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Influence of BaO on Pd/Al_2O_3-based catalysts in C_2H_4 and CO oxidation as well as in NO reduction

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Abstract

In this study, Pd/Al_2O_3 and Pd/BaO/Al_2O_3 metallic monoliths were used to investigate the effect of BaO in C_2H_4 and CO oxidation as well as in NO reduction. A FT-IR gas analyser was used to study the activity of the catalysts. Several activity experiments carried out with dissimilar feedstreams revealed that BaO enhances CO and C_2H_4 oxidation as well as NO reduction reactions in rich conditions. This effect is due to BaO, which causes a decrease in the ethene poisoning of palladium. In lean conditions BaO is present in the form of $Ba(OH)_2$ which reacts with oxidised NO releasing water. Therefore, NO was stored during the lean reaction.

Keywords: Barium oxide (BaO); Carbon monoxide; Ethene; Nitrogen oxides; Palladium

1. Introduction

Automotive exhaust gases contain harmful oxidation and reduction products such as carbon monoxide (CO), nitrogen oxides (NO_x), and unburned hydrocarbons (HCs). Under lean operating conditions, conventional three-way catalysts (TWCs) are not efficient enough to clean NO_x from exhaust gas streams. The removal of NO_x from the exhaust gas is significant because nitrogen oxides are suspected to cause many health and environmental problems [1]. Moreover, the legislation concerning emission control is increasingly stringent, and therefore, it is necessary to discover new improvements to the performance of the catalysts to remove all the pollutants present in the exhaust gases.

Promoters are used to improve the properties of a catalyst such as activity, selectivity, and stability. Recently, barium oxides (BaO) are studied as a NO_x storage material [2–8]. The NO_x storage reduction (NSR) concept is based on lean operating and short rich operating cycles in the engine [2]. During the lean period, NO_x is oxidised over a noble metal catalyst and then stored on a storage compound (such as on BaO, $BaCO_3$ or $Ba(OH)_2$) as nitrite and nitrate compounds ($Ba(NO_2)_2$ and $Ba(NO_3)_2$) [3]. During the short rich period, these compounds are released and diffused on noble metal sites and reduced to N_2. The NO_x storage capacity is enhanced with the increasing alkalinity of the element. The problem of a strong alkaline catalyst is that the conversion of hydrocarbons is reduced [4]. Under the lean conditions, it has been shown that NO_2 has a crucial role in the storage of NO_x [9]. The oxidation of NO is higher on Pt-containing catalysts than on Pd-based catalysts [9]. However, Pd catalysts have significant catalytic properties, such as a high three-way catalytic activity and an excellent light-off characteristic [10].

The aim of this investigation was to study the role of BaO in CO and C_2H_4 oxidation as well as in NO reduction reactions over Pd/Al_2O_3 containing catalysts. The research was carried out by performing activity experiments in a fixed-bed catalytic reactor by using several model reactions. The catalytic activities of the Pd/Al_2O_3 and Pd/BaO/Al_2O_3 catalysts were measured and compared.

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2. Experimental

Metallic monoliths, Pd/Al_2O_3 and $Pd/BaO/Al_2O_3$, were used to study the NO reduction as well as CO and C_2H_4 oxidation. The amount of Pd in the washcoat was 1 wt.% in both cases. The BaO content in the washcoat was 2 wt.%. The FT-IR (Gasmet^{TM} FT-IR Gas Analyser) was used to analyse the gaseous compounds: C_2H_4, H_2O, CO, CO_2, NH_3, NO, N_2O, and NO_2. The nitrogen balance was calculated as follows: $N_{bal} = NO_{inlet} - NO_{outlet} - NO_{2\ outlet} - 2N_2O_{outlet}$ [5]. Oxygen concentration was determined by using a paramagnetic oxygen analyser (ABB Advance Optima). 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). The dispersion values were 18% and 12% for the Pd/Al_2O_3 and $Pd/BaO/Al_2O_3$ catalysts, respectively. The Pd particle size was estimated to be about 6 and 10 nm for the Pd/Al_2O_3 and $Pd/BaO/Al_2O_3$ catalysts, respectively.

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 (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.

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 [11].

Four model reactions ($C_2H_4 + NO$, $C_2H_4 + NO + O_2$, $CO + C_2H_4 + NO$ and $CO + C_2H_4 + NO + O_2$) were studied. The redox characteristics of the gas mixture were identified by the stoichiometric number, S (oxidising–reducing components ratio), calculated using Eq. (1).

$$S = \frac{[O_2] + [NO]}{[CO] + 3[C_2H_4]} \tag{1}$$

In the feed gas mixture, the following constant concentrations were used: 0.05 vol.% C_2H_4, 0.09 vol.% NO, and 1 vol.% CO. 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. $C_2H_4 + NO \rightarrow CO_2 + CO + NH_3 + N_2O + N_2$

Based on Eq. (1), the $C_2H_4 + NO$ reaction occurred under rich conditions ($S = 0.60$). The light-off temperatures of C_2H_4 and NO were lower for the $Pd/BaO/Al_2O_3$ catalyst than for the Pd/Al_2O_3 catalyst (see Table 1). However, the final conversion of C_2H_4 reached the values of 82% and 88%, respectively. For both catalysts the final conversions of NO_x reached the value of 98%. A decrease in NO and C_2H_4 light-off curves was observed over the Pd/Al_2O_3 and $Pd/BaO/Al_2O_3$ catalysts at around 250 °C (see Figs. 1a and 2a). The yields of CO, N_2O, N_2 and CO_2 also decreased at the same temperatures (Figs. 1a and 2a). The formation of NH_3, which started at around 270 °C, indicates with the formation of CO that C_2H_4 adsorbs and dehydrogenates on the catalyst surface. The limiting availability of oxygen explains the formation of NH_3 and CO. The oxygen which is formed as a result of NO dissociation is mostly consumed during the C_2H_4 oxidation to CO and CO_2, while a part of nitrogen reacts with hydrogen to form NH_3. Over the $Pd/BaO/Al_2O_3$ catalyst the maximum amounts of NH_3, N_2O and CO_2, were higher but the maximum amounts of CO and N_2 were lower than over the Pd/Al_2O_3 catalyst. The higher amount of N_2O over the $Pd/BaO/Al_2O_3$ catalyst compared to that over the Pd/Al_2O_3 catalyst is consistent with the results of Lietti et al. [3] who explained that the reduction of $Ba(NO_2)_2$ and $Ba(NO_3)_2$ species by hydrogen leads to the formation of N_2O and BaO. According to them, water is also formed in the reduction but it is adsorbed onto the Ba sites in the form of $Ba(OH)_2$. This may also explain why the formation of water was not observed in our measurements, and therefore, e.g. in situ DRIFT and transient studies are needed.

Table 1
Light-off temperatures (T^{50}-values (°C))[a] for NO, CO and C_2H_4 in studied reactions over the Pd/Al_2O_3 and $Pd/BaO/Al_2O_3$ catalysts

Catalysts	Pd/Al_2O_3			$Pd/BaO/Al_2O_3$		
	C_2H_4	NO	CO	C_2H_4	NO	CO
$C_2H_4 + NO$	409	335	–	385	331	–
$C_2H_4 + NO + O_2$	272	n.d.	–	273	n.d.	–
$C_2H_4 + NO + CO$	430	375	n.d.	438	357	n.d
$CO + C_2H_4 + NO + O_2$	217	n.d.	214	191	n.d.	188

In the feed gas mixture, the following constant concentrations were used: 0.05 vol.% C_2H_4, 0.09 vol.% NO, and 1 vol.% CO. n.d. = not detected, because no light-off occurred.

[a] Defined as a temperature of 50% conversion of C_2H_4, NO, and CO.

3.2. $C_2H_4 + NO + O_2 \rightarrow CO_2 + CO + H_2O + N_2O + NO_2 + N_2$

The $C_2H_4 + NO + O_2$ reactions were studied under lean conditions ($S = 6.33$). Figs. 1b and 2b present the $C_2H_4 + NO + O_2$ reaction on the Pd/Al_2O_3 catalyst and on the $Pd/BaO/Al_2O_3$ catalyst, respectively. There were no significant differences between the light-off temperatures of C_2H_4 for the studied catalysts (see Table 1). The maximum NO conversion was a bit lower over the $Pd/BaO/Al_2O_3$ catalyst (21%) than over the Pd/Al_2O_3 catalyst (23%). The amount of NO_2 formed was higher for the Pd/Al_2O_3 catalyst than for the $Pd/BaO/Al_2O_3$ catalysts, but the amounts of N_2O and N_2 were almost the same. Instead, the formation of water over the $Pd/BaO/Al_2O_3$ catalyst was higher than over the Pd/Al_2O_3 catalysts. The Pd/Al_2O_3 catalyst consumed more oxygen but formed equal amounts of CO_2 than the $Pd/BaO/Al_2O_3$ catalyst. Formation of CO was quite low (see Figs. 1b

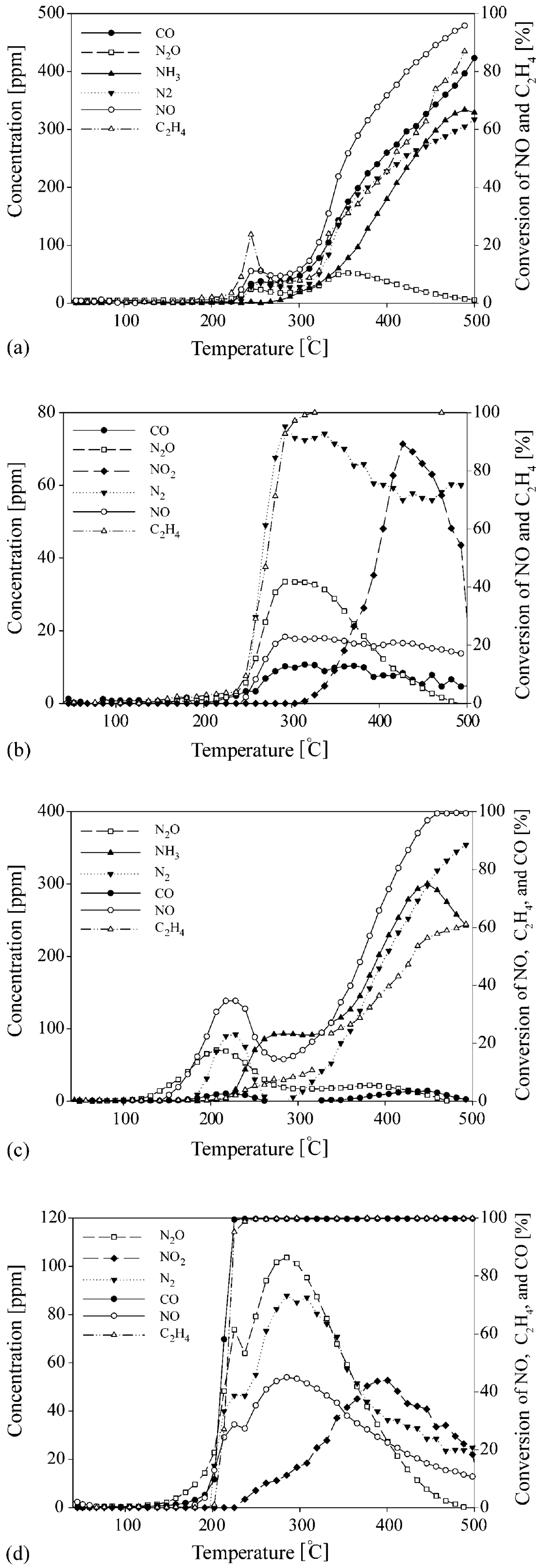

Fig. 1. The conversion curves of NO and C_2H_4 (on the right) and the concentration curves of CO, N_2O, NH_3 or NO_2, and N_2 (on the left) for (a) C_2H_4 + NO and (b) C_2H_4 + NO + O_2 reactions as well as the conversion curves of NO, C_2H_4, and CO (on the right) and the concentration curves of N_2O, NH_3 or NO_2, and N_2 (on the left) for (c) C_2H_4 + NO + CO and (d) C_2H_4 + NO + CO + O_2 reactions as a function of temperature over the Pd/Al_2O_3 catalyst.

and 2b), because surface oxygen was in excess of accessible carbon. The reason for the lower NO_2 formation in the case of $Pd/BaO/Al_2O_3$ catalyst is that during the lean operation conditions Ba is probably present in the form of $Ba(OH)_2$ and/or $BaCO_3$. NO is first oxidised over the noble metal, and the NO_2 formed reacts with $Ba(OH)_2$ or $BaCO_3$ to form nitrates [3]. $Ba(OH)_2$ is more probable than $BaCO_3$ in our case because the amount of CO_2 formed during the reaction was not so high.

3.3. $CO + C_2H_4 + NO \rightarrow CO_2 + NH_3 + N_2O + N_2$

The CO + C_2H_4 + NO reaction occurred in rich conditions ($S = 0.08$). As can be seen in Table 1, the light-off temperature of NO was ca. 20 °C lower over the $Pd/BaO/Al_2O_3$ catalyst than over the Pd/Al_2O_3 catalyst. Moreover, BaO enhances the CO conversion compared to the Pd/Al_2O_3 catalyst. This was observed as a higher maximum conversion of CO for the $Pd/BaO/Al_2O_3$ catalyst than for the Pd/Al_2O_3 catalyst. Instead, there were no significant differences between the light-off temperatures of C_2H_4 for the studied catalysts (see Table 1). The NO + CO reaction was the prevailing one at low temperatures, because the light-off of CO and NO started at around 160 °C for both catalysts (Figs. 1c and 2c). C_2H_4 started to react at 200 °C and reached finally a 60% conversion. Both catalysts had maximum conversion for NO and CO at 225 °C. At the same temperatures, the amounts of N_2O, N_2 and CO_2 had maxima. The formation of NH_3 started at 220 °C. The formation of CO_2 and N_2O started to decrease in the same temperature range, where C_2H_4 started to react and the formation of NH_3 was observed. At 250 °C, the conversions of CO and NO started to decrease and the amounts of N_2, CO_2, and N_2O decreased. Instead, the formation of NH_3 at these temperatures was more enhanced than the formation of the other products. The formation of NH_3 occurred similarly in the case of C_2H_4 + NO (Section 3.1). Over the $Pd/BaO/Al_2O_3$ catalyst the maximum amounts of NH_3 and N_2O were higher, but the maximum amount of N_2 was lower than over the Pd/Al_2O_3 catalyst. The same kind of effect for N_2O was observed also in the case of the C_2H_4 + NO reaction (see Section 3.1). Equal amount of CO_2 was formed for both catalysts. If the light-off temperatures of NO and C_2H_4 are compared in the C_2H_4 + NO and CO + C_2H_4 + NO reactions (see Table 1), it can be concluded that the presence of CO in the gas mixture increases the competition of the same adsorption and dissociation sites. This was observed as higher light-off temperatures of C_2H_4 and NO during the CO + C_2H_4 + NO reaction.

3.4. $CO + C_2H_4 + NO + O_2 \rightarrow CO_2 + H_2O + N_2O + NO_2 + N_2$

The CO + C_2H_4 + NO + O_2 reaction was carried out in rich conditions ($S = 0.83$). Figs. 1d and 2b present the results over Pd/Al_2O_3 and $Pd/BaO/Al_2O_3$ catalysts, respectively.

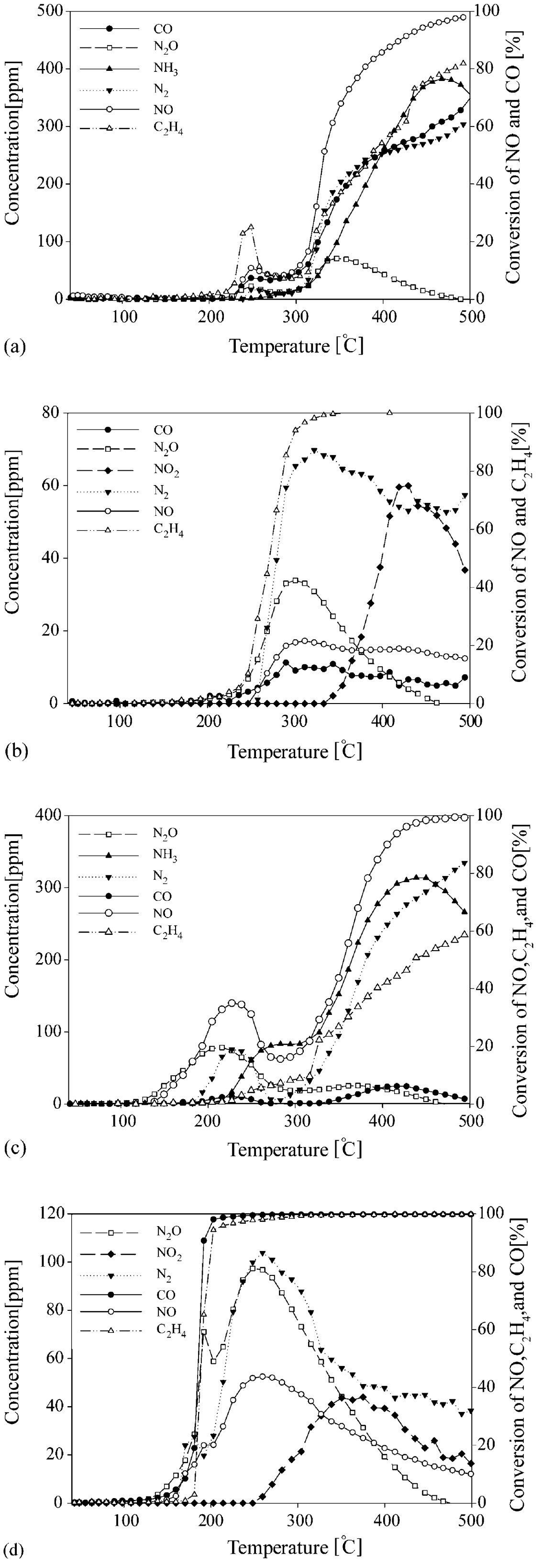

Fig. 2. The conversion curves of NO and C_2H_4 (on the right) and the concentration curves of CO, N_2O, NH_3 or NO_2, and N_2 (on the left) for (a) $C_2H_4 + NO$ and (b) $C_2H_4 + NO + O_2$ reactions as well as the conversion curves of NO, C_2H_4, and CO (on the right) and the concentration curves of N_2O, NH_3 or NO_2, and N_2 (on the left) for (c) $C_2H_4 + NO + CO$ and (d) $C_2H_4 + NO + CO + O_2$ reactions as a function of temperature over the $Pd/BaO/Al_2O_3$ catalyst.

The light-off temperatures of C_2H_4 and CO were lower for the $Pd/BaO/Al_2O_3$ catalyst than for the Pd/Al_2O_3 catalyst (see Table 1). However, the maximum conversion of NO (45%) was the same for both catalysts. The amount of NO_2 formed over the $Pd/BaO/Al_2O_3$ catalyst was only one half of the amount of NO_2 over the Pd/Al_2O_3, and almost the same amounts of N_2 and N_2O were formed over both catalysts. This observation is the same as in the case of the $C_2H_4 + NO + O_2$ reaction (see Section 3.2). The presence of BaO in the washcoat decreases the oxygen consumption. The amount of CO_2 formed over both catalysts was equal. However, more water was formed over the $Pd/BaO/Al_2O_3$ catalyst than over the Pd/Al_2O_3 catalyst.

4. Discussion

The removal of nitrogen oxides from exhaust gases is a major goal when designing new catalytic materials for lean-burn applications. For this reason, attention has been paid to study N-containing compounds such as NO, NO_2, N_2O, and N_2. In oxygen rich reactions (lean) formation of the NH_3 was not observed, because the reducing agent (C_2H_4) was completely oxidised. In addition, no formation of CO was observed in the $C_2H_4 + O_2$ reactions, as expected, because there was enough oxygen available on the surface for total oxidation. Based on Table 1, where the light-off temperatures (T^{50}-values) of C_2H_4, NO, and CO are presented, it can be concluded that the reducing agents react rather with oxygen than with NO. Thus, there is a lack of reductants for the NO reactions. In addition, at low temperatures (<200 °C), CO was a more effective reductant than ethene. This effect can be seen by comparing the results presented in Figs. 1 and 2. NO reduction by propene over the Pd/Al_2O_3 catalyst goes via intermediates like NCO, acetates, formates and nitrates [12]. According to Fridell et al. [6], BaO enhances HC oxidation by causing a decrease in the propene (or propene derived species) poisoning of platinum. This effect explains the lower light-off temperatures of C_2H_4 for the $Pd/BaO/Al_2O_3$ catalyst than for the Pd/Al_2O_3 catalyst.

NO_2 is a very significant compound in several NO_x removal techniques, such as in NO_x traps. In our case NO_2 was formed in reactions, where oxygen is a reactant. Formation of NO_2 occurs either via $NO + O^* \rightarrow NO_2 + {}^*$ (Eley–Ridel) or via $NO^* + O^* \rightarrow NO_2{}^* + {}^*$ (Langmuir–Hinselwood) mechanisms. Both mechanisms can occur at the same time. However, the latter mechanism is more common than the former one [2]. Important steps in NO oxidation are the adsorption and desorption of oxygen. Therefore, the detection of NO_2 is a sign of Pd–O and Pd–O_2 species on the surface [13]. The formation of Pd–O and Pd–O_2 species seems to be dependent on the acidity/alkalinity of the support material [7]. Large amounts of these species can deactivate the surface of the catalyst in NO oxidation and NO_2 dissociation reactions. However, the participation of active oxygen species in NO_x storage reactions is significant [3]. The role of Al_2O_3 as an acidic support material is also significant. Al_2O_3 receives electrons from palladium, and thus the electron density in Pd decreases. During the oxidation palladium donates electrons to oxygen. When BaO, which is a more alkaline compound than alumina, is added to the Pd/Al_2O_3 catalyst, it favours the oxidation of palladium [4].

BaO-containing catalysts consumed less oxygen from the feedstream than the Pd/Al_2O_3 catalyst, due to the oxidised form of barium (BaO) in all the cases. However, the maximum amount of water formation was high for the $Pd/BaO/Al_2O_3$ catalyst. This effect may be caused by the formation of $BaCO_3$ and $Ba(OH)_2$ adsorption sites on the oxidised surface during the reaction [14]. The fresh, calcined catalyst contains $BaCO_3$, which in a dry environment leads to the formation of BaO. The presence of hydrogen leads to the formation of $Ba(OH)_2$. It has been reported by Lietti et al. [3] that NO_x storage occurs first at BaO, then at $Ba(OH)_2$, and finally at $BaCO_3$. However, during the NO_x storing process to nitrates or nitrites over the last two mentioned adsorption sites it is accompanied by the release of CO_2 and H_2O. The displacement of surface carbonate species by NO_x is likely due to the lower acidity of CO_2 than NO_x species [8].

5. Conclusions

BaO promotes the C_2H_4 and CO oxidation reactions in rich conditions via the formation of $Ba(OH)_2$ species. In lean conditions, BaO enhances the formation of water, because NO is stored on $Ba(OH)_2$. In order to fully understand the surface phenomena and NO_x storage over these catalysts, e.g. in situ DRIFT and transient studies are needed.

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