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NO_x abatement in the exhaust of lean-burn natural gas engines over Ag-supported γ-Al_2O_3 catalysts

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ABSTRACT

A series of Ag catalysts supported on γ-Al_2O_3, including two different γ-Al_2O_3 supports and various Ag loadings (2–8 wt.%), was prepared, characterized (SEM, TEM, BET, physisorption, TPR, NH_3-TPD) and tested for the selective catalytic reduction of NO_x by CH_4 for lean-burn natural gas engines exhausts. The catalysts containing 2 wt.% Ag supported on γ-Al_2O_3 were found to be most efficient for the NOx reduction into N_2 with a maximal conversion of 23% at 650 °C. This activity was clearly linked with the ability of the catalyst to concomitantly produce CO, via the methane steam reforming, and NO_2. The presence of small AgOx nanoparticles seems to be crucial for the methane activation and NOx reduction.

1. Introduction

Natural gas, mainly composed of methane, is one of the cleanest burning hydrocarbon fuels. Due to its high carbon to hydrogen ratio, the CO_2 emissions per unit of produced energy are limited. This property, combined with the worldwide abundance of natural gas reserves, makes it an appealing alternative fuel [1–3]. The utilization of natural gas as a fuel in the transportation sector can partially substitute diesel powered heavy-duty vehicles. Several studies have shown that natural gas engines present reduced particulate matter (PM) emissions compared to diesel engines, associated with a slight decrease in the CO_2 emissions [4, 5]. Therefore, the development of natural gas heavy-duty vehicles can contribute to the decrease of the PM emissions in urban areas and is a powerful strategy to decrease CO_2 and pollutant emissions. However, this technology must keep with the Euro VI emission legislations, applicable from September 2014, which limit the NOx emission level below 0.46 g/kWh for heavy-duty vehicles using natural gas as a fuel. Therefore, an effective catalytic post-treatment is required to reduce the emissions of unburnt CH_4, CO and NOx. The selective catalytic reduction of NOx by urea (urea-SCR) can be efficiently implemented using noble-metal free catalysts [6]. Even if the urea-SCR requires an additional tank of urea and a controlled injection and decomposition of urea, this technology is now commonly developed for heavy-duty vehicles. Nevertheless, the corrosion and leakage of ammonia are still problematic. A more straightforward and economical approach is to directly reduce NOx with unburnt methane contained in the exhaust. The selective catalytic reduction of NOx by CH_4 (CH_4-SCR) could remove simultaneously CH_4 and NOx but is quite challenging and up to date there is no technology available. Noble metal-based catalysts supported mainly on zeolites, alumina or zirconia have been were investigated for CH_4-SCR in the presence of oxygen [7–12]. Recently, a synergic effect was reported by using a bimetallic Pd–Pt supported on sulfated zirconia. A bi-functional mechanism was proposed with the NO oxidation to NO_2 occurring on Pt and coupled with the reduction of NO_2 by CH_4 on Pd [13]. However, the balance between the PGM cost, their performance and durability are still insufficient for practical applications.

Alternative materials could be the Ag-based catalysts especially at higher reaction temperatures [14, 15] and in the presence of water [16–18]. In addition, the selectivity to N_2 over Ag-based catalytic systems is relatively high, leading to inexpensive materials, which are more attractive compared to noble metal catalysts [19]. Many studies have been performed on silver supported γ-alumina catalysts but

Table 1
Main properties of Ag/Al_2O_3 catalysts.

Sample	BET surface area ($m^2\ g^{-1}$)	Ag content (wt.%)	Pore diameter (nm)	Pore volume (cm^3/g)	Acidity (μmol $NH_3 \cdot m^{-2}$)
Al_2O_3C	150	–	7	0.35	0.83
Al_2O_3P	203	–	5	0.33	0.69
2AgC	154	1.95	7	0.35	0.73
2AgP	198	1.75	5	0.34	0.79
4AgP	185	3.5	5	0.32	
8AgP	172	7.3	5	0.30	

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mainly by using alkenes as reducing agents [20–25]. Only few studies are dealing with CH_4-SCR on Ag supported γ-Al_2O_3 systems in the literature [26–29]. The competition between the reduction of NOx with methane and the methane combustion is driving the catalytic performances [30]. The nature of Ag species is the most crucial parameter affecting the catalytic performance for CH_4-SCR [14, 18, 20, 26, 29]. According to the literature data, silver oxide species finely dispersed on γ-Al_2O_3 seem to be the most active site for CH_4-SCR while metallic silver particles or Ag_n^0 clusters lead to the methane combustion.

The objective of this study is to investigate the catalytic performances of Ag supported γ-Al_2O_3 catalysts for the CH_4-SCR of NOx by using operating conditions comparable to those encountered in lean-burn natural gas engine exhausts. A series of catalysts, including two different γ-Al_2O_3 supports and various loadings of Ag, has been synthesized and characterized using several techniques (SEM, TEM, BET, physisorption, TPR, NH_3-TPD). The catalytic performance for the CH_4-SCR of NOx was monitored as a function of temperature, partial pressures of methane and H_2O.

2. Experimental

2.1. Catalyst preparation

Two different γ-alumina supports have been used to disperse the Ag nanoparticles. The first one was prepared by the precipitation method (denoted as Al_2O_3P) from an aqueous solution 1 M of aluminum nitrate, $Al(NO_3)_3 \cdot 9H_2O$ (Sigma-Aldrich) at pH of ca. 9.0–10, controlled by addition of a NH_4OH (Sigma-Aldrich) solution 0.5 M. The precipitated $Al(OH)_3$ was washed three successive times with distilled water to remove nitrate and ammonium ions. The sample was dried at 110 °C overnight and then calcined in air at 700 °C for 6 h. This temperature was selected because this is the highest one encountered in a lean-burn natural gas engine exhaust.

The second support was a porous powder provided by PYLOTE (denoted as Al_2O_3C). The Ag/γ-Al_2O_3 catalysts containing different Ag loadings were prepared by the wet impregnation method from an aqueous solution of $AgNO_3$ (Sigma-Aldrich). All catalysts have been dried at 110 °C for one night and then calcined in air at 700 °C for 6 h. Table 1 gives the list of investigated catalysts with their specific code.

2.2. Characterization of the catalysts

The Ag loading in the catalysts after the calcination step at 700 °C was measured by using the inductively coupled plasma atom emission spectroscopy. Nitrogen adsorption isotherms of the samples were measured at −196 °C (77 K) with a Tristar 3000 volumetric sorption analyzer. Prior to measurement, the samples (ca. 200 mg) were outgassed at 250 °C under vacuum. The specific surface area was calculated from the resulting isotherms using the BET method.

Scanning electron microscopy (SEM) was performed using a JEOL JSM 5800LV SEM electron microscope linked to an energy-dispersive X-ray spectrometer (EDX) equipped with a SieLi diode (PGT). The samples were deposited onto a scotch carbon and metalized by sputtering. A gold film ensures a good conductivity for the observations.

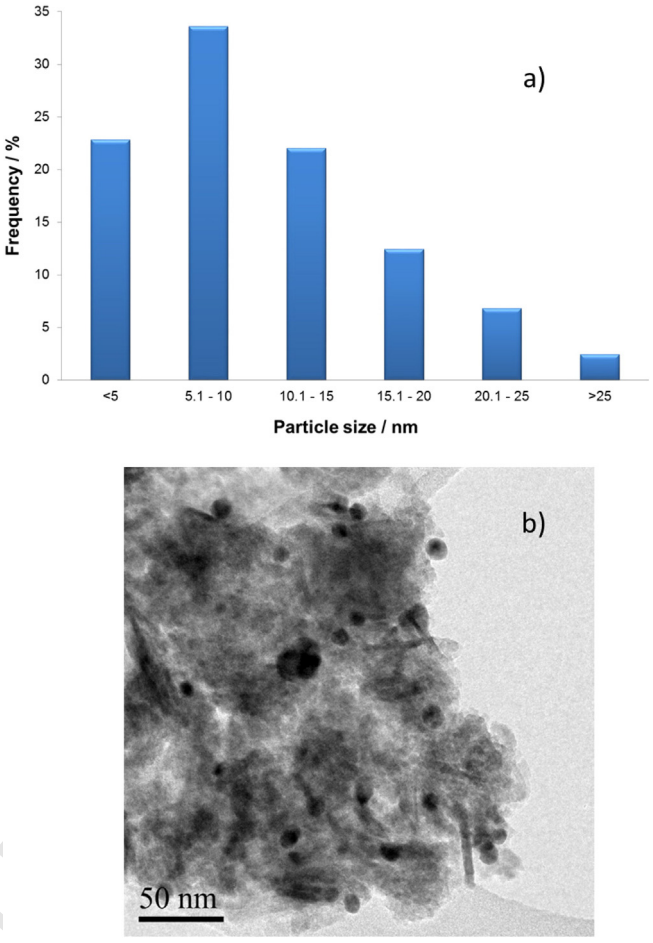

Fig. 2. TEM photograph (a) and particle size distribution (b) of 2AgP catalyst.

Transmission electron microscopy (TEM, JEOL 2010 LaB6) was used to determine the morphology of the solid and the silver particle size distribution. The mean diameter was calculated using Eq. (1).

$$D = \sum NiDi / \sum Ni \quad (1)$$

where Ni is the number of Ag particles with a diameter Di. The ImageJ 1.44 software was used to measure Ag nanoparticle size from at least 10 TEM images and 250 nanoparticles.

Temperature programmed reduction (TPR) measurements have been performed in a U-shaped quartz catalytic reactor. An appropriate

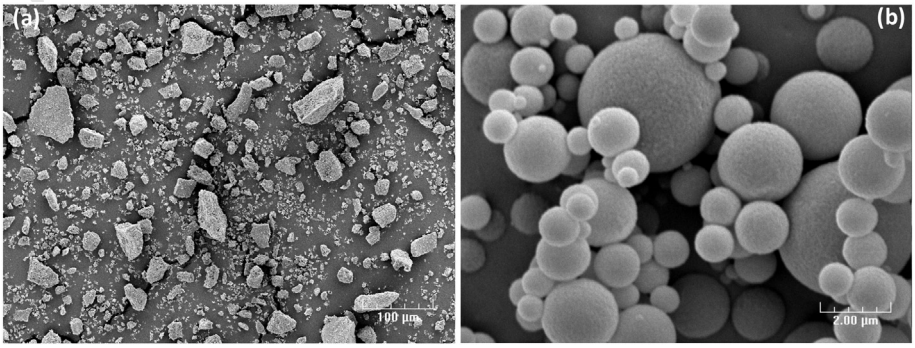

Fig. 1. SEM photographs of the bare supports: (a) Al_2O_3P and (b) Al_2O_3C.

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