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Selective reduction of NO_x by hydrogen and methane in natural gas stationary sources over alumina-supported Pd, Co and Co/Pd catalysts
Part A. On the effect of palladium precursors and catalyst pre-treatment

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Abstract

The aim of the present work is to study the selective reduction of NO_x from natural gas sources. The unburned methane can be used as reductant. Another reductant such as hydrogen can be created in situ, using a microreformer. The results suggest that the NO_x are reduced by H_2 at low temperature, when methane is not activated and at higher temperature the methane is then the main reductant. However, the catalytic behaviour depends on the metal precursor and the catalyst treatment. The most prominent result is obtained on the palladium catalyst prepared from $Pd(NH_3)_4(NO_3)_2$ precursor. Comparing the reduction and the calcination step in the course of catalyst preparation, one can conclude that calcination lead to the higher activity in deNO_x, since reduced catalysts are oxidized during the deNO_x process.

Keywords: deNO_x; Hydrogen; Methane; Palladium precursor; Cationic species

1. Introduction

Nowadays, the harmful effects of emission of nitrogen oxides are completely recognized. Emission of NO_x ($NO + NO_2$) from vehicles and stationary sources are responsible for serious environmental problems. The deNO_x is the specific post-treatment for the reduction of nitrogen oxides present in the exhaust streams in lean-burn conditions. The SCR of NO_x by methane is a very attractive technology for the decreasing of NO_x from stationary sources, because natural gas (methane) is readily available.

Initially, Li and Armor [1] found that the most active catalysts for NO_x removal by methane in oxygen excess were based on cobalt supported on several zeolites. Bimetallic cobalt and palladium loaded zeolites exhibited much more resistance to water vapor than monometallic Co-zeolites [2–5]. Although they are more resistant, these catalysts also deactivate under long-term hydrothermal conditions. Another main obstacle of SCR of NO by methane is the low selectivity between the reaction with NO and O_2 [6,7]. This obstacle is important in the case of Pd, since Pd is very active for total oxidation of methane [8]. The used of Pd supported on acidic materials such as zeolites for he SCR of NO_x by methane, is correlated with the stabilization of the Pd^{2+} ions on acidic materials, which have low activity for methane oxidation [9]. Therefore, other acidic materials have been tested, such as sulphated zirconia and sulphated alumina [10,11]. Recently, a general three-function model for deNO_x catalysis [12–17] was also proposed for metals in cationic form. The authors claimed that three functions are necessary for the deNO_x process to occur: (i)

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oxidation of NO to NO_2; (ii) mild oxidation of methane to alcohol and aldehyde, in the presence of NO_2; (iii) reduction of NO to N_2, assisted by the deep oxidation of the alcohol and aldehyde to CO_2.

Moreover, many authors report that H_2 is a very effective reductant under lean conditions [18–23]. Pt and Pd based catalysts have been examined by Ueda et al. [19], for $H_2/NO/O_2$ reaction, under lean burn condition (5% O_2) in presence of 10% of H_2O. All Pd-based catalysts displayed two distinct conversion maxima for the reduction of NO, one centred at 100 °C and the second at 300 °C. At low temperature, the peak results from the reaction between H_2 and NO, while the peak at high temperature would be the result of the reaction between H_2 and NO_2 produces in situ. The maximum of NO_x conversion varies significantly with the choice of the support. Pd/TiO_2 shows the best activity, while for Pd/Al_2O_3, the total of NO_x conversion does not exceed 10%. Pieterse and Booneveld [22] reported the study of NO_x reduction by the reducing agents H_2, CO, CH_4, in presence and absence of O_2, H_2O and CO_2 on Zeolite MOR catalysts impregnated with palladium and cerium. This bimetallic catalyst provides high NO_x conversion showing high nitrogen selectivity (~90%) with H_2 and CO under lean burn conditions, which is assigned to a synergic co-operation between CO and H_2. Engelmann-Pirez et al. [23] have showed that alumina- or perovskite-supported palladium catalysts are efficient for NO_x abatment in a mixture $H_2/NO/O_2$ at low temperature (<150 °C). The authors proposed that the active phase is metallic palladium. The influence of the precursor kind of catalysts on the course of NO_x reduction by CO has been investigated by Nazimek and Cwikla-Bundyra [24]. The authors showed that the NO_x reduction by CO depends on the kind of precursor. Indeed, $Pd(NO_3)_2$ precursor leads to the higher reactivity compared to chlorinated precursors. This paper reports a study on the influence of metal precursor and the influence of calcination or reduction on the SCR of NO_x by methane or hydrogen. Finally, the influence of methane and hydrogen used alone or both as reducing agents are studied.

2. Experimental

2.1. Catalysts synthesis

Catalysts were prepared by wet impregnation of crushed and sieved γ-Al_2O_3 ($0.8\ mm < d < 1.2\ mm$) (Procatalyse, specic surface area of 190 $m^2\ g^{-1}$, pore volume of 0.7 $cm^3\ g^{-1}$). Three different palladium precursors were used: (1) $Pd(NH_3)_4(NO_3)_2$ (5%) aqueous solution, (2) $Pd(NO_3)_2$ hydrate (99%), and (3) $PdCl_2$ hydrate (99%). The metal salts were dissolved to prepare the precursor suspension. To prepare the catalyst containing chloride, HCl (1 M) was used in order to dissolve the salt at RT in water. The pH of the solution was about 1.9.

The precursor's suspension was maintained under stirring at 333 K for 3 h. After complete removal of water by evaporation under reduced pressure, the catalysts were dried overnight with air at 393 K and calcined with air at 773 K for 2 h [16]. The as-prepared catalysts are labelled $Pd_{Pd(NH_3)_4)(NO_3)_2}$ $(X)/Al_2O_3$, $Pd_{PdCl_2}(X)/Al_2O_3$ and $Pd_{Pd(NO_3)_2}$ $(X)/Al_2O_3$.

2.2. Characterization of catalysts

The catalysts were characterized by XRD, transmission electron microscopy (TEM), and UV–visible–near-infrared (NIR). The specific surface area was also measured using a home made apparatus. Elemental analysis was performed by the "Service Central d'Analyses du CNRS" in order to determine the cobalt and palladium contents and cobalt-supported catalysts. Powder X-ray diffraction (XRD) was carried out on a Siemens model D-500 diffractometer with Cu Kα radiation. High-resolution transmission electron microscopy (HRTEM) was performed to determine the particle size of cobalt or palladium particles on alumina and to check their dispersion. HRTEM studies were performed on a JEOL-JEM 100 CXII apparatus associated with a top entry device and operating at 100 kV. EDS analysis was performed with the same apparatus using a LINK AN 10000 system, connected to a silicon–lithium diode detector, and multichannel analyser. EDS analyses were obtained on large domains of samples (150 nm × 200 nm to 400 nm × 533 nm). Diffuse reflectance spectra were recorded at room temperature between 190 and 2500 nm on a Varian Cary 5E spectrometer equipped with a double monochromator and an integrating sphere coated with polytetrafluoroethylene (PTFE). PTFE was the reference.

2.3. Catalytic measurements

The catalytic reaction was performed with the three reaction mixtures: (i) 150 ppm NO, 7 vol.% O_2, 0 vol.% CO_2, 9000 ppm CH_4, 0 vol.% H_2O, 0 ppm H_2, in Ar as balance; (ii) 150 ppm NO, 7 vol.% O_2, 0 vol.% CO_2, 0 ppm CH_4, 0 vol.% H_2O, 1500 ppm H_2, in Ar as balance; (iii) 150 ppm NO, 7 vol.% O_2, 0 vol.% CO_2, 9000 ppm CH_4, 0 vol.% H_2O, 1500 ppm H_2, in Ar as balance. The NO mixture was supplied by air liquide as 1 vol.% NO, and 99 vol.% Ar (<10 ppm other gases). The O_2 mixture contained 100 vol.% O_2 (air liquide). The CH_4 mixture contained 5 vol.% CH_4, and 95 vol.% Ar (air liquide). The total gas flow was maintained at 0.25 L min^{-1} NTP. Each of the gas mixtures was metered using calibrated electronic mass flow controllers (Brooks, Model 5850E). Taking a catalyst density of about 0.7 g/cm^3, the gas hourly space velocity (GHSV) was 50,000 h^{-1}. Catalytic experiments were carried out in a glass microreactor containing quartz wool supporting the sample. The bed temperature was measured using K-type thermocouple affixed to the outer reactor surface. The temperature was controlled using an electronic controller (Eurotherm 2408). The reactor outflow was analyzed using a set of specific detectors. An Eco Physics CLD 700 AL NO_x chemiluminescence analyzer (for NO and total NO_x (i.e. $NO + NO_2$)) allowed the simultaneous detection of NO, NO_2 and NO_x. An Ultramat 6 IR analyzer was used to monitor N_2O and a FID detector was used to follow the total concentration of hydrocarbons (HC). Temperature Programmed Desorption (TPD) experiments were carried out in Ar/O_2 (7 O_2 vol.% in Ar as balance, 0.250 L min^{-1}) with a heating rate of 5 °C min^{-1}, up to 500 °C, over pre-treated samples. Before TPD gas mixture was pre-adsorbed (150 ppm NO, 7 vol.% O_2 in Ar as balance,