Catalysis Today 191 (2012) 65–74

Contents lists available at SciVerse ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Effect of Ag, Pd and Co promoters on the Selective Catalytic Reduction (SCR) of NO_x by ethanol over sulfated ceria-zirconia catalysts

Alexandre Westermann, Bruno Azambre*, Alain Koch

Laboratoire de Chimie et Méthodologies pour l'Environnement (LCME), Institut Jean Barriol, Université Paul Verlaine – Metz, Rue Victor Demange 57500 Saint- Avold, France

ARTICLE INFO

Article history:
Received 14 September 2011
Received in revised form
14 December 2011
Accepted 19 December 2011
Available online 2 February 2012

Keywords:
Nitrogen oxides
$Ce_xZr_{1-x}O_2$
TPSR
DRIFTS
Sulfates
$DeNO_x$

ABSTRACT

In this study, our purpose was to investigate to what extent the deposition of some metal promoters such as Pd, Co and Ag may alter the performances of EtOH-SCR sulfated ceria-zirconia catalysts and the complex network of reactions pertaining to the reaction mechanism. In the case of Pd and Co, the characterization of metal-promoting species by X-Ray Diffraction (XRD), thermogravimetry (TGA) and DRIFTS of adsorbed CO revealed the presence of highly-dispersed cationic species coexisting with small clusters (< 1–2 nm), whereas for Ag an unstable bulk Ag_2SO_4 phase was also detected before the SCR test. Specific temperature-programmed surface reactions (TPSR) and steady-state profiles of a dozen of gaseous species monitored under 1920 ppm NO + 3020 ppm C_2H_5OH + 5% O_2 conditions were confronted to the temperature profiles of adsorbed species obtained by *in situ* DRIFTS. Under isothermal conditions, $DeNO_x$ yields of 40, 37 30 and 30% at 350–400 °C were obtained respectively for the sulfated support (SCZ28) and the Co($1.03_{wt\%}$)/SCZ28, Ag($3.00_{wt\%}$)/SCZ28 and Pd($0.24_{wt\%}$)/SCZ28 catalysts. TPSR data were then deeply discussed according to the nature of the metal deposited. This allowed us to reveal that the promoter effect can be sometimes either positive or negative depending on the temperature range investigated and the occurrence of deactivation processes.

1. Introduction

Compared with other post-treatment technologies such as NO_x adsorbers or urea-SCR, the intrinsic advantages of a lean-NO_x catalyst technology, such as HC-SCR, are its simplicity in terms of engine control, after treatment system and infrastructure implementation requirements. The reductant efficiency in the catalytic reduction of NO_x to N_2 by hydrocarbons usually follows the order: alkanes < alkenes < oxygenated [1]. Among the class of oxygenated compounds, ethanol is one of the most interesting for mobile applications because on the one hand, it can be produced from renewable energy sources and blended with gasoline and/or diesel fuel, and on the other hand, it is less toxic than ammonia. With this reductant, high activities and selectivities to N_2 were achieved at medium temperatures (300–400 °C) over Ag/Al_2O_3 [2] but also on Ag- or Ba-Y zeolites [3,4]. Among the other investigated catalysts, ion-exchanged zeolites, such as Fe-, Co- or Cu- on BEA and Ag- on ZSM-5 have also shown some interest despite their lower activity [5–7].

The mechanism of NO_x reduction with oxygenates on silver-promoted catalysts, namely Ag/Al_2O_3, has been investigated by many authors [2,3,8–10], but still remains partly unclear towards some points. This is widely due to the ill-defined state of silver during the HC-SCR reaction, which is strongly affected by interdependent parameters such as: the initial silver loading and salt used as precursor, the characteristics of the support, the reaction temperature, the concentration of reactants/contaminants (C-containing, NO_x, O_2, H_2, SO_2, H_2O...) at the solid/gas interface. It has been proposed that Ag species in the +1 oxidation state promote the SCR reaction by increasing the yield of enolic/enolate species, which transform to the key isocyanate (—NCO) intermediates by reaction with NO_2 [2,10]. On the other hand, metallic silver clusters were found rather inactive for NO_x reduction while promoting the NO oxidation to NO_2 and the HC depletion by total oxidation [8].

Apart from the considerable body of data available on Ag/Al_2O_3, literature studies devoted to the role of promoters and mechanisms of EtOH-SCR on other catalytic systems are much more scarce. In [11], we aimed to investigate the performances in ethanol-SCR of novel sulfated ceria-zirconia (SCZ) catalysts prepared by direct sulfation of the $Ce_xZr_{1-x}O_2$ nanopowders (with x = 0, 0.2, 0.5, 0.8 and 1) in sulfuric acid. By comparison with the sulfated single oxides, the sulfated mixed oxides with intermediate Ce molar contents (typically between 0.2 and 0.8) displayed a superior behaviour, with $DeNO_x$ yields of the order of 40–50% between 300 and 400 °C [8]. The sulfation treatment was also found to be beneficial since it promoted the mild oxidation of the reductant instead of its total oxidation to CO_2. The SCR-active sites on SCZ materials could possibly consist of $[Ce(O,Zr)_n\cdots H]^{x+}$ adducts in the vicinity of a surface

---

* Corresponding author. Tel.: +33 387939106; fax: +33 87939101.
E-mail address: bazambre@univ-metz.fr (B. Azambre).

0920-5861/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2011.12.030

sulfate or bisulfate species [8,12]. The intrinsic activity of Ce sites was found to be slightly higher when associated with tetragonal structures (or intermediate compositions) than with the cubic ones (Ce-rich compositions). By contrast, the sulfated zirconia catalyst with a monoclinic structure was found to be almost completely inactive under the same conditions [8].

Due to their intrinsic SCR activity, SCZ supports can be considered as a starting point to develop more complex, *i.e.* promoted, SCR catalysts. Hence, the aim of this article is to assess to what extent the reaction pathways and performances of SCZ catalysts could be affected by the presence of supported promoters such as Pd, Co and Ag. We focused on these metals because, on the one hand, Pd and Co supported SCZ catalysts showed an honourable activity in CH_4-SCR [13] and on the other hand, Ag is obviously interesting for ethanol-SCR [2,3]. In this study, the conditions of formation of important SCR intermediates produced during temperature-programmed surface reactions (TPSR) and steady-state experiments are investigated in order to assess the role of each promoter and to establish structure–properties relationships.

2. Experimental

2.1. Catalysts

The $Ce_{0.21}Zr_{0.79}O_2$ (CZ) nanopowder (S_{bet} = 180 m^2/g) was kindly supplied by Rhodia (La Rochelle, France). The sulfated ceria-zirconia material (labeled SCZ28 hereafter) was obtained by: (i) reacting the CZ material (5 g) with a 0.5 M H_2SO_4 solution (100 mL) for 45 min; (ii) washing the slurry with diluted 0.05 M H_2SO_4; (iii) drying at 70 °C under vacuum for 24 h and calcination in air at 500 °C for 2 h. The resulting material has a specific surface area of 185 m^2/g and a sulfate density of 2.0 SO_4^{2-}/nm^2.

Metal-supported catalysts were prepared by incipient wetness impregnation of the ceria-zirconia mixed oxide using an appropriate amount of $Pd(Cl)_2$, $Ag(NO_3)$ and $Co(NO_3)_2$ precursors (product from Aldrich) dissolved in NH_3 in order to obtain a Pd, Ag and Co loading of 0.24, 3.00 and $1.03_{wt\%}$ respectively. After drying, the catalysts were calcined at 500 °C under static air for 2 h.

2.2. Reactivity studies

TPSR and steady-state isothermal experiments were carried out in a tubular quartz reactor itself placed in a Carbolite MTF furnace regulated with a Eurotherm temperature controller. Standard conditions for ethanol-SCR tests were 1920 ppm NO + 3020 ppm C_2H_5OH + 5% O_2 (He balance); $m_{catalyst}$ = 0.2 g; GHSV = 50,000 h^{-1}. Certified gases (NO/He, NO_2/He, O_2 and He) were fed from compressed cylinders provided by Air Liquide and their concentrations were adjusted with Brooks 5850S mass-flow controllers. Constant ethanol concentration (calculated from Antoine coefficients) was supplied to the reacting stream by means of a bubble tower purged by He flow and immerged in a thermostated bath at 2 °C (accuracy ±0.1 °C). Before reaching the catalyst bed (consisting of the pelletized catalyst powder crushed and sieved to 0.5–1 mm and two quartz wool plugs), all the fed gases were allowed to pass through a home-made glass mixture chamber for further dilution and better homogeneity of the reacting stream. The composition of the reactor outflow was continuously monitored using a heated FTIR gas cell (Cyclone Series – Specac, optical pathlength = 2 m, v = 0.19 L) coupled to a Varian Excalibur 4100 FTIR spectrometer with a DTGS detector. The temperature of the gas cell was maintained at 110 °C to avoid any condensation of the reactants/products during the tests. FTIR spectra, referenced to a He background, were recorded using a 2 cm^{-1} resolution and co-addition of 50 scans. These parameters allowed to obtain satisfying signal/noise ratio as well as a sufficient time resolution (the sampling rate was 1 spectrum per 10 °C intervals during the TPSR) but also to detect the fine gas structure in most cases for identification purposes.

Prior to catalytic tests, the catalysts were pre-treated from 25 to 500 °C under 5% O_2 in He (ν = 20 °C/min) to remove most of adsorbed impurities. After cooling down to 35 °C (under He), the standard gas mixture was sent through the catalyst and the temperature was ramped from 35 to 500 °C (TPSR experiments, ν = 5 °C/min). Then, the temperature was decreased progressively from 500 to 150 °C by dwells of 50 °C to measure the SCR activity of the catalysts under steady-state conditions (in our conditions after 1 h at each temperature). On the whole set of catalytic experiments, up to 22 different N- and C-compounds were detected and identified using different FTIR spectral libraries. 10 compounds (ethanol, acetaldehyde, ethene, CO, CO_2, ethylnitrite, NO, NO_2, N_2O and NH_3), among the most important ones in terms of amounts sent/produced (with the exception of HCN that could not be accurately calibrated), were quantitated from their areas or absorbances in FTIR spectra using certified standards or other methodologies. Complex signal treatment procedures using different steps of spectral subtractions were often required to get rid of spectral interferences between some compounds. The quantification accuracy was checked systematically using C- and N-balances. In most cases, the sum of the computed concentrations closely corresponded to the concentrations of the C- and N-feeds. Due to the presence of rather high amounts of ethyl nitrite below 150 °C, we chose to include this compound in the measurement of the NO_x conversion:

$$NO_x\,\text{conversion}\,(\%) = \frac{[NO_x]_{in} - ([NO] + [NO_2] + [C_2H_5ONO])_{out}}{[NO_x]_{in}} \times 100$$

The selectivity to N_2 was calculated as follows:

$$N_2\ \text{selectivity}\,(\%) = \frac{([NO]_{in} - [NO]_{out}) + [NO_2] + 2[N_2O]}{[NO]_{in} - [NO]_{out}} \times 100$$

The nature of adsorbed species occurring during the SCR reaction was investigated by DRIFTS in function of the temperature. Diffuse reflectance (DR) spectra were recorded in the 4000–700 cm^{-1} range (resolution 4 cm^{-1}, 100 scans) on a Varian Excalibur 4100 FTIR spectrometer equipped with a MCT detector, a "Graseby Specac" optical accessory and a Spectra-Tech environmental cell. After an *in situ* pre-treatment at 400 °C under He flow, the catalysts were allowed to cool down to 35 °C and then exposed to a flow mixture (unless otherwise stated) of 1920 ppm NO + 3020 ppm C_2H_5OH + 5% O_2 (He balanced) for 1 h (adsorption step). After this adsorption step, the temperature was raised by dwells of 50 °C up to 380 °C under the same atmosphere (TPSR conditions). At each temperature, difference spectra were obtained by using the single-beam spectra of the corresponding non-reacted catalyst as reference.

2.3. Characterization studies

X-Ray Diffraction (XRD) analyses were carried out thanks to a Bruker-AXS diffractometer with the Cu K_α radiation (1.5405 Å). Powdered diffraction patterns were recorded between 25° and 65° (2θ) using increments of 0.01° and a counting time of 0.1 s.

Thermogravimetric (TG) and derivative (DTG) profiles corresponding to the evolution of sulfate species existing on the different promoted SCZ materials were determined using a Mettler-Toledo TGA/SDTA851e TG analyzer. The heating program consisted of heating the catalysts (50 mg) under Ar flow (20 mL/min) from 25 up to 1100 °C (ν = 10 °C/min).