

High specific surface area YSZ powders from a supercritical CO₂ process.

Utilization as catalytic supports for gases oxidation and reduction reactions.

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INTRODUCTION

In heterogeneous catalysis, the increase of support surface area and the decrease of particle size of metal catalysts are two major concerns in order to improve the performances of the catalytic material. In other respects, the preparation of heterogeneous catalysts using supercritical carbon dioxide has been recently stressed as providing catalysts with higher activity compared with catalysts prepared using standard methods [1]. In previous papers, we described the preparation of yttrium stabilized zirconia (YSZ) nanoparticles via a supercritical carbon dioxide aided sol-gel process [2,3]. Actually, the nanocrystalline YSZ particles synthesized in supercritical carbon dioxide are therefore of great interest for catalytic application because of the high surface area, but also the crystalline nature of the powders and its extremely low agglomeration state.

YSZ is known to be an O²⁻ conductor due to the presence of oxygen vacancies inside its crystallographic structure. It has received specific attention as a catalytic support especially in studies of Electrochemical Promotion of Catalysis (EPOC). The role of surface oxygen vacancies on YSZ support covered with Pt nanoparticles has been recently evidenced for both H₂ and CO chemisorptions [4]. These results anticipate a good redox catalytic activity for this kind of catalyst. The aim of the work presented in this paper is to show the enhanced catalytic activity of a NO_x storage/reduction (NSR) catalyst based on YSZ nanopowder synthesized in supercritical carbon dioxide. The catalytic activity of precious metal catalysts on this powder was studied versus a commercial YSZ powder usually used as a catalyst support. The impact of supercritical synthesized YSZ for NO_x conversion has been specially investigated in a NO_x TRAP configuration on a diesel particulate filter produced by Saint-Gobain.

POWDER SYNTHESIS AND CHARACTERIZATION

Powder synthesis

The ceramic powders are synthesized under CO₂ supercritical conditions by a batch process. The experimental set-up is schematically represented in Figure 1. A batch reactor has been specially designed to produce several hundred grams of nanosized powders. In a preparative step, a sol containing yttrium and zirconium acetates, mixed with isopropanol in presence of nitric acid is prepared at room temperature. The yttrium proportion is calculated so as to obtain partially stabilized zirconia at a 3 mol % with respect to ZrO₂. The powder synthesis is done by injecting this sol in the autoclave containing CO₂ in supercritical condition: the temperature and pressure is increased respectively to 350°C and 300 bar. The sol is injected into the autoclave at 1,4 m.s⁻¹ and the autoclave is stirred at 400 rpm for 60 minutes. At the end of the reaction, the autoclave is vented and the powder recovered.

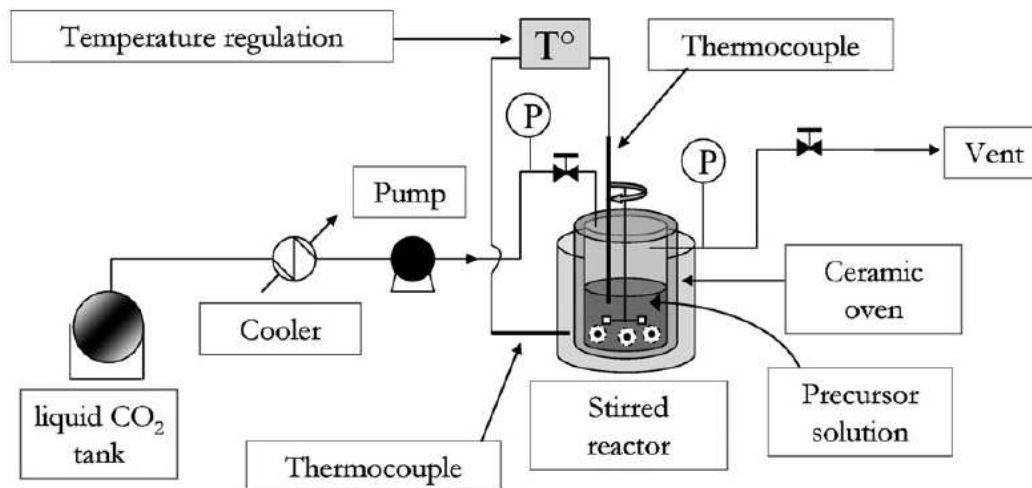


Figure 1 : Schematic representation of the reactor used for the synthesis of YSZ powders

Powder characterization

The nano-crystalline nature of the YSZ particles is evidenced by TEM analysis and XRD measurements. X-Ray diffraction pattern (Figure 2) is acquired using a X'Pert (PANalytical-Cu K_α radiation) equipped with a HTK2000 high temperature chamber. The powder is dispersed in ethanol and deposited on a Pt strip responsible for the two narrow and intense peaks at $2\theta = 39.6^\circ$ and 46° . The other peaks can be indexed to yttrium stabilized zirconium oxide. The large diffraction peaks indicate that the YSZ particles are in the nanometer range. After heat treatment at 1200°C in air, the peaks narrow due to particle size increase. The diffraction peaks can be indexed to the tetragonal YSZ structure.

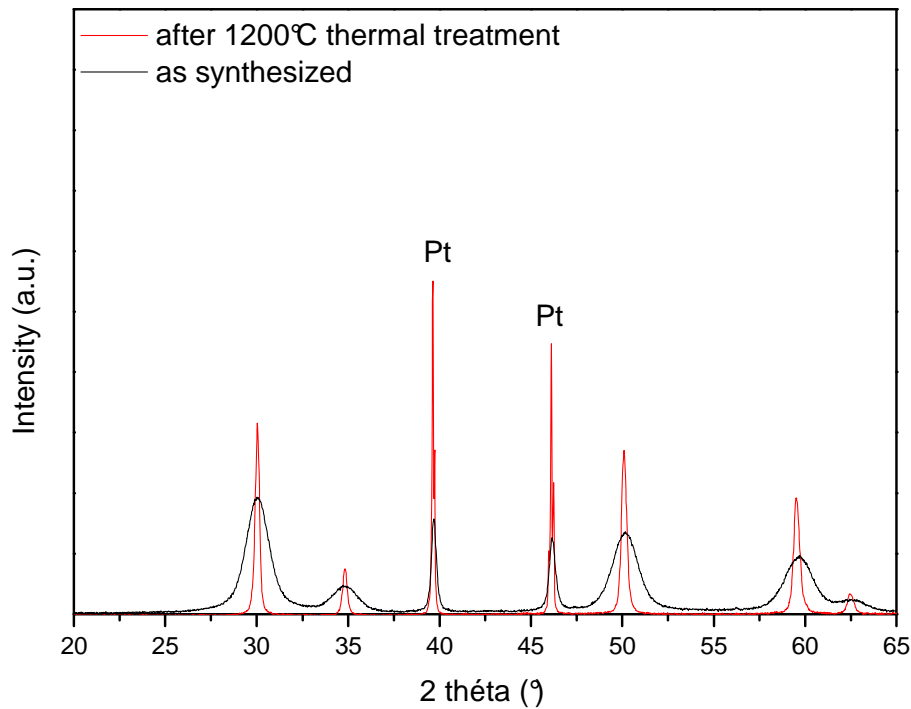


Figure 2 : XRD diffraction patterns of as synthesized SC-3YSZ and after 1200°C thermal treatment

TEM observations (JEOL 2010 LaB6) of the as synthesized powders (SC-3YSZ) show that it is composed of uniform and well crystallized 5nm sized nanoparticles (Figure 3-a). Specific surface area is determined by the BET method using nitrogen adsorption/desorption at 77K (Micromeritics-ASAP 2010) after outgassing at 250°C. Due to its nanosized nature, the powder exhibits a very high specific surface area: 142 m²/g. Such large specific surface area coupled with the crystalline nature of the as synthesized particles is extremely interesting for catalytic applications. For comparison, Figure 3-b shows the TEM image of the widely used commercial YSZ powder from Tosoh TZ3Y. Its particle size is about 50 nm and the developed SSA close to 15 m²/g. In the following, the impact on catalyst support performance of the nanosized YSZ powder prepared in supercritical carbon dioxide (SC-3YSZ) is investigated and compared with the commercial TZ3Y powder.

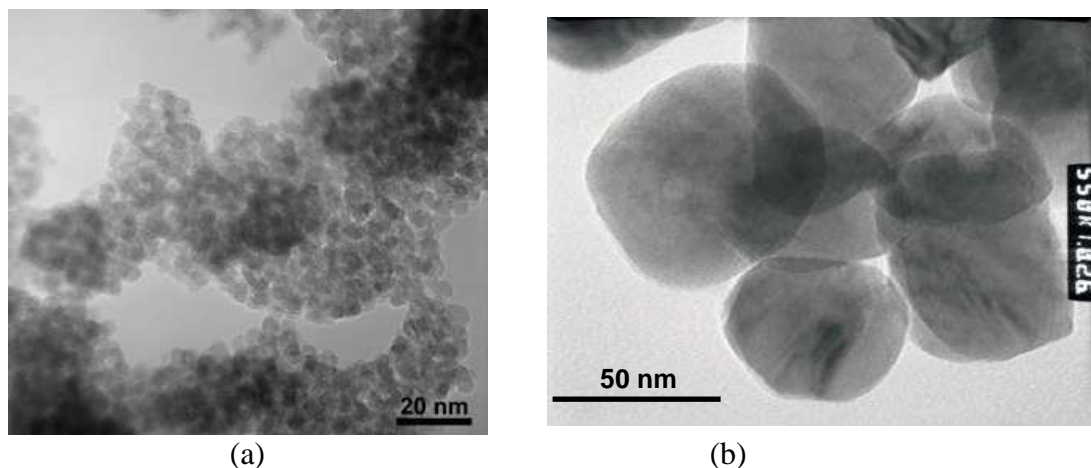


Figure 3 : TEM images of – a) SC-3YSZ (b) commercial Tosoh TZ3Y

CATALYTIC ACTIVITY

Catalyst preparation

Structured catalytic systems (monoliths) were obtained by wash-coat catalyst deposition on a SiC-DPF (Diesel Particle Filter) produced by Saint-Gobain. The monolithic support (Figure 4) consists of a SiC structure constituted by longitudinal square channels ($\sim 1.5 \times 1.5$ mm) open in both sides and separated by thin walls (~ 0.4 mm).

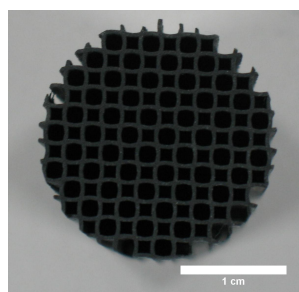


Figure 4: SiC monolith

Table 1: Fraction of SC-3YSZ in the as deposited wash coat

Sample	DPF A	DPF B	DPF C	DPF D	DPF E
$X_{\text{SC-3YSZ}}$	0	0.5	0.6	0.8	1

Different catalyst loads (Table 1) are obtained by mixing the commercial Tosoh TZ3Y powder with the SC-3YSZ powder and wash-coating on the SiC monoliths. The wash-coat suspensions are prepared by dispersing the YSZ powders in desionized water in presence of acetic acid. After thermal treatment at 400°C , Pt and Rh (0.3% w/w in regard to the as deposited wash-coat) were deposited using $(\text{NH}_3)_2\text{Pt}(\text{NO}_2)_2$ and $\text{Rh}(\text{NO}_3)_3$ as precious metal precursors and stabilized by thermal treatment at 500°C .

All the tested catalytic systems had an equivalent load of catalyst around 22 g/L of DPF.

NO_x storage/reduction (NSR) cyclic activity measurements

Experimental

The NSR cyclic measurements were conducted on the DPF-catalytic systems with previous activation at 600 °C in presence of 10% O₂/He (~10 L/h; 2h) and then 100 % H₂ (~3.2 L/h; 1h). Constant flows (40 L/h) of lean reaction mix (500 ppm NO/ 1000 ppm C₃H₆ / 6.7% O₂ and He as balance) or rich reaction mix (500 ppm NO/ 1000 ppm C₃H₆ and He as balance) were introduced alternately. The cycling experiments with a lean period of 3 min and a rich period of 2 min were performed at 300 °C. The catalysts were exposed to 12 lean/rich cycles. The NO_x conversion for a complete representative cycle was calculated according to the following formula:

$$\% \text{ NO}_x \text{ conversion} = 100 \times (\text{NO}_{x, \text{in}} - \text{NO}_{x, \text{out}}) / \text{NO}_{x, \text{in}} \quad (1).$$

The global NO_x conversion into N₂ (selectivity of the process) was estimated considering the production of N₂O during a complete cycle:

$$\% \text{ NO}_x \text{ conversion into N}_2 = 100 \times (\text{NO}_{x, \text{in}} - \text{NO}_{x, \text{out}} - \text{N}_2\text{O}_{\text{out}}) / \text{NO}_{x, \text{in}} \quad (2).$$

Results and discussion

NO_x storage/reduction (NSR) catalyst technology reduces NO_x by a cycling operation, where NO_x is first trapped by the catalyst in a lean phase. Once the NO_x trapping capacity is reached, the NO_x in the outlet feed will increase. This is followed by a hydrocarbon rich phase in order to reduce the NO_x by the hydrocarbons on the catalyst. Once a sufficiently low oxygen concentration is reached, the NO_x will decrease by reduction into NO₂ and N₂.

For the catalysts employed in this work, the principal NO_x storage component can be related with the surface oxygen vacancies generated in the YSZ structure [5]. The evolution of NO_x in the outlet feed as a function of the time was followed for the 5 catalyst loads prepared with increasing quantity of SC-3YSZ. Figure 5-a shows the evolution of NO_x during the first twelve lean/rich cycles. An enlargement of cycles 2-4 is shown in Figure 5-b.

The NO_x profiles appear stable over the analysed cycles, except for DPF-A. In a general way, the efficiency of the NSR process on the evaluated systems depends on the SC-3YSZ fraction. Lowest NO_x storage/reduction capacity is obtained for sample DPF-A, followed by DPF-B and then, very similar profiles are obtained for DPF-C, DPF-D and DPF-E systems. As expected, an increase in the surface area of the storage component (in this case, the YSZ catalytic support) has a positive effect on the NO_x storage capacity of the catalysts. This trend can be related with the effect exerted by a high surface area catalytic support on the dispersion and stability of the deposited metallic phases (Pt and Rh), which also enhances the spillover of the surface species between the precious metal and storage component [6,7].

At the beginning of the lean condition, the NO_x level keeps to essentially zero, suggesting the complete uptake of NO_x by the catalyst - except for DPF-A. This complete uptake behavior was sustained for several seconds, and then the NO_x level is gradually increasing with time and it reaches a stable value which maximum depends on the catalytic system. The profiles are very similar to those reported by Epling et al. [8,9], who divided the profiles into three zones. First, for an initial period of time, complete uptake of NO_x is attained. Then, NO_x starts

to be detected in the outlet, but still uptake of NO_x occurs for some period of time. During this time period, the trapping rate of NO_x decreased continuously. At the last stage of adsorption, the NO_x profile starts to become flat, which indicates the saturation of the catalyst surface. The difference in the NO_x concentration between the inlet and outlet gases at this point can be attributed to the selective NO_x reduction by hydrocarbons on Pt of the NSR catalyst [10].

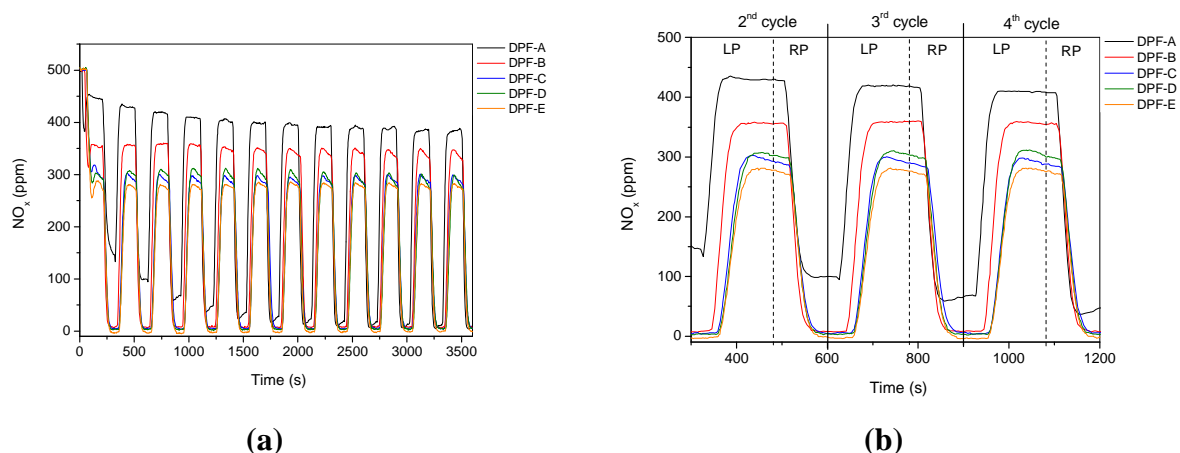


Figure 5: Evolution of NO_x concentrations under cyclic lean-rich conditions at 300 °C. (a) 12 cycles (b) enlargement for 2nd to 4th cycle

Table 2 summarizes the results obtained for the 4th cycle as a function of SC-3YSZ fraction ($X_{\text{SC-3YSZ}}$). t_{100} is the duration in seconds of the first zone in the lean phase profile, where the NO_x uptake by the catalyst is complete, C_{NO_x} is the total NO_x conversion during one complete lean-rich cycle and $S_{\text{NO}_x\text{-N}_2}$ the conversion of NO_x into N_2 for the same cycle, which represent the process selectivity.

Table 2: Catalytic parameters evaluated on the studied catalytic systems (cycle No. 4)

Monolith	$X_{\text{SC-3YSZ}}$	t_{100} (s)	C_{NO_x} (%)	$S_{\text{NO}_x\text{-N}_2}$ (%)
DPF-A	0	-	49	22
DPF-B	0.5	46	62	30
DPF-C	0.6	56	69	33
DPF-D	0.8	56	69	56
DPF-E	1.0	56	72	59

In a general manner, the increase in $X_{\text{SC-3YSZ}}$ fraction increases the efficiency of the catalytic parameters described in Table 2. At the reaction temperature, the effectiveness of the NO_x conversion is not limited by the rate of NO oxidation to NO_2 . It principally depends on the metallic dispersion and the number of storage sites on the catalyst surface. Therefore, t_{100} increases to about 10 seconds between DPF-B and DPF-C, after which it remains almost constant. This result can be associated to the saturation of the surface active sites available for the NO oxidation to NO_2 (Pt dispersion). Accordingly, taking into account that the available storage surface on the catalyst is getting larger with the $X_{\text{SC-3YSZ}}$ fraction increase, the height of the NO_x concentration plateau at the end of the lean phase is inversely proportional to the catalyst surface area (Figure 5). As a result, NO_x conversion and selectivity were improved as a function of the high surface area material fraction on the catalytic systems.

The analysis of CO₂ concentration profile in the outlet gas flow provides interesting information on the oxidation capacity during the lean phase. Propylene was chosen as the reductant in this system because it has a relatively low light-off temperature and clean burn characteristics [11]. Figure 6 shows CO₂ concentration profiles versus time the NSR process. The high amount of CO₂ produced in the course of the lean phase corresponds to the propylene catalytic combustion in presence of oxygen. When the flow is switched to rich phase composition, the CO₂ concentration decreases very fast due to the absence of oxygen. At the end of the rich phase, the level of CO₂ produced is related to the selectivity of the catalytic reduction process of NO with propylene. For the tested systems, the propylene conversion in the lean phase is almost complete showing the high oxidation capacity of the catalysts, except for DPF-A sample. During the rich phase the quantity of detected CO₂ corresponds to the amount expected from the process. The strong peak of CO₂ concentration at the beginning of the lean phase is attributed to carbon deposition during the rich phase. The production of CO was evidenced only in during the course of the rich phase, when there is no oxygen in the feed. Here also, the presence of SC-3YSZ powders in the catalytic loads strongly enhances the oxidation capacity of the catalytic system in order to eliminate hydrocarbons during the lean phase without producing carbon monoxide.

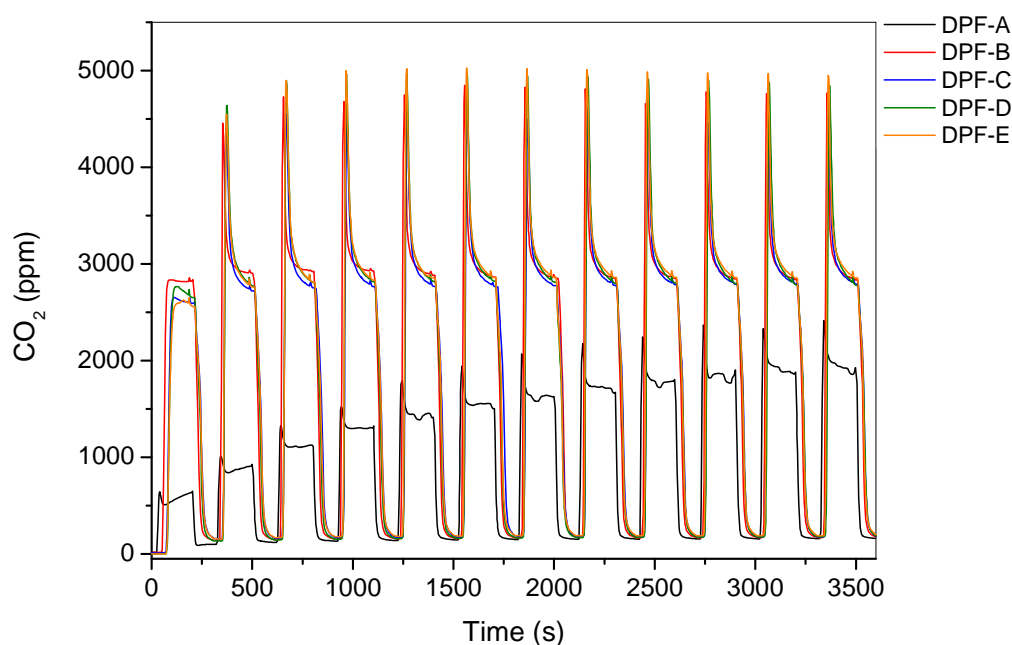


Figure 6: CO₂ concentration profiles obtained at 300°C during the NSR process

CONCLUSION

Nanosized SC-3YSZ particles were synthesized under supercritical conditions. The properties of the particles, i.e. high surface area, crystalline and low agglomeration state make them promising materials as catalyst supports. To evaluate the impact of YSZ nanoparticles

synthesized under supercritical conditions, mixtures of SC-3YSZ and commercial Tosoh TZ3Y were wash-coated on SiC monoliths industrially used for diesel particle filters and, after precious metal induction, studied for NO_x storage/reduction activity. In a general manner, the high-surface SC-3YSZ fraction deposited on the system has a positive influence on its catalytic properties for the NO_x-TRAP process. For the reaction conditions used, the metal dispersion on the YSZ supports with the highest specific surface areas drives the NO_x conversion and selectivity to N₂ of the process. In conclusion, the use of supercritical CO₂ medium for the synthesis of metal oxide catalyst supports demonstrates significant improvement of catalytic performance when compared with catalyst supports prepared using standard methods.

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