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Effect of carbon black combustion on NO_x trap catalyst performances

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ABSTRACT

The effect of carbon–NSR catalyst contact on the ability of the catalyst to store NO_x is investigated. The catalysts used are model catalysts composed of Pt and/or Ba supported on Al_2O_3 (2%Pt/γ-Al_2O_3, 20%BaO/γ-Al_2O_3 and 2%Pt–20%BaO/γ-Al_2O_3). It is shown that the presence of carbon black in the catalytic bed involves a decrease of the NO_x storage capacity (NSC) of the catalysts. Participation of a direct reaction between carbon particles and NO_x storage sites to form carbonate adsorbed species is proposed. However, the loss of NSC measured in the presence of carbon varies as a function of the catalyst composition. It is shown that the presence of platinum limits the influence of carbon–catalyst contact. The influence of the proximity between the storage sites, Pt sites and their contact with carbon is discussed.

1. Introduction

The diesel engines are considered as one of the main source of soot and NO_x emissions. As these pollutants have adverse effects on the environment and human health, their emissions standards have become increasingly stringent over the last decade. Therefore, treatment techniques for the exhaust gases were developed.

In order to control soot emissions, technologies like Diesel Particulate Filter (DPF) [1,2] and Continuously Regeneration Trap (CRT) [3,4] are used. To reduce NO_x emission in an oxygen-rich environment, Selective Catalytic Reduction (SCR) or NO_x Storage Reduction (NSR) technologies [5–8] were developed. However, in order to decrease the size of the aftertreatment devices assembled along the exhaust line and the back pressure induced, '4 way catalytic converters' were recently developed [9,10]. In these systems, soot treatment, NO_x reduction and CO and hydrocarbons oxidation functions are coupled on a single monolith. The first commercialized '4 way catalytic converters' was developed by Toyota [9,10] known as Diesel Particulate NO_x Reduction (DPNR). This system is composed of a particulate wall-flow filter coated with a NSR catalyst layer and works under cyclic conditions, as a NSR catalyst. Particulate filter regeneration is supposed to be effective during the lean phase, due to the presence of NO_x and the excess of oxygen in the exhaust gas, similarly to that occurring in the CRT technology (soot combustion by direct and cooperative reactions [11–17]). It is also claimed that soot oxidation occurs during the rich phase [9].

As it is expected that combination of the NSR and CRT technologies modifies their behavior, recent studies investigated the reaction mechanism of 4 way catalytic materials [18–24]. Most of these investigations concluded that NO_x storage function enhances soot combustion either by decreasing soot oxidation temperature and/or by increasing locally NO_2 gas phase concentration [18–23]. On the other hand, several authors [11,22–24] observed that the NO_x storage capacity of the NSR catalyst is partially inhibited by the presence of soot. Artioli et al. [24], in a recent paper, proposed that the presence of soot has a destabilizing effect on the NO_x adsorbed species on a model Pt–Ba/Al_2O_3 catalyst due to the reaction between soot particles and the nitrate species which are mobile on the surface.

The aim of the present study is to investigate more precisely the effect of carbon–NSR catalyst contact on the ability of the catalyst to store NO_x. The catalysts used are model catalysts composed of Pt and/or BaO on Al_2O_3 (2%Pt/γ-Al_2O_3, 20%BaO/γ-Al_2O_3 and 2%Pt–20%BaO/γ-Al_2O_3). For this purpose, the activity of the materials toward NO_x storage was measured in a fixed bed reactor at 573 K in the presence and in the absence of carbon black in the catalytic bed.

2. Experimental

2.1. Catalyst preparation

The 2 wt%Pt/γ-Al_2O_3 (noted Pt/Al_2O_3) and 20 wt%BaO/γ-Al_2O_3 (noted Ba/Al_2O_3) catalysts were prepared by wet impregnation of alumina (Alfa Aesar, 220 $m^2\,g^{-1}$) with an aqueous solution of barium nitrate (Fluka, 99% purity) (70 g/L) or a solution of

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platinum (II) acetylacetonate (Alfa Aesar, Pt 48% min) (8.2 g/L in ethanol 4 vol./dichloromethane 1 vol.) respectively. The preparation of the 2%Pt–20%BaO/γ-Al_2O_3 (noted Pt–Ba/Al_2O_3) catalyst involve the impregnation of alumina with the barium nitrate solution then with the platinum acetylacetonate solution. After drying in air at 383 K during 14 h, the catalysts were calcined at 973 K for 2 h under 20%b.v. O_2 in N_2.

2.2. Reactivity tests

The catalytic activity of the different catalysts for NO_x adsorption and carbon oxidation was measured in a fixed bed quartz reactor (internal diameter 16 mm). The NO_x storage capacity of the materials was studied in the presence and in the absence of soot by performing isothermal NO_x adsorption/temperature programmed desorption (TPD) cycles. A commercial carbon black, Vulcan 6 from Cabot with a specific surface area equal to 106 $m^2\,g^{-1}$, was used in this study as a model for soot particles. The use of commercial soot for laboratory studies is favored as diesel soot contains soluble organic fraction (SOF) whose composition varies as a function of the origin of the soot and then influences its reactivity. In contrary, model soot can be obtained in large quantities with reproducible characteristics. Catalytic tests with pure catalyst were carried out on a sample of 1.2 g in the reactor. For the experiments performed in the presence of soot, 200 mg of carbon black was firstly crushed in a mortar for 10 min, in order to obtain particle with a diameter between 30 μm and 50 μm. These carbon black particles are then physically mixed with 1.2 g of catalyst with a spatula in order to obtain a loose contact between the two materials (carbon black and catalyst). The fixed bed was heated in an electrical furnace driven by a temperature programmer controller. The gas temperature was measured by a thermocouple, located within the bed of catalyst or catalyst–carbon mixture allowing the subsequent temperature monitoring.

For the pure catalyst, the sample was firstly reduced at 573 K for 20 min using 2%b.v. H_2 in N_2. Then the gas flow was switched to N_2. After the stabilization of the temperature and concentration signals, the gas flow was switched to the reactive gas mixture containing 300 ppmv NO + 10%b.v. O_2 in N_2 or 300 ppmv NO_2 + 10%b.v. O_2 in N_2. The NO_x storage phase is maintained until saturation of the catalyst and then the reactive gas mixture was switched to pure N_2. Subsequently Thermal Programmed Desorption (TPD) of stored NO_x was performed. TPD was carried out by heating the sample at a rate of 5 K/min from the adsorption temperature (573 K) to 873 K under pure N_2. The catalyst samples have been conditioned by performing a few NO_x adsorption/TPD cycles in order to obtain a reproducible behavior (typically 4 cycles). Note that each NO_x adsorption/TPD cycle were separated by the reducing surface treatment under 2%H_2 in N_2 at 573 K. In the following sections, the catalyst samples conditioned by four NO_x adsorption/TPD cycles will be named ‘conditioned’ sample. A typical result of NO_x storage and desorption test over the conditioned Pt–Ba/Al_2O_3 catalyst is shown in Fig. 1.

In order to evaluate the influence of the presence of soot on NO_x adsorption capacity of the catalysts, the carbon–catalyst mixtures conditioned as described above was placed on the quartz frit of the reactor. Three NO_x adsorption/TPD cycles were performed, in the same experimental conditions as those carried out with pure catalyst sample.

In all experiments, the total gas flow rate was 60 NL h^{-1}, controlled by mass flow meters. The total pressure in the set-up was kept at 1 atm.

The outlet gas was analyzed using an infrared ROSEMOUNT NGA 2000 analyzer to quantify the outlet NO, NO_2, CO and CO_2 molar fractions.

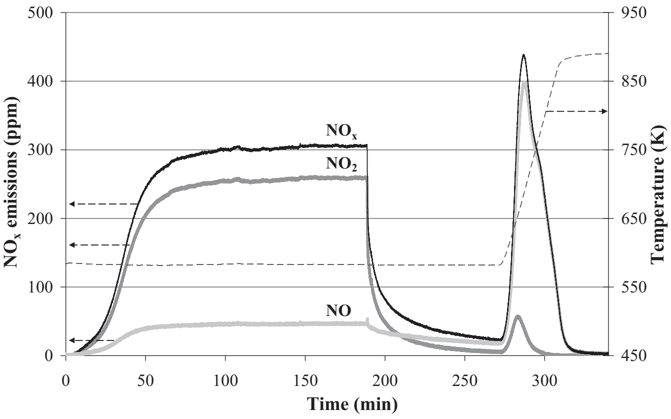

Fig. 1. Outlet concentration of NO and NO_2 versus time. Left: NO_x storage (exposure under 300 ppmv NO and 10%b.v. O_2 at 573 K and 60 NL h^{-1}); right: temperature (dotted line).

3. Results

3.1. Storage without carbon black

The NO_x storage capacities (NSCs) of the catalysts, determined by NO_x adsorption and desorption cycles under 300 ppmv NO or NO_2 + 10%b.v. O_2 at 573 K in N_2, are shown in Table 1. It is important to note that a nitrogen balance from the quantity of NO_x adsorbed during the lean phase and NO_x desorbed during TPD was obtained. So that one may assert that no significant amount of N_2O or N_2 is formed in these conditions. As mentioned in the literature [25], alumina presents an important NSC (210 μmol/g_{cat}) using NO_2 in the gas mixture. On Ba/Al_2O_3 the amount of NO_x stored in these conditions is however double (430 μmol/g_{cat}). It is also important to note that in the presence of NO instead of NO_2 in the reactive gas, no adsorption was detected either on Al_2O_3 or Ba/Al_2O_3 materials (not shown). From the NO_x emission signal obtained during the TPD on Al_2O_3 material, and taking into account the BaO content in the Ba/Al_2O_3 catalyst, a deconvolution of the TPD signal obtained on the Ba/Al_2O_3 catalyst was performed (Fig. 2). This deconvolution highlights that the NO_x storage on Ba/Al_2O_3 catalyst takes place on two distinctive type of sites: alumina and barium with a contribution of 40% and 60% respectively.

The NSC measured on the Pt/Al_2O_3 catalyst (Table 1) reveals that the presence of platinum does not promote the NO_x storage on Al sites. On the contrary, the introduction of Pt on the Ba/Al_2O_3 catalyst allows an increase of 30% of the NSC reaching the value of 560 μmol/g_{cat}. Thus, the presence of platinum seems to promote the access of NO_x to Ba sites.

The NO_x storage behavior of platinum based catalysts (Pt/Al_2O_3 and Pt–Ba/Al_2O_3) is however affected when NO is used in the reactive gas instead of NO_2. Surprisingly, the decrease in the amount of

Table 1
NO_x storage capacity (NSC in μmol/g_{cat}) in the presence and in the absence of carbon black and rate of loss of NSC (Δ_{NSC} in %) due to the presence of carbon (300 ppmv NO or NO_2, 10%b.v. O_2, 60 NL h^{-1}).

Catalyst	Gas composition	NSC (μmol/g_{cat})		Δ_{NSC} (%)
		Without soot	With soot	
Al_2O_3	NO_2/O_2	210	120	43%
Ba/Al_2O_3	NO_2/O_2	430	195	55%
Pt/Al_2O_3	NO/O_2	140	140	0%
	NO_2/O_2	200	165	18%
Pt/Ba/Al_2O_3	NO/O_2	500	430	14%
	NO_2/O_2	560	500	11%