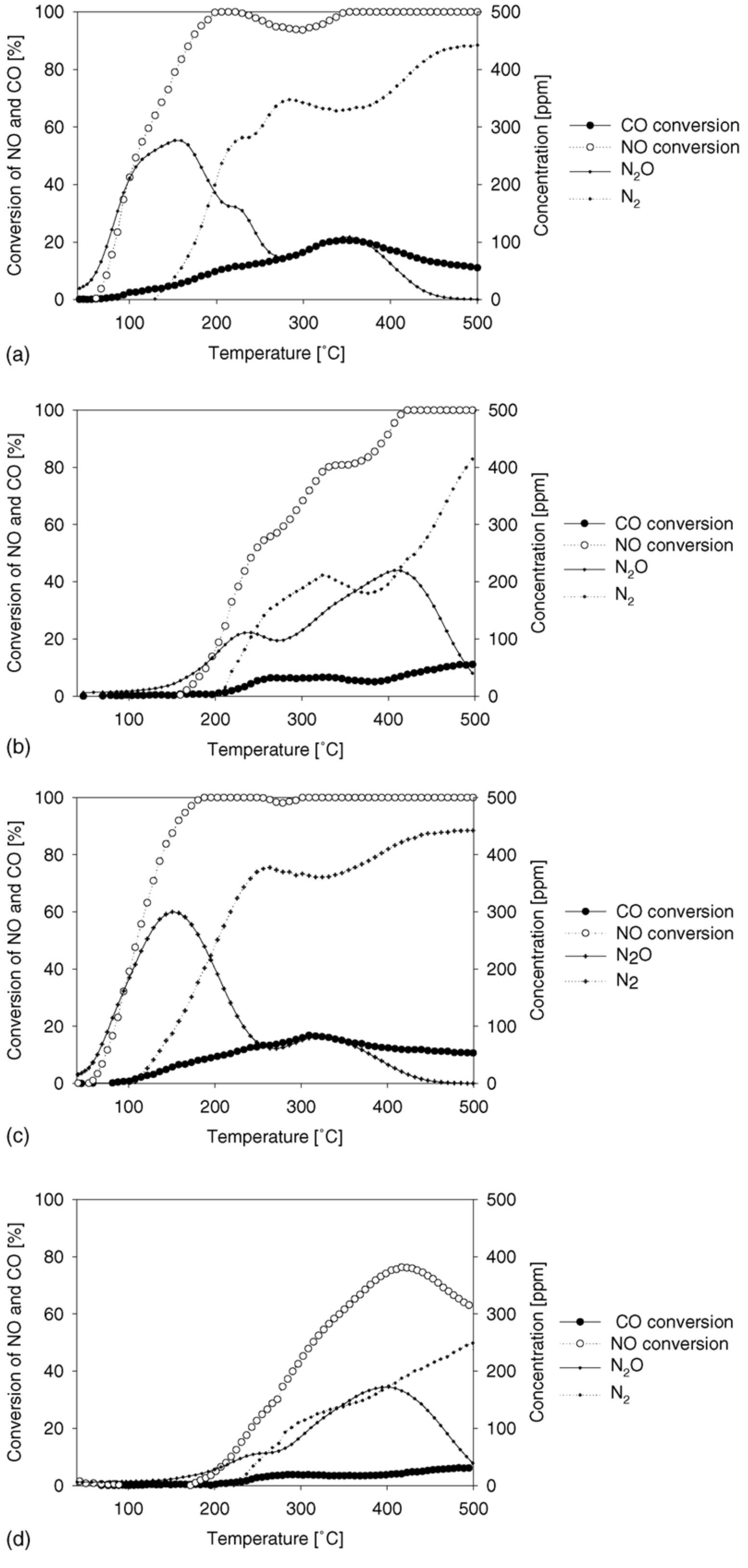

Fig. 1. NO and CO conversion (on the left) and N_2 and N_2O concentration (on the right) curves as a function of temperature for (a) fresh and (b) aged Pd/(OSC + Al_2O_3) catalysts and for (c) fresh and (d) aged (Pd + OSC)/Al_2O_3 catalysts during the CO + NO reaction.

Table 2
The light-off temperatures[a] of NO and CO in the studied reactions for the fresh and aged Pd/(OSC + Al_2O_3) and (Pd + OSC)/Al_2O_3 catalysts

	Pd/(OSC + Al_2O_3)				(Pd + OSC)/Al_2O_3			
	Fresh		Aged		Fresh		Aged	
	CO	NO	CO	NO	CO	NO	CO	NO
CO + NO	n.d.	108	n.d.	243	n.d.	110	n.d.	315
CO + NO + O_2	123	n.d.	208	n.d.	142	n.d.	227	n.d.

n.d.: not detected, because no light-off occurred.

[a] A temperature of 50% conversion of CO and NO.

catalyst at around 350 °C probably due to the oxidised state of Pd caused by NO adsorption and dissociation reactions. The PdO state decreases the activity of CO oxidation [7,13]. Pd particles, which are in close contact with alumina are readily reduced [7,13], which might explain why CO was oxidised better over the Pd/(OSC + Al_2O_3) catalyst.

As can be seen in Fig. 1, a significant decrease in catalytic activity is observed after the agings both in CO oxidation and NO reduction reactions. The aged Pd/(OSC + Al_2O_3) catalyst had a much lower light-off temperature than the aged (Pd + OSC)/Al_2O_3 catalyst (see Table 2). At 500 °C, N_2 selectivities were 92% and 86%, respectively. N_2O and N_2 concentration curves behaved the same way as for the fresh catalysts. The maximum amount of N_2O formed was higher over the aged Pd/(OSC + Al_2O_3) catalyst than over the (Pd + OSC)/Al_2O_3 catalyst, and, in both cases, lower than for the fresh catalyst. As shown in Fig. 1, the maximum conversion of CO was lower over the (Pd + OSC)/Al_2O_3 catalyst than over the Pd/(OSC + Al_2O_3) catalyst. At higher temperatures the conversion of CO increases, whereas for a fresh catalyst it decreased.

In all cases, the formation of CO_2 was observed in the beginning of the measurement. This is a result of direct reaction of CO with oxygen originating from the oxygen storage material [3]. The maximum amount of CO_2 formed was finally at higher temperatures equal for all the studied catalysts. Vacant sites for NO adsorption are formed as a result of the reduction of ceria by oxygen transfers, and NO decomposes readily on reduced ceria [3]. A dynamic OSC technique allows the detection of the oxygen available for redox processes on a time scale of seconds [1]. The fresh catalysts have almost the same oxygen storage capacity at 400 °C. For aged catalysts, the Pd/(OSC + Al_2O_3) catalyst stored oxygen better than the (Pd + OSC)/Al_2O_3 catalyst. This can be due to the Pd particle size (see Table 1), which is an important parameter under dynamic conditions [14]. In general, for the aged catalysts the reactions are slower at low temperatures than at high temperatures.

3.2. $CO + NO + O_2 \rightarrow CO_2 + NO_2 + N_2O$

CO + NO + O_2 reaction was studied in lean conditions ($S = 1.81$). The main results are presented in Fig. 2, where the light-off curves of NO and CO as well as the concentration curves of NO_2 and N_2O are presented for fresh and aged catalysts. The formation of N_2 was not observed, which can be explained by the lack of adjacent vacant sites for NO dissociation. As can be seen in Fig. 2, the formation of N_2O behaved the same way as presented in Section 3.1. The formation of NO_2 started at around the same temperatures where CO reached its maximum conversion for all other cases except for the aged (Pd + OSC)/Al_2O_3 catalyst (see Fig. 2d).

For both fresh catalysts the maximum amount of N_2O formed was the same. Over the Pd/(OSC + Al_2O_3) catalyst, the formation of NO_2 was slightly more pronounced than over the (Pd + OSC)/Al_2O_3 catalyst. As can be seen in Fig. 2, a significant decrease in catalytic activity was observed after the agings in NO reduction reactions. Over the aged catalysts the formation of N_2O was around 50% lower than over the fresh catalysts. On the aged (Pd + OSC)/Al_2O_3 catalyst the formation of N_2O was almost 50% smaller than on the aged Pd/(OSC + Al_2O_3) catalyst. On the aged (Pd + OSC)/Al_2O_3 catalyst the amount of formed NO_2 was much smaller than on the aged Pd/(OSC + Al_2O_3) catalyst. Therefore, over the Pd/(OSC + Al_2O_3) catalyst NO reacted more probably to N_2O and NO_2 than over the (Pd + OSC)/Al_2O_3 catalyst regardless the catalyst being fresh or aged (see Fig. 2).

CO reacts with O_2 rather than with NO. As can be seen in Table 2, the light-off temperature of CO was about 20 °C lower for the fresh and aged Pd/(OSC + Al_2O_3) catalyst than for the (Pd + OSC)/Al_2O_3 catalyst. As expected, for the aged catalysts the light-off temperature of CO shifted to the higher temperatures. CO oxidation over the aged (Pd + OSC)/Al_2O_3 (see in Fig. 2d, at 225 °C), in contrast to other catalysts, appears to proceed in two different steps. Below 225 °C the CO conversion increased relatively rapidly and then it slowly increased upon increasing temperature. Martínez-Arias et al. [15] have presented dissimilar activity results for the aged Pd/(Ce,Zr)/Al_2O_3 catalyst. They concluded that as a consequence of the sintering of both Pd and Ce–Zr mixed oxides the number of active sites decreased and caused a high CO coverage on the surface.

More oxygen was consumed over the fresh Pd/(OSC + Al_2O_3) catalyst than over the fresh (Pd + OSC)/Al_2O_3 catalyst. The same kind of behaviour was also observed for the aged catalysts. The formation of CO_2 behaved in the same way as presented in Section 3.1.

4. Discussion

Palladium is assumed to be present initially in an oxidised form for both catalysts, as a result of oxidising pretreatment that was applied to the samples. In order to fully ensure the chemical state of Pd before the measurements, XPS measurements would have been needed.

The chemical state of the catalyst will change during the conversion measurement which is due to NO and CO

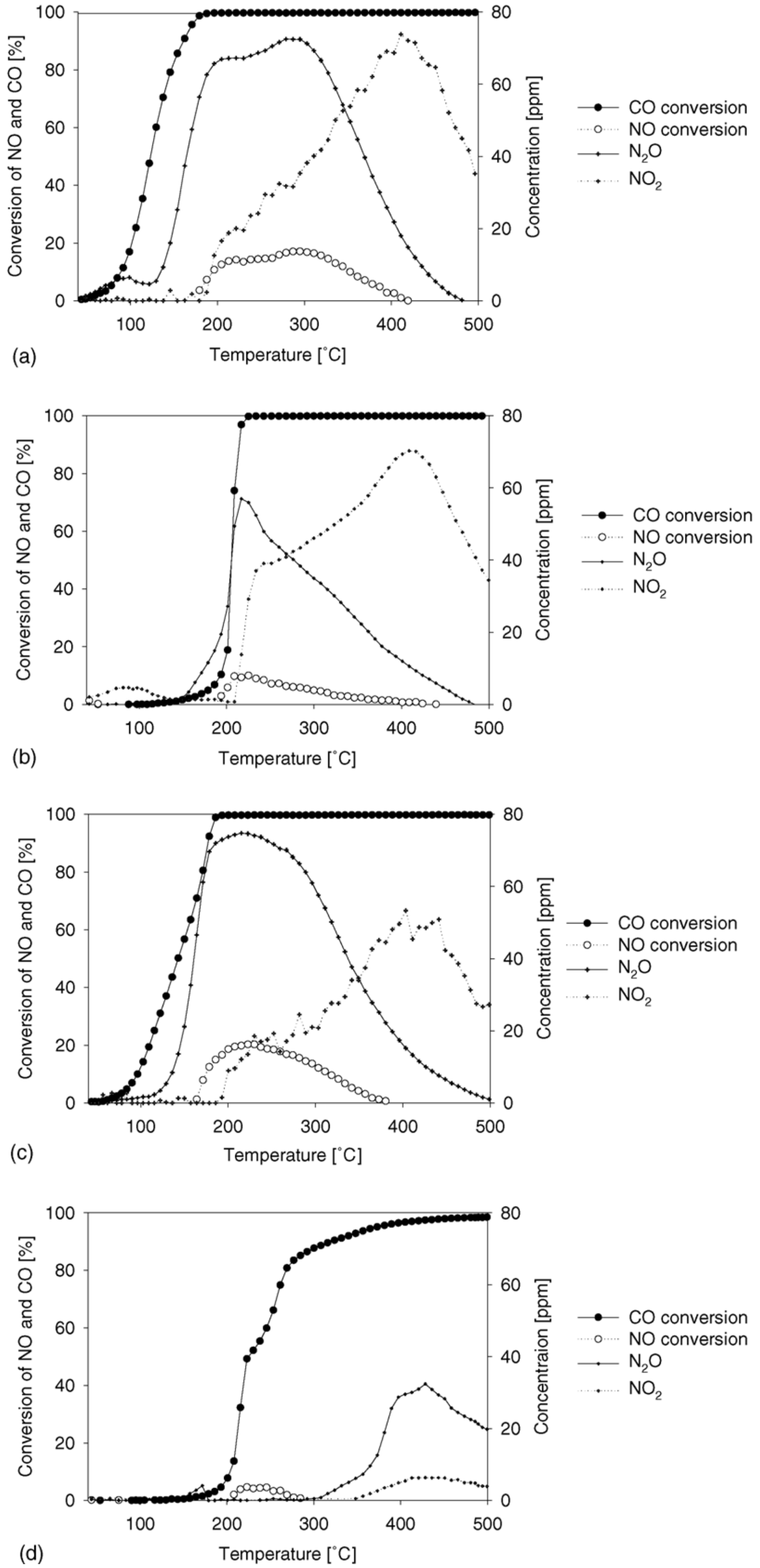

Fig. 2. NO and CO conversion (on the left) and NO_2 and N_2O concentration (on the right) curves as a function of temperature for (a) fresh and (b) aged Pd/(OSC + Al_2O_3) catalysts and for (c) fresh and (d) aged (Pd + OSC)/Al_2O_3 catalysts during the CO + NO + O_2 reaction.

adsorption as well as NO dissociation reactions on the catalyst. This effect could be due to the fact that ceria has a strong metal support interaction (SMSI) with Pd, which could also affect the chemical state by promoting bulk and surface reduction with enhanced reactivity towards CO and NO [16]. In this paper, two fresh and aged catalysts were compared by activity measurements. The difference of these catalysts was mainly how Pd and OSC material were added into the catalyst.

In Pd–OSC-based catalysts, the most active sites involve interactions between Pd and Ce–Zr mixed oxides [1,2]. In both studied reactions, NO dissociates over both fresh catalysts, because the formation of N_2O and N_2 or NO_2 as reaction products was observed. The formation of N_2O or NO_2 was higher when Pd was added during the preparation of the catalyst on the OSC material than when Pd was added on OSC/Al_2O_3. Therefore, over the former catalyst the Pd–Ce interaction with oxygen vacancies was stronger than over the latter catalyst. Upon aging, the amount of active sites on the surface decreased more on the $(Pd + OSC)/Al_2O_3$ catalyst than on the $Pd/(OSC + Al_2O_3)$ catalyst which explains much lower NO and CO activities on the $(Pd + OSC)/Al_2O_3$ catalyst compared to the $Pd/(OSC + Al_2O_3)$ catalyst (see Fig. 1b and d).

Because the amount of CO was much higher compared to the amount of NO, during the NO + CO reaction, all NO was reduced. Therefore, alumina supported PdO particles can be reduced by CO at room temperature [4]. CO adsorbs more strongly on metallic palladium than on Pd oxide. High surface coverage of CO consumed active surface. Over the fresh $Pd/(OSC + Al_2O_3)$ catalyst the CO conversion was higher than over the fresh $(Pd + OSC)/Al_2O_3$ catalyst. Therefore, the OSC material in the $(Pd + OSC)/Al_2O_3$ catalyst keeps Pd in an oxidised state.

Martínez-Arias et al. [8] reported in their catalytic activity tests over $PdO/\gamma\text{-}Al_2O_3$ catalysts that Pd loading has an effect on the NO reduction reaction. They deduced from their results that NO dissociation is most favoured over the large Pd particles. As was mentioned above, for the two reactions studied, NO reduction was more effective over the fresh $(Pd + OSC)/Al_2O_3$ catalyst than over the fresh $Pd/(OSC + Al_2O_3)$ catalyst. In the former catalyst, the particle size as fresh was somewhat larger than for the latter catalyst (see Table 1). As can be seen in Table 1, the Pd particle size increased during the aging process as a consequence of sintering of Pd and Ce–Zr mixed oxides [1,15]. Sintering explains the lower catalytic activity by decreasing the number of such active sites on the aged catalysts. On the other hand, our aging procedure was done at quite high temperatures, which also changes the BET surface areas (see Table 1) and possibly also the chemical state of palladium [17]. This kind of thermal deactivation of the catalysts is due to the collapse of surface area, sintering of Pd particles and phase transitions observed in the bulk material [17]. For the aged catalysts, oxygen consumption in $CO + NO + O_2$ reaction was higher than over the fresh ones. This effect is due to the loss of active sites on the surface by thermal deactivation.

5. Conclusions

In this paper, it is shown that in the case of fresh catalysts, NO adsorption and dissociation reactions during the $CO + NO + O_2$ reaction occur at lower temperatures when Pd was added into the OSC material than into the alumina and OSC material mixture. The effect is due to a strong Pd–OSC interaction, during which the oxygen vacancies are formed for further reactions. However, upon aging the number of active sites decreased due to the thermal deactivation, which is caused by sintering of the Pd particles. The size of Pd particles affected also the oxygen storage capacity, in particular at low temperatures.

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