Stability and activity of Pd-, Pt- and Pd–Pt catalysts supported on alumina for NO oxidation

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ABSTRACT

The association of palladium and platinum supported on alumina was studied for diesel oxidation catalyst application. The effect of propene, water and their combination on NO oxidation activity was investigated in flow reactor over Pt/Al_2O_3, Pd/Al_2O_3 and two $Pt–Pd/Al_2O_3$ catalysts, prepared by co-impregnation and sequential impregnation of the metals. Contrary to Pd/Al_2O_3, activity improvement due to the repetition of activity test was observed on Pt/Al_2O_3 and both $Pt–Pd/Al_2O_3$. Metal sintering during activity test was revealed by CO chemisorption. The bimetallic catalysts reached their final stability and activity before Pt/Al_2O_3. The presence of water decreased the NO oxidation activity of all catalysts and the propene completely inhibited NO oxidation at low temperature until propene combustion occurred. The addition of palladium to Pt/Al_2O_3 was found very efficient to oxidize propene and therefore significantly limited the inhibition of NO oxidation by propene. A mechanism was proposed to explain the NO oxidation promotion lying behind the addition of Pd. DRIFT measurements and flow reactor experiments showed that propene was less stable and able to react with surface nitrates on Pd-containing catalyst at low temperature (175 °C). On Pt/Al_2O_3, however, the propene consumption proceeded initially through selective catalytic reduction of NO, which took place at higher temperature (240 °C). In this way, propene combustion and consequently NO oxidation occurred at lower temperature on bimetallic catalysts than on Pt/Al_2O_3.

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1. Introduction

In diesel exhaust after treatment, the catalyst is exposed to a complex gas mixture, the composition of which varies with the engine load, and is sometimes subjected to high temperature. Under these harsh conditions, sintering of Pt/Al_2O_3 oxidation catalysts has been observed and attributed to both thermal and chemical effects [1–4]. The addition of palladium in the DOC formulation has led to higher resistance against metal particle sintering [5–9], without altering the NO oxidation [6,10] despite the low activity of Pd-catalysts for this reaction. Another issue is the presence in the exhausts of various compounds that can interfere with the considered reaction by, for instance, competing for the catalytic active sites. Among these DOC poisons, residual SO_2 has been widely studied [11–16] but mutual inhibition of reactants to be oxidized has also raised interest. CO and NO have been found to affect each others' oxidation [17–19] as well as CO and C_3H_6 [20]. The presence of hydrocarbons decreases NO oxidation activity of Pt/Al_2O_3 and vice versa [21–23]. However, inhibition of NO oxida-

tion by hydrocarbons has only been investigated on Pt/Al_2O_3, which needs to be extended to catalysts with different active phase in order to increase the knowledge about inhibition mechanism and to develop a catalyst formulation capable of limiting this inhibition.

In this work the effect of water and propene on Pt/Al_2O_3, Pd/Al_2O_3 and bimetallic $Pt–Pd/Al_2O_3$ DOCs was investigated using NO oxidation as probe reaction. The stability of the catalysts in operating conditions was also addressed and DRIFT spectroscopy was used to get a deeper understanding about the reaction mechanisms. In addition, H_2 TPR were performed before and after NO oxidation experiments in order to examine the reproducibility of different oxygen species on the surface.

2. Experimental

2.1. Catalysts preparation

2.1.1. Pt/Al_2O_3 and Pd/Al_2O_3

Two monometallic catalysts containing 1 wt% Pt and 1 wt% Pd respectively have been prepared according to the same procedure. A slurry consisting of pre-calcined γ-alumina (Puralox SBa-200, Sasol, 2.5 h at 750 °C) and purified deionized "MilliQ" water (Millipore) was maintained under stirring while the pH was monitored.

A ratio of 16 mL water per gram of alumina was used. Nitric acid was then added drop-wise to reach a stable pH of ca. 4. A solution containing the PGM was prepared by dilution of the appropriate amount of metal precursor, $Pt(NO_3)_2$ and $Pd(NO_3)_2$, respectively, in 40 mL MilliQ water. It was then added drop-wise to the stirred alumina slurry. During this operation, the pH decreased. After ca. 2 h under stirring, the solution was frozen by using liquid N_2 and dried overnight under vacuum to sublimate the water. The collected catalyst powder was calcined at 500 °C for 2 h.

2.1.2. Pt–Pd/Al₂O₃ by co-impregnation of Pt and Pd

One bimetallic catalyst containing both platinum and palladium was prepared by wet impregnation, freezing and drying, as described for the monometallic catalysts. However, the solution added to the alumina slurry contained both $Pt(NO_3)_2$ and $Pd(NO_3)_2$, in such proportion to obtained a total PGM loading of 1 wt% with a Pt/Pd mass ratio of 3. This catalyst was referred to as PtPd-CoImp in the present manuscript.

2.1.3. Pt–Pd/Al₂O₃ by sequential impregnation of Pt and Pd

A second bimetallic catalyst containing Pt and Pd in the same proportion as PtPd-CoImp (1 wt% PGM, Pt/Pd = 3) was prepared by sequential impregnation. First 0.75 wt% Pt/Al₂O₃ was prepared as described above in the case of monometallic Pt/Al₂O₃. After calcination at 500 °C, the catalyst powder was mixed with MilliQ water in the proportion 16 mL/g cat and the pH was decreased by addition of HNO₃ to ca. 4. A 10 mL solution containing the palladium precursor was prepared and added drop-wise. The catalyst was then frozen, dried and calcined for two hours at 500 °C. This catalyst was named PtPd-Seq.

2.1.4. Monolith preparation

The four catalysts studied were washcoated onto honeycomb-structured cordierite monoliths by dipping a pre-calcined (2 h at 600 °C in air) monolith in a catalyst powder suspension. The monoliths were 2 cm long and had a 2 cm diameter and a channel density of 400 cpsi. The catalyst powder was mixed with a binder (boehmite Disperal P2, Sasol, 80 wt% catalyst/20 wt% binder) and dispersed in a solution made of 50 wt% ethanol and 50 wt% water. The liquid-to-solid mass ratio of the slurry was around 7 to ensure the deposition of a sufficient amount of washcoat and avoid channel clogging. After each dipping, the monolithic sample was dried with a hot air gun at ca. 90 °C until the liquid phase in the channels disappear. Drying at 550 °C was then performed for one minute. During the first drying step, the sample was continuously rotated with care to ensure the homogeneous wetting of the channels. The dipping and drying process was repeated until ca. 0.5 g washcoat was deposited. The monoliths were then calcined in oven at 550 °C in air for two hours.

2.1.5. Flow reactor experiments

A flow reactor was used to measure the activity and selectivity of the samples. It consists of a horizontal quartz tube in which the monolith was placed and the gas mixture, supplied by Bronkhorst® mass flow controllers, flowed. The reactor was heated by a resistance connected to a Eurotherm temperature controller. Quartz wool was wrapped around the reactor to provide thermal insulation. A MultiGas™ 2030 FTIR continuous gas analyzer (MKS) was connected to the reactor outlet and monitored the concentrations of the various gas constituents.

Initially, the samples were exposed to a degreening treatment in the flow reactor, consisting of 2 h at 500 °C using 500 ppm NO, 8% O_2 in Ar and a total flow of 3000 mL/min. Thereafter, the dispersion was measured using CO-chemisorption, the details of which are described in the following section. After, the dispersion measurement the catalysts were subjected to repeated thermal cycles under a gas flow of 3000 mL/min containing 500 ppm NO, 8% O_2

and argon as carrier gas. The temperature was increased and then decreased at a controlled rate of 5 °C/min from 150 °C to 500 °C, describing one cycle. Four cycles, were performed in one run. In the second cycle, 5% H_2O was included in the gas mixture previously described so as to study the effect of water. In the third cycle, the combined effect of water and propene on NO oxidation was addressed; therefore 500 ppm C_3H_6 was added to the second cycle gas mixture. Finally water was turned off during the fourth cycle in order to study the effect of propene in dry conditions. This procedure was designed in order to study the effect of water, C_3H_6 – a model hydrocarbon – and the combination of water and propene on the NO oxidation activity of the Pt, Pd and bimetallic Pt–Pd catalysts. Before each cycle the catalyst was pre-treated with 10% O_2 in Ar at 450 °C for 10 min followed by 30 min reduction at 450 °C in 2% H_2, with a total flow of 1000 mL/min.

The cycle run described above was repeated three times in order to assess the reproducibility of the results, as well as the aging and stability of each catalyst.

2.2. Catalyst characterization

2.2.1. BET and CO chemisorption

Chemisorption of CO was used to assess the metal dispersion of mono-metallic catalysts since the amount of surface metal atoms can be correlated to the amount of CO chemisorbed. After reduction of the catalyst at 450 °C in a H_2 flow (2% in Ar) for 30 min, the reactor was cooled rapidly to 25 °C. After flushing with argon for 10 min, 100 ppm CO in Ar was flowed for 20 min to measure the CO adsorption. Physisorbed CO was then flushed with Ar for 500 s and a second 100 ppm CO pulse (10 min) was carried out to quantify the weakly bonded CO. During these measurements a total flow of 1000 ml/min was used.

However, the dispersion of bimetallic Pt–Pd catalysts cannot be inferred from CO chemisorption without important assumptions since the adsorption stoichiometry of CO on Pt and Pd is different. Attempt of calculating the dispersion, in the bimetallic cases, would require detailed information about the presence of alloy particles, their composition and, more importantly, the exact composition of their surface. For these reasons, the results of CO chemisorption were merely reported as the ratio CO_{ads}/M, M being the amount of noble metal, in mol.

The surface area was determined by physisorption of nitrogen at liquid nitrogen temperature and calculated according to the BET method. After degassing the powder samples at 250 °C for 2 h under vacuum, the measurement was performed on a Micromeritics TriStar 3000 chemisorption instrument.

2.2.2. Temperature-programed reduction (TPR)

TPR was performed to characterize the reducibility of the catalysts after exposure to oxygen-rich gas flow. About 0.05 g of catalyst powder (0.1 g in the case of Pt/Al₂O₃ catalyst) was loaded in a vertical tubular quartz reactor (inner diameter = 5 mm) on a sintered quartz bed. A controlled gas mixture flowed downward through the catalyst bed while a mass spectrometer (Hiden Analytical) enabled to measure the time-resolved hydrogen concentration of the outlet gas flow. Prior to the TPR, the catalysts were degreened for 2 h at 500 °C under a flow containing 500 ppm NO and 8% O_2 with Ar as inert balance. After this treatment, the catalysts were reduced at 450 °C for 30 min in 2% H_2. Then, the catalysts were exposed to O_2 (8% balanced with Ar) at 450 °C for 30 min and during subsequent cooling to 25 °C (10 °C/min). After a one-hour argon flush, the pre-oxidized catalysts were exposed to 500 ppm hydrogen (balanced with Ar) for 30 min at 25 °C and during a subsequent temperature ramping step to 450 °C (10 °C/min). The catalysts were then aged for 2 h at 500 °C (500 ppm NO and 8% O_2 with Ar as inert balance) to mimic the effect of one NO oxidation activity measurement. The