

NO_x abatement by HC-assisted SCR over combustion synthesised-supported Ag catalysts

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Introduction

The reduction of nitrogen oxides emissions has become one of the greatest challenges in environment protection. In the forthcoming years, the US, Europe, and Japan governments will strengthen the legislation to reduce the amount of emitted nitrogen oxides (NO_x). NO_x are serious pollutants that cause not only the formation of acid rain but also photochemical smog. They can generate secondary contaminants through interaction with other primary pollutants, which also result from the combustion of fossil fuels in stationary sources such as industrial boilers, power plants, waste incinerators, and gas turbines, diesel and lean-burn gasoline engine [1, 2]. Particularly, the Diesel engine has the advantage of lower consumption of fuel and CO/HC emissions than the conventional spark-ignition engine, but it has the disadvantage that a large amount of NO_x is emitted in the presence of excess oxygen. Among the technical approaches developed, the direct decomposition of NO_x and its reduction with hydrocarbons (HC) are the most attractive ones since virtually no additional reactants from those currently available on board are needed [3].

Materials and Methods

A series of catalyst supports (CeO₂, La₂O₃, ZrO₂) were prepared via a highly exothermic and self-sustaining reaction, the so-called "Solution Combustion Synthesis" (SCS) method [4]. The Ag-based catalysts (CeO₂-2%Ag, La₂O₃-2%Ag, ZrO₂-2%Ag) were prepared according to the same route, by adding also AgNO₃ to the precursors solution in order to obtain a catalyst with 2% in weight of silver [5]. This technique enables a low-cost and convenient "one-step" process, catalysts with a rather high surface areas and purity. All the catalysts were then ground in a ball mill at room temperature and characterized by different analysis: XRD, BET, FESEM, TEM, AAS and Temperature Programmed Desorption or Reduction (TPD/R). The activity of the prepared catalysts was analysed by Temperature Programmed Reaction (TPRe), according to the following standard operating procedures: a gas mixture (750 ppm NO; 750 ppm C₃H₆ or C₆H₆, 7 vol% O₂, He = balance) was fed at the constant rate of 1.67 ml·s⁻¹ to the catalytic fixed-bed reactor (W/F = 0.30 g·s/cm³) enclosed in a quartz tube placed in an electric oven. The reaction temperature was controlled through a PID-regulated oven and increased to 550°C at a 5 °C·min⁻¹ rate. The outlet gas composition was

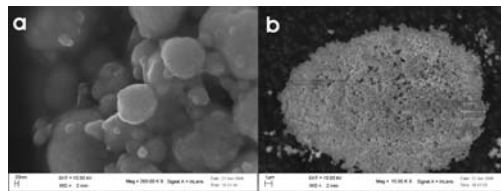


Figure 1. FESEM view of the CeO₂-2%Ag catalyst crystals: (a) 250000x; (b) 10000x.

monitored through both a CO/CO₂/NO_x/N₂O NDIR analyzer and a NO/NO₂ chemiluminescence analyzer as a function of the bed temperature.

Results and Discussion

Figure 1.a illustrates a FESEM picture of the CeO₂-2%Ag catalyst produced via SCS. It regards one of the two catalysts which showed the highest activity among those prepared. However, it is quite representative of all the crystal sizes (30-150 nm) of the prepared catalysts. As far as the microstructure of the catalyst crystals agglomerates is concerned, Figure 1.b shows how it is rather foamy. By employing this direct observation technique no Ag particles could be observed. This is a sign of good dispersion. All samples were found to be pure by XRD analyses. No secondary phases could be detected by this technique.

Table 1. Specific surface area and catalytic activity results of the synthesized catalysts

Catalyst	Ag (% wt)	BET [m ² /g]	HC = C ₃ H ₆		HC = C ₆ H ₆	
			T _p [°C]	% NO to N ₂	T _p [°C]	% NO to N ₂
ZrO ₂	--	7.1	-	0	345	4
ZrO ₂ -2%Ag	2	4.6	360	29	340	38
La ₂ O ₃	-	4.9	-	0	335	70
La ₂ O ₃ -2%Ag	2	3.6	335	50	350	99
CeO ₂	-	74	280	34	315	41
CeO ₂ -2%Ag	2	16.3	350	71	320	88

The surface areas and catalytic activity results for all of the catalysts are listed in Table 1. The peak temperature of the maximum NO to N₂ conversion is reported as T_p. The presence of Ag was always found to lead to a decrease of the BET specific surface area values of the pure support oxides. In all cases, the performance of the Ag-deposited catalysts was better, than that of the support oxides alone. Moreover, using benzene as reducing agent a higher NO to N₂ conversion was obtained. The zirconia based catalysts delivered the worst performance with a maximum NO reduction to N₂ lower than 40 %. Conversely, CeO₂-2%Ag and La₂O₃-2%Ag catalysts could both ignite benzene or propene combustion and NO reduction at temperatures close to 250°C, which have to be considered well inside the range of normal operating temperatures of a diesel engine (180-400°C). The NO_x to N₂ selectivity was quite good for all catalysts since the maximum N₂O or NO₂ production was always below 20 ppm. TPD/R results confirmed that Ag⁺ appears to be more important than Ag for effective N₂ formation. Moreover, by comparing the results of all the investigated catalysts, one can also anticipate that the catalytic activity may not result exclusively from Ag, as the support itself may be involved in the reaction mechanism at least in the cases of ceria and lanfana. In the full presentation, some promising results obtained by structuring the catalysts in catalytic filters for the treatment of diesel engines and waste incinerators flue gases will be discussed.

References

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