



Research Paper

Macroporous carrier-free Sr-Ti catalyst for NO_x storage and reductionVirginia Alcalde-Santiago^a, Arantxa Davó-Quiñonero^a, Ion Such-Basáñez^b, Dolores Lozano-Castelló^a, Agustín Bueno-López^{a,*}^a Department of Inorganic Chemistry, University of Alicante, Carretera de San Vicente s/n. E03080, Alicante, Spain^b Technical Research Services (SSTTI), University of Alicante, Carretera de San Vicente s/n. E03080, Alicante, Spain

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ABSTRACT

A novel concept is presented, consisting of a macroporous carrier-free catalyst. As a proof of concept, a novel Cu-containing Sr-Ti NSR catalyst with a macroporous network has been synthesized, and its maximum NO_x storage capacity (1500 μmolNO_x/g_{catalyst}) significantly surpasses that of conventional Pt/Ba/Al₂O₃ formulations (~600–800 μmolNO_x/g_{catalyst}). This high NO_x storage capacity is achieved because the active phases (mainly SrCO₃ and Cu-containing Sr-Ti perovskites, as deduced by XRD) are not diluted in an inert carrier, and this can be done because the macroporous structure obtained using a polymethylmethacrylate colloidal crystal template allows the access of gases to the particles bulk. *In situ* DRIFTS experiments showed that NO_x were chemisorbed on the novel Cu-containing Sr-Ti macroporous catalyst as a mixture of nitrite and nitro species, and this suggests that several NO_x chemisorption pathways are simultaneously taking place probably involving chemisorption of both NO and NO₂. Additionally, this novel catalyst is totally selective towards N₂ formation as NO_x reduction product, without traces of N₂O nor NH₃. CO₂ and H₂O compete with NO_x for being chemisorbed on the catalyst, and this hinders the utilization of this catalyst in real diesel exhausts. However, we believe that this new concept of macroporous carrier-free catalyst could be extended to other heterogeneous catalyzed reactions or materials to avoid the diluting effect of the catalyst support.

1. Introduction

Heterogeneous catalytic reactions are an important and complex class of chemical reactions where, usually, reactants and products are gases or liquids and the reaction takes place on the surface of a solid catalyst [1,2]. In these systems, the amount of active sites on the catalyst surface where the fluid molecules are chemisorbed and transformed plays a key role. In order to maximize the amount of active sites exposed to the fluid, the active phases of heterogeneous catalysts are often dispersed on a high-surface area solid carrier. This allows stabilizing small particles of the active compounds, improving their surface/bulk ratio. However, this presents the drawback that the active phases are diluted, and it would be desirable to design catalysts with appropriate solid state, surface, and morphological properties but avoiding the diluting effect of the support.

A particular application where dilution of the active phases presents great disadvantages is NO_x storage and reduction (NSR). NSR is one of the most suitable technologies for NO_x removal in diesel exhausts, which is a hot topic of ongoing research [3–6]. It operates in cycles where NO_x are continuously chemisorbed on a catalyst that is periodically regenerated by feeding pulses of a reductant. Conventional

NSR catalysts, like Pt/Ba/Al₂O₃ formulations, combine a NO_x storage compound (typically an alkali compound) with a noble metal to accelerate NO oxidation to NO₂. In this application, high NO_x storage capacity is required, and dispersion and dilution of the active phases has a negative impact in NO_x chemisorption.

To avoid dispersion of the active phases, a novel concept is introduced in this paper. It comprises the preparation of macroporous carrier-free NSR catalysts by using a colloidal crystal template, which allows the access of gases to the particles' bulk. The utilization of colloidal crystal templates has demonstrated to be a suitable synthetic route to obtain solid catalysts with a macroporous structure [7,8], therefore improving the diffusion of gases in heterogeneous catalytic reactions [9–15]. However, macroporous catalysts prepared with colloidal crystal templates have never been tested for NO_x storage and reduction.

The catalyst prepared in this study is a copper-containing Sr-Ti mixed oxide, mainly consisting of an intimate mixture of SrCO₃ and Sr-Ti perovskites. This mixture of phases has been specially designed to combine the high NO_x chemisorption capacity of the former phase with the NO oxidation capacity of the latter [16,17]. The design and synthesis of specific tailor-made mixed oxides able to perform complex

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functions is one of the main topics of research in the field of heterogeneous catalysis, and strontium titanates are mixed oxides with relevant catalytic applications [18–23]. The storage and reduction of NOx has been reported on copper-containing SrTiO₃ [20], this catalyst being also active to accelerate diesel soot combustion [21]. Doped strontium titanates have been also proposed as potential materials for anodes in solid-oxide fuel cell operating directly on hydrocarbon fuels, because of the resistance towards carbon formation [24], for photocatalytic production of H₂ [25], and for propane [26] and methane [27] oxidation.

The goal of this study is to demonstrate the high NOx storage capacity of the macroporous carrier-free catalyst prepared, and that stored NOx can be properly reduced to N₂.

2. Experimental details

2.1. Catalysts preparation

As a proof of concept, three catalysts have been prepared and tested, which are referred to as SrTi-macro, SrTiCu-macro and SrTi-ref. The catalysts SrTi-macro and SrTi-ref have the same composition, but the former has been prepared by infiltration of the metal precursors in a polymethylmethacrylate (PMMA) colloidal crystal template, which is removed by calcination, while the latter has been obtained by calcination of a mixture of precursors. The catalyst SrTiCu-macro is similar to SrTi-macro but doped with copper.

Polymethylmethacrylate (PMMA) colloidal crystals were prepared by polymerisation in boiling aqueous solution of methylmethacrylate, methacrylic acid and divinylbenzene in 100:1:5 vol ratio. Potassium persulfate was used to initiate the polymerization, which was conducted for 75 min. After cooling, the colloidal crystals of PMMA spheres were conformed by centrifugation.

For preparation of SrTi-macro, 5 g of PMMA template was impregnated with a 1:1 water:etanol solution of strontium nitrate (1.15 g of strontium nitrate per gram of PMMA). After drying, titanium tetraisopropoxide (0.48 g per gram of PMMA) diluted in 2-propanol was impregnated and the solid was dried at 80 °C. The Sr:Ti atomic ratio used was 3.2, that is, there is an excess of Sr with respect to that required to yield the SrTiO₃ perovskite. The goal was to prepare a mixture of phases combining SrCO₃ (with high NOx storage capacity) and SrTiO₃ (with high NO oxidation capacity). This was confirmed by XRD and microFRX (see below). The catalyst referred to as SrTiCu-macro was prepared following the same procedure, but in this case, copper nitrate was impregnated into PMMA together with strontium nitrate (strontium nitrate:copper nitrate weight ratio 34.5). The impregnated PMMAs were calcined at 650 °C for 1 h (heating rate of 1 °C/min) and the temperature was increased afterwards at 10 °C/min up to 850 °C. The reference catalyst, (SrTi-ref) was prepared with the same composition than SrTi-macro but without PMMA template.

For comparison, a reference 1%Pt/10%Ba/Al₂O₃ catalyst was also prepared. Ba(CH₃COO)₂ was loaded on commercial γ -alumina (Alfa Aesar 99.97%) by wetness impregnation using a water solution to reach 10 wt.% Ba, and after drying at 80 °C overnight, the same procedure was repeated with Pt(NH₃)₄(NO₃) for 1 wt.% Pt loading. Finally, the catalyst was dried at 100 °C for 4 h and calcined at 550 °C for 4 additional hours.

2.2. Catalysts characterization

SEM images were obtained in a JEOL microscope, model JSM-840.

The porous structure of the catalysts was studied by mercury intrusion porosimetry and N₂ adsorption-desorption at –196 °C. N₂ adsorption-desorption isotherms were obtained in an automatic volumetric system (Autosorb-6, Quantachrome) and data were evaluated by calculating BET surface areas. The catalysts were outgassed at 150 °C for 4 h before the N₂ adsorption measurements.

Mercury porosimetry analysis was performed in a Poremaster 60 GT

(Quantachrome). This equipment is capable of intruding mercury up to 60000 psi reaching pores with diameters of 3.6 nm. All powdered samples were submitted to a prior outgassing treatment at 50 °C under vacuum (10 Torr) for 12 h. Samples were then analyzed in low pressure mode and high pressure mode consecutively. A contact angle (θ) of 140 °C and a value of mercury surface tension (γ) of 0.48 J/m² were used. Intrusion pressure relates inversely to the pore diameter through the Washburn equation but has to be reminded that pore diameter obtained relates to the entrance of the pore while pore diameter through the channel may vary [28]. Mercury porosimetry of powder samples is complex due to the occurrence of interparticle and intraparticle intrusions as well as bed packing effects. Such effects are considered to occur up to a pressure of 50 psia, which corresponds to a pore diameter of 2133 nm. For the sake of clarity, interparticle filling region is not shown (diameter greater than 2100 nm). Also, intrusion in pores smaller than 10 nm is not shown, as most probably is affected by compressibility of the sample.

The nature of the different crystallographic phases present on the catalysts was studied by XRD, and the composition by Micro-FRX. Diffractograms were obtained in a Rigaku Miniflex II diffractometer, using CuK α radiation ($\lambda = 0.15418$ nm), between 10 and 60° (2 θ) with a step of 0.025°. Micro-XRF measurements were performed in an Orbis Micro-XRF Analyzer from EDAX. Areas of 300 μ m in diameter were analyzed and three different spots were measured and averaged to obtain the mean composition of each catalyst.

The reducibility of the catalysts was studied by H₂-TPR experiments, which were performed in a Micromeritics Pulse Chemisorb 2705 device. 40 mg of catalyst were loaded on a tubular quartz reactor with 5 mm inner diameter coupled to a thermal conductivity detector. The heating rate was 10 °C/min from room temperature to 1000 °C and the gas flow was 40 ml/min with 5 vol.% H₂ in Ar. A cold trap was placed before the TCD, consisting of a mixture of isopropyl alcohol and liquid nitrogen (temperature –89 °C).

2.3. NOx chemisorption and NSR experiments

NOx chemisorption-desorption experiments were performed in temperature ramp conditions in a fixed-bed reactor coupled to specific NDIR-UV gas analyzers for NO, NO₂ and O₂ monitoring (Fisher–Rosemount, models BINOS). A gas stream (500 ml/min; GHSV = 30000 h^{–1}) with 500 ppm NO + 5% O₂ in N₂ was used, and the experiments consisted of heating the reactor from room temperature up to 800 °C at 10 °C/min. The catalysts were kept at room temperature under the reaction gas mixture for 15 min before heating, but chemisorption in these conditions was null for all catalysts.

In situ DRIFTS isothermal experiments were performed at 450 °C with catalysts SrTi-macro and SrTiCu-macro, to identify the nature of the chemisorbed NOx species. An infrared spectrometer Jasco, model FT/IR-4100, was used with a reaction cell that allows temperature and gas flow composition control. The cell was designed to allow the gas flow through the catalytic bed, consisting of 100 mg of undiluted catalyst. The temperature was increased up to 450 °C in inert gas (Ar), and after 30 min a background spectrum was recorded and subtracted from further spectra. Then, the inert gas was replaced by 100 ml/min of a gas stream with 500 ppm NO + 5% O₂ in Ar and the chemisorbed species were monitored as a function of time.

Isothermal NOx storage and NSR experiments were carried out in a fixed-bed reactor coupled to a mass spectrometer Pfeiffer Vacuum (model OmniStar) running at 1 s frequency. The experiments were performed with 80 mg of the catalyst SrTiCu-macro diluted with 300 mg of SiC. The temperature was increased up to 450 °C in Ar flow, and then the inert gas was replaced by the reaction gas mixture (100 ml). The NOx chemisorption experiments were carried out with 500 ppm NO + 5% O₂ in Ar. The NSR experiments were also performed with 500 ppm NO + 5% O₂ in Ar and with 500 ppm NO + 5% O₂ + 5% CO₂ + 5% H₂O in Ar. All gases were added to the mixture

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