Available online at www.sciencedirect.com

ScienceDirect

Catalysis Today 137 (2008) 288–291

CATALYSIS TODAY

www.elsevier.com/locate/cattod

DRIFT study of the interaction of NO and O_2 with the surface of $Ce_{0.62}Zr_{0.38}O_2$ as $deNO_x$ catalyst

Małgorzata Adamowska [a,b,d,*], Andrzej Krztoń [a], Mieczysława Najbar [c], Patrick Da Costa [d], Gérald Djéga-Mariadassou [d]

[a] Centre of Polymer and Carbon Materials, Polish Academy of Sciences, 34 M. Curie-Skłodowskiej str., 41-819 Zabrze, Poland
[b] Silesian University of Technology, Faculty of Chemistry, 9 Strzody str., 44-100 Gliwice, Poland
[c] Jagiellonian University, Faculty of Chemistry, 3 Ingardena str., 30-060 Kraków, Poland
[d] Laboratoire de Réactivité de Surface, Université P. et M. Curie, CNRS UMR 7609, 4 Place Jussieu, Casier 178, 75 252 Paris Cedex 05, France

Abstract

Gas–solid interactions and surface intermediates evolution after NO adsorption onto calcined $Ce_{0.62}Zr_{0.38}O_2$ were investigated. The results of adsorption and temperature-programmed desorption of NO were explained using diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) coupled with temperature-programmed experiments in environmental cell. Surface NO-containing species such as nitrites and nitrates were identified during evolution of NO on the surface of $Ce_{0.62}Zr_{0.38}O_2$ solid solution at low and high temperature. The ceria–zirconia solid solution was found to be active in $deNO_x$ reaction in the presence of a ‘‘toluene, propene and propane’’ mixture.

Keywords: $deNO_x$; Ceria–zirconia; TPD; DRIFTS; Toluene

1. Introduction

Nitrogen oxides emitted in atmosphere (NO, NO_2 and N_2O) have negative environmental impact. Nitrogen oxides contribute to photochemical smog, acid rains, global warming and ozone layer weakening [1–4]. Nearly all anthropogenic NO_x (95%) derive from transport (49%) and gas or coal power plants (46%). Two main methods for removal of NO_x from emission gases are employed [5]:

(1) The three-way catalyst (TWC) developed for mobile sources [6].
(2) The selective catalytic reduction with ammonia (NH_3-SCR), which is applied mainly for big stationary sources such as power plants.

Three-way catalysts are capable of simultaneously and efficiently converting CO, hydrocarbon (HC) and NO_x to CO_2, H_2O and N_2. The catalyst is generally constituted by a metallic phase of Pt, Pd and Rh deposited on a high specific surface area support such as γ-alumina doped with ceria, zirconia and other basic oxides (BaO, La_2O_3, etc.) [6].

Selective catalytic reduction by ammonia is the main industrial catalytic technology for abatement of nitrogen oxides emission from coal combustion. However, the use of ammonia as a reductant is undesirable for a number of reasons (cost of large scale NH_3-SCR reactors, necessity of ammonia storage, risk of environmental contamination). More attractive and alternative reducing agents than ammonia could be hydrocarbons [7–8].

A large number of catalysts have been evaluated in the SCR by hydrocarbons (HC-SCR). These catalysts are mainly metal ion-exchanged zeolithes (e.g. Cu–, Co–, Fe–, Pt–) and supported platinum group metals (PGMs) such as Pt, Pd, Rh, Ag, on various metal oxides (e.g. Al_2O_3, TiO_2, CeO_2) [9].

Ceria-based oxides have attracted much attention because of their high oxygen storage capacity (OSC) and unique redox properties. CeO_2 is able to undergo rapid reduction/oxidation cycles according to the reaction: $2CeO_2 \leftrightarrow Ce_2O_3 + {}^1\!/_2O_2$. However, pure CeO_2 is rarely used because of its poor thermal stability [10–14]. The addition of zirconium to ceria leads to

---

* Corresponding author at: Centre of Polymer and Carbon Materials, Polish Academy of Sciences, 34 M. Curie-Skłodowskiej, 41-819 Zabrze, Poland. Tel.: +48 32 271 60 77; fax: +48 32 231 28 31.
E-mail address: malgorzata.adamowska@wp.pl (M. Adamowska).

0920-5861/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2008.01.013

improvements in ceria oxygen storage capacity, redox properties, thermal resistance and better catalytic activity at lower temperatures [10–14].

This work reports some results related to the TPD and DRIFT data for NO adsorption on the surface of the most active $Ce_{0.62}Zr_{0.38}O_2$ solid solution. It is then interesting to investigate the interaction of NO and O_2 with the surface of $Ce_xZr_{1-x}O_2$, because NO adsorption and its subsequent oxidation is the first crucial step of $deNO_x$ reaction according to Djéga-Mariadassou's $deNO_x$ model [15]. This step has to be considered for designing the most efficient $deNO_x$ catalyst.

2. Experimental

The ceria–zirconia $Ce_xZr_{1-x}O_2$ ($x = 0.17$, 0.62, 0.8) solid solutions, obtained via hydrothermal synthesis from nitrate precursors, were provided by Rhodia Company. Before each TPD, FTIR and catalytic experiment, the samples were calcined *in situ* in air for 2 h at 500 °C. The samples for XRD, BET and TPR measurements were previously calcined in the same conditions but outside equipment.

Powder X-ray diffraction (XRD) was performed on a Siemens model D-500 diffractometer with Cu K_α radiation. Measurements were carried out for 2θ ranging from 10° up to 90°.

The specific surface area (S_{BET}) measurements and surface characterization were performed by BET method using N_2 adsorption/desorption at 77 K (Micromeritics ASAP 2010).

Temperature-programmed reduction (TPR) experiments were performed using 50 mg samples of $Ce_xZr_{1-x}O_2$ from room temperature up to 950 °C at 7.5 °C/min, under a mixture of 5% (v/v) H_2/Ar with a flow rate of 0.5 dm^3/h. Hydrogen consumption was measured with a thermal conductivity detector (TCD); water was trapped in a dry ice-cooled trap; TCD calibration with mixture of 5% (v/v) H_2/Ar was performed prior to each experiment.

Catalytic isothermal steady-state experiments for all the solid solutions were performed in the 170–500 °C temperature range in the flowing gas mixture containing: 250 ppm NO, 247 ppm (1000 ppm C_1) hydrocarbon mixture (50 ppm propane, 133 ppm propene, 64 ppm toluene) and 5% (v/v) O_2 in argon. Such a mixture represents incompletely burned hydrocarbons always present in the flue gas from coal boilers, with a quantity similar to that of NO. The reactor outflow was analyzed using the combination of four different detectors (an Eco Physics CLD 700 AL chemiluminescence NO_x analyzer (for NO and total NO_x), Ultramat 6 IR analyzers (for N_2O, CO and CO_2) and one FID detector (FIDAMAT 5E) (for total concentration of hydrocarbons).

Temperature-programmed desorption (TPD) was performed after NO adsorption at room temperature in the presence of oxygen (250 ppm NO and 5% (v/v) O_2/Ar). TPD was carried out from RT up to 500 °C with a heating rate of 3 °C/min in 5% (v/v) O_2/Ar.

DRIFT spectra were recorded in the range of 700–4000 cm^{-1} using a BRUKER IFS 66 V spectrometer, equipped with a MCT detector and a Spectra-Tech Collector high-temperature environmental cell, fitted with ZnSe window. Prior to each experiment, the sample was placed in a crucible located in the high-temperature cell, heated up to 400 °C in the 20% (v/v) O_2/Ar flowing mixture, during 2 h, and followed by cooling to room temperature. The gas mixture, containing 250 ppm of NO in 5% (v/v) O_2/Ar, was passed through the sample during 2 h at room temperature for adsorption and the temperature-programmed desorption was then carried out up to 400 °C with steps every 50 °C with a 10 °C/min heating rate.

3. Results and discussion

3.1. $Ce_xZr_{1-x}O_2$-mixed oxides properties

The specific surface area of ceria–zirconia samples changes in the following order: ca. 185 m^2/g for $Ce_{0.8}Zr_{0.2}O_2$, 131 m^2/g for $Ce_{0.62}Zr_{0.38}O_2$ and 184 m^2/g for $Ce_{0.17}Zr_{0.83}O_2$. The average pore diameter ranges from 3.9 to 10.2 nm. According to the IUPAC classification, the studied supports present mesoporosity.

On the basis of XRD patterns, $Ce_{0.8}Zr_{0.2}O_2$ and $Ce_{0.62}Zr_{0.38}O_2$ were isostructural with cubic CeO_2, while $Ce_{0.17}Zr_{0.83}O_2$ was identified as a mixture of tetragonal and monoclinic phases. According to Thammachart et al. [16], $Ce_xZr_{1-x}O_2$ preferably crystallizes in a cubic structure if x is equal or lower than 0.5.

Reducibilities of the samples $Ce_{0.8}Zr_{0.2}O_2$ and $Ce_{0.62}Zr_{0.38}O_2$ were better than that of the sample $Ce_{0.17}Zr_{0.83}O_2$. It is known that introduction of zirconium (for $x \leq 0.5$) to cerium oxide causes increase of mobility of oxygen ions as a result of substitution of the Ce^{4+} cation by the smaller Zr^{4+} one (lattice distortion), which favors structural defect formation.

3.2. Catalytic $deNO_x$ activity

The catalytic performance of ceria–zirconia-mixed oxides $Ce_xZr_{1-x}O_2$ ($x = 0.17$, 0.62, 0.8) was determined by steady-state experiments in the presence of hydrocarbons mixture (Fig. 1). Results show that all supports are active in $deNO_x$ reaction. Maximal NO_x conversion depends on x value and reaches 19% at 324 °C for $Ce_{0.17}Zr_{0.83}O_2$, 22% at 312 °C for $Ce_{0.8}Zr_{0.2}O_2$ and 27% at 322 °C for $Ce_{0.62}Zr_{0.38}O_2$, respec-

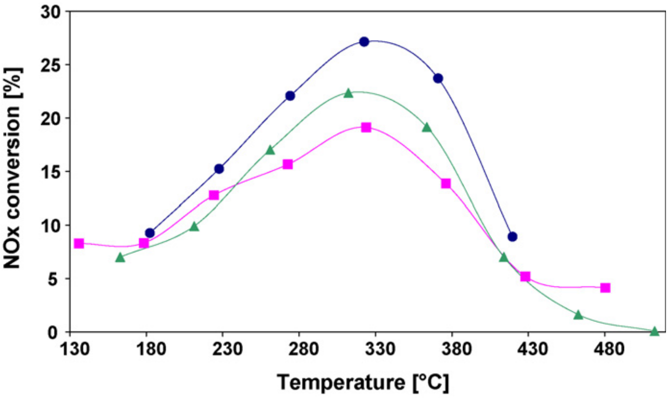

Fig. 1. Evolution of NO_x conversion to N_2 in the course of steady-state $deNO_x$ reaction on $Ce_{0.8}Zr_{0.2}O_2$ (▲), $Ce_{0.62}Zr_{0.38}O_2$ (●), $Ce_{0.17}Zr_{0.83}O_2$ (■) in the presence of 247 ppm hydrocarbon mixture (propane, propene and toluene), 250 ppm NO, 5% O_2, GHSV = 30,000 h^{-1}.

tively. The conversion of NO_x to N_2 shows a dependence on the reducibility of $Ce_xZr_{1-x}O_2$ as a function of the ceria/zirconia ratio. Thus, deNO$_x$ conversion is controlled by the facility of oxygen vacancies formation. It can thus be thought that oxygen vacancies leads to the so called ‘‘coordinatively unsaturated sites’’ (‘‘cus’’) permitting NO, HC and water adsorptions on cerium cation active sites. NO oxidation being the first step of the earlier proposed mechanism of HC-deNO$_x$ could result in an increase of oxygen vacancies population [17].

3.3. Study of surface NO-containing species

According to Djéga-Mariadassou [15], the temperature of NO dissociation can be predicted by TPD of the NO_x adsorbed on catalyst surface. Fig. 2 shows the TPD profile of NO_x species in Ar/O_2 flow from $Ce_{0.62}Zr_{0.38}O_2$ sample. Three NO desorption peaks at 94, 185 and 450 °C are observed. The TPD plot shows that there are three sites of NO adsorption. We assume that the active sites depend on different degrees of support unsaturation with different cerium oxidation states (reduction). So we can distinguish three steps of support reduction: almost completely oxidised support, partially reduced system cation – vacancy and almost completely reduced system cation – two vacancies. So the strength of NO bonding with the ceria surface depends on the degree of support reduction (unsaturated sites).

Fig. 3 shows DRIFT spectra of adsorbed species over $Ce_{0.62}Zr_{0.38}O_2$ in flowing NO + O_2/Ar at room temperature as a function of time of exposure. Only one strong band is observed at 1186 cm^{-1} and few weak bands at 1323, 1438 and 1598 cm^{-1}. The NO_2^- and NO_3^- ions formed are negatively charged fragments and there are several possibilities of their formation on the surface. According to Hadjiivanov [18], when NO_2^- is coordinated with the cation via oxygen atom, the corresponding species are called nitrito compounds. The bands corresponding to the nitrito monodentate species are usually observed at 1470–1375 cm^{-1} (νN=O) and at 1206–1065 cm^{-1} (νN–O). While the bands corresponding to nitrito bidentate groups are most often observed at 1315–1265 cm^{-1} (ν_s) and at 1203–1176 cm^{-1} (ν_{as}). When NO_2^- is coordinated via its N atom, the respective species are called nitro compounds ((ν_s) 1350–1250 cm^{-1} and 1650–1375 cm^{-1} (ν_{as})). Regarding NO_3^-, it is also coordinated by one or two of its oxygen atoms. Nitrates monodentates are observed at 1530–1480 and 1290–1250 cm^{-1}, nitrates bidentates at 1585–1500 and 1300–1260 cm^{-1} while nitrates bridging at 1650–1600 and 1225–1170 cm^{-1}. According to [19] NO_3^- ions are preferably formed at high temperature. The strong band observed during in NO + O_2/Ar at 1186 cm^{-1} can be attributed to both nitrite and nitrate anions. Since NO adsorption was realized at room temperature, so we postulate that nitrite anion (NO_2^-) was mainly formed during adsorption which was coordinated with surface cation via one or two oxygen atoms. Week bands may be ascribed to nitrite anions binding with the surface cations in another way [19].

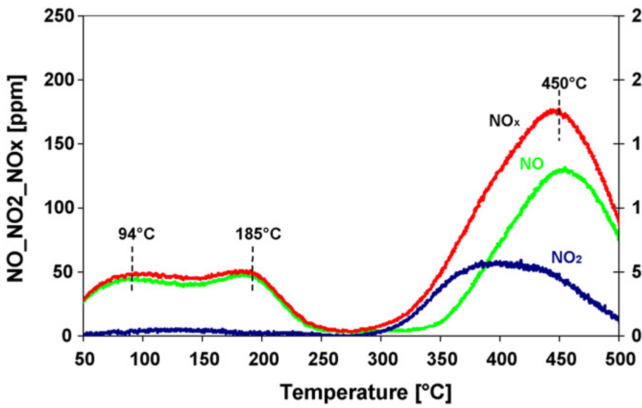

Fig. 2. TPD profile in the presence of 250 ppm of NO, 5% O_2, evolution of NO_x, NO and NO_2 on $Ce_{0.62}Zr_{0.38}O_2$.

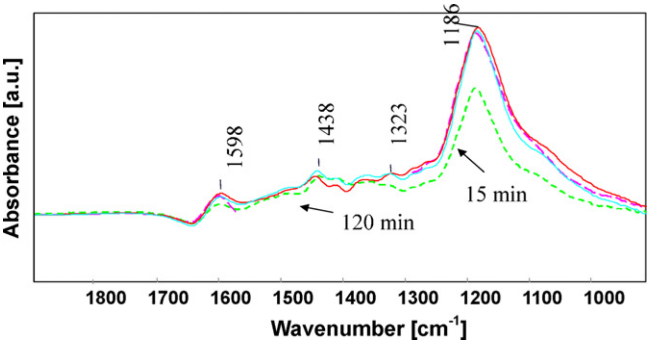

Fig. 3. DRIFT spectra of adsorbed species over support $Ce_{0.62}Zr_{0.38}O_2$ in following NO + O_2 at room temperature.

Fig. 4 shows DRIFT spectra recorded at different temperatures under O_2/Ar flow, after RT adsorption of NO/O_2 in Ar on $Ce_{0.62}Zr_{0.38}O_2$ sample. Surface NO-containing species such as nitrites and nitrates were identified. Those species were formed during low- and high-temperature evolution of NO on the surface of $Ce_{0.62}Zr_{0.38}O_2$ solid solution. Martínez-Arias et al. [19] have shown that NO_2^- formation is connected with the transfer of an (unpaired) electron from the NO molecule to the ceria surface. During desorption, we can

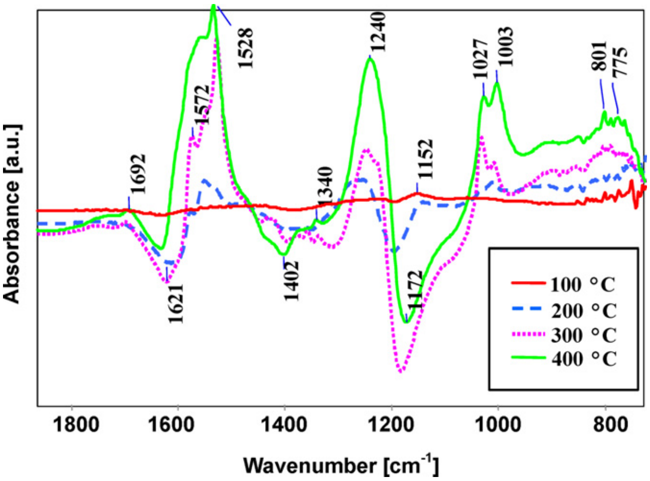

Fig. 4. DRIFT differential spectra recorded at different temperature under 5%O_2/Ar, after RT adsorption of NO (250 ppm) and O_2 (5%) in Ar on $Ce_{0.62}Zr_{0.38}O_2$.

observe simultaneously the disappearance of the strong band around 1186 cm^{-1} and the weak band around 1438 cm^{-1} and the appearance of bands with maxima at 775, 801,1003, 1027, 1240 and 1528 cm^{-1}, whose intensities increase with temperature. Bands around 1027, 1240 and 1528 cm^{-1}can be attributed to chelating or bidentate nitrate. Therefore, we can claim that the nitrites are transformed to nitrates as temperature increases.

Adamski and Sojka [20] have shown that various nitrates were the final products of NO transformation on $Ce_xZr_{1-x}O_2$ in the presence of O_2, giving rise to the strong bands in the region 1295–1625 cm^{-1}, typical of mono- and polydentate or bridging forms.

On the basis of DRIFT results we can explain more precisely results of adsorption and temperature-programmed desorption of NO. At room temperature, we did not observe the presence of NO_2 in the gas phase (graph not shown). During TPD experiments, at lower temperature, we observe NO desorption which probably comes from the partial decomposition of nitrites, as follows:

$$3NO_2{}^- \rightarrow NO_3{}^- + O^{2-} + 2NO$$

As a consequence, we only observe NO in the gas phase (TPD) and the decay of nitrites bands with, simultaneously, the formation of nitrates bands. However, neither NO nor NO_2 are detected in the gas phase at 250–300 °C.

It seems that the nitrites are transformed to nitrates as temperature increases, according to reaction:

$$NO_2{}^- + O^{2-} \rightarrow NO_3{}^- + 2e^-$$

Above 300 °C, NO_2 desorption (nitrates decomposition) was observed. At high temperature, in the gas phase, NO_2 formed is immediately reduced, in the presence of ceria–ziconia, to NO in accordance with thermodynamic equilibrium:

$$2NO_{2(g)} = 2NO_{(g)} + O_{2(g)}$$

These reactions are realized thanks to exceptional property of cerium oxides which are capable to change easy oxidation degree from +IV to +III, dependent on conditions.

4. Conclusions

The interaction of NO and O_2 with the surface of $Ce_{0.62}Zr_{0.38}O_2$ was investigated. The TPD experiments evidenced that there are three sites for adsorption of NO (“cus”). The nature of the surface species formed upon NO adsorption was determined by DRIFT method. Surface NO-containing species such as nitrites and nitrates are formed during low- and high-temperature evolution of these species on the surface of $Ce_{0.62}Zr_{0.38}O_2$ solid solution. At room temperature, the nitrite anions ($NO_2{}^-$) are mainly formed during adsorption and coordinated with surface cation via one or two oxygen atoms. The nitrites are transformed to nitrates as temperature increases and releasing NO and NO_2, respectively. The ceria–zirconia solid solution was found to be active in $deNO_x$ reaction in the presence of a “toluene, propene and propane” mixture.

Acknowledgments

This work was carried out in the framework of the Polish–French Program Jumelage “Materiaux catalytiques pour l’environnement” supported by CNRS and PAN and French Embassy in Poland (bursary of French Government for Miss Małgorzata Adamowska) and in the framework of EUREKA ! 3230 project “STATIONOCAT”. J.M. Krafft is kindly acknowledged for his help in DRIFT experiments.

References

[1] J.M. Armor, Catal. Today 26 (1995) 99.
[2] Y. Yokoi, H. Uchida, Catal. Today 42 (1998) 167.
[3] E.A. Efthimiadis, G.D. Lionta, C. Christoforou, I.A. Vasalos, Catal. Today 40 (1998) 15.
[4] H. Bosch, F. Janssen, Catal. Today 2 (1988) 369.
[5] V.I. Pârvulescu, P. Grange, B. Delmon, Catal. Today 46 (1998) 233.
[6] N. Hickey, Catal. Today 77 (2003) 419.
[7] R. Burch, J.P. Breen, F.C. Meunier, Appl. Catal. B: Environ. 39 (2002) 283.
[8] M. Wojciechowska, S. Lomnicki, Clean Products Process 1 (1999) 237.
[9] K.A. Bethke, M.C. Kung, B. Yang, M. Shah, D. Alt, C. Li, H.H. Kung, Catal. Today 26 (1995) 169.
[10] Y. Nagai, T. Yamamoto, T. Tanaka, S. Yoshida, T. Nonaka, T. Okamoto, A. Suda, M. Sugiera, Catal. Today 74 (2002) 225.
[11] P. Fornasiero, R. Di Monte, G. Ranga Rao, J. Kašpar, S. Meriani, A. Trovarelli, M. Graziani, J. Catal. 151 (1995) 168.
[12] G. Ranga Rao, P. Fornasiero, R. Di Monte, J. Kašpar, G. Valic, G. Balducci, S. Meriani, G. Gubitosa, A. Cremona, M. Graziani, J. Catal. 162 (1996) 1.
[13] J. Kašpar, P. Fornasiero, M. Graziani, Catal. Today 50 (1999) 285.
[14] A. Trovarelli, M. Boaro, E. Rocchini, C. Leitenburg, G. Dolcetti, J. Alloys Compd. 323–324 (2001) 584.
[15] G. Djéga-Mariadassou, Catal. Today 90 (2004) 27.
[16] M. Thammachart, V. Meeyoo, T. Risksomboon, S. Osuwan, Catal. Today 68 (2001) 53.
[17] M. Adamowska, S. Muller, P. Da Costa, A. Krztoń, P. Burg, Appl. Catal. B: Environ. 74 (2007) 278.
[18] K.I. Hadjiivanov, Catal. Rev. Sci. Eng. 42 (2000) 71.
[19] A. Martínez-Arias, J. Soria, J.C. Conesa, X.L. Seoane, A. Rcoya, R. Cataluña, J. Chem. Soc. Farad. Trans. 91 (11) (1995) 1679.
[20] A. Adamski, Z. Sojka, Catal. Today 119 (2007) 120.