ISCRE25
FLORENCE 2018
BRIDGING
SCIENCE & TECHNOLOGY
The 25th International Symposium
on Chemical Reaction Engineering
20-23 May 2018
Florence, Italy
www.aidic.it/iscre25

Effect of noble metal on the hydrothermal resistance of coupled NSR-SCR for automobile exhaust aftertreatment

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Highlights

- Hydrothermal resistance of coupled NSR-SCR system is investigated.
- Nobel metal dispersion in the NSR catalyst is directly related with NOx elimination.
- Pd behaves better than Pt for NOx removal and N_2 production in the coupled NSR-SCR.
- Pd-based NSR catalysts have lower hydrothermal resistance than Pt in NSR-SCR.

1. Introduction

The demand of improving fuel efficiency of light vehicles and the need to decrease CO_2 emissions have recently led to the introduction of lean-burn engines in Europe. However, the presence of excess of oxygen under lean-burn conditions strongly makes the conventional three-way catalysts inefficient to remove NOx from exhaust gases. In this context, two promising solutions remain under research: NOx storage and reduction (NSR) and NOx selective catalytic reduction (SCR).

With the NSR technology, a limited NOx storage capacity is achieved and some NO may leave the converter, and also NH_3 may release during the regeneration of the trap, especially if H_2 is used as reductant [1]. However, an NH_3-SCR catalyst placed downstream of the NSR trap, if appropriately tuned, can complete the reaction between NO and NH_3, much increasing the pollutant removal efficiency [1]. In order to avoid pressure drop, structured catalysts are required for the cleanup of automobile engine exhausts. In addition, these catalysts must highly resist hydrothermal deactivation. In this work, the hydrothermal resistance of combined NSR-SCR catalytic system is investigated with both fresh and aged monolith catalysts under simulated cycled lean-burn environment.

2. Methods

SCR catalyst was prepared by washcoating a 64 cpsi cordierite monolith with powder 4%Cu/CHA, following the procedure described elsewhere [2]. On the other hand, two NSR monolith catalysts, 1%Pt-15%BaO/Al_2O_3 and 1%Pd-15%BaO/Al_2O_3, were prepared according to our previously reported procedure [2]. The prepared catalysts were submitted to accelerated aging under 5% H_2O in Ar during 16 h at 750 °C. The NOx storage–reduction experiments for the single-NSR and coupled NSR-SCR configuration were also described elsewhere [2]. All prepared samples have been textural and chemically characterized, as powders by ICP-AES, N_2 adsorption-desorption, X-ray diffraction, programmed temperature techniques (H_2-TPR and NH_3-TPD) and X-ray photoelectron spectroscopy (XPS).

The activity and selectivity tests were performed in a vertical downflow stainless steel reactor, inside which the monolith catalysts were placed. The reaction temperature was varied from 140 to 380 ºC. The SCR experiments were performed with the following feedstream composition: 750 ppm NO, 750 ppm NH_3 and 6% O_2 using Ar as the balance gas. When running the system under cycled NSR conditions, the composition of the lean gas mixture for NOx storage was 750 ppm NO and 6% O_2, using Ar as the balance gas, for 150 s; during the subsequent 20 s rich period, oxygen was replaced by hydrogen (4% H_2) maintaining 750 ppm of NO in the feedstream. The total flow was set at 2,900 ml min^{-1}, which corresponds to a GHSV of 28,620 h^{-1}. The NO, NO_2, N_2, NH_3 and N_2O concentration at the reactor exit were monitored every 40 ºC, once stabilized the analysis for at least 10 min, by FTIR multigas (MKS 2030) and MS quadrupole (MKS Cirrus) analyzers.

3. Results and discussion

Table 1 quantifies the surface area, Pt/Pd dispersion, pore volume and acidity for fresh and aged catalysts. It can be observed that the aging process reduces surface area and pore volume slightly for the prepared catalysts, while acidity and metal dispersion suffer from higher decrease in NSR catalysts.

Table 1. Physico-chemical properties of the prepared granulated form catalysts, fresh and after severe hydrothermal aging.

Catalyst	Surface area, m^2/g	Pt/Pd dispersion, %	Pore Vol., mm^3/g	Acidity, ml NH_3
1%Pt-15%Ba/Al_2O_3 Fresh	152	17.2	477	2.58
1%Pt-15%Ba/Al_2O_3 Aged	136	5.20	459	1.85
1%Pd-15%Ba/Al_2O_3 Fresh	161	25.6	468	7.85
1%Pd-15%Ba/Al_2O_3 Aged	140	4.50	426	3.46
4%Cu-CHA Fresh	579	-	287	3.31
4%Cu-CHA Aged	481	-	248	2.95

Figure 1 shows a) NOx conversion, b) N_2 yield and c) NH_3 yield for fresh coupled NSR-SCR system as well as after ageing, as a function of the reaction temperature. On one hand, palladium promotes DeNOx activity in the whole temperature range, due to the higher metal dispersion observed in Table 1, attaining NOx conversion values about 95% at intermediate temperature. Similarly, Pd-based catalyst showed the highest N_2 production at every temperature, except for around 220 ºC, where the excess production of NH_3 (Figure 1c) penalizes the N_2 yield. However, it has been verified that a lower H_2 concentration during the rich period could reduce this problem. On the other hand, with the Pt-based catalyst, at the exit of NSR-SCR configuration a negligible amount of NH_3 is produced at 200 °C and above. Also, for both catalysts, very few amount of N_2O at any temperature, and small quantity of NO_2 is produced only at highest temperatures (not shown). Finally, although Cu/CHA catalysts presented high hydrothermal stability [3], in NSR catalysts the presence of Pd penalized hydrothermal stability, in line with Pd dispersion decrease observed in Table 1.

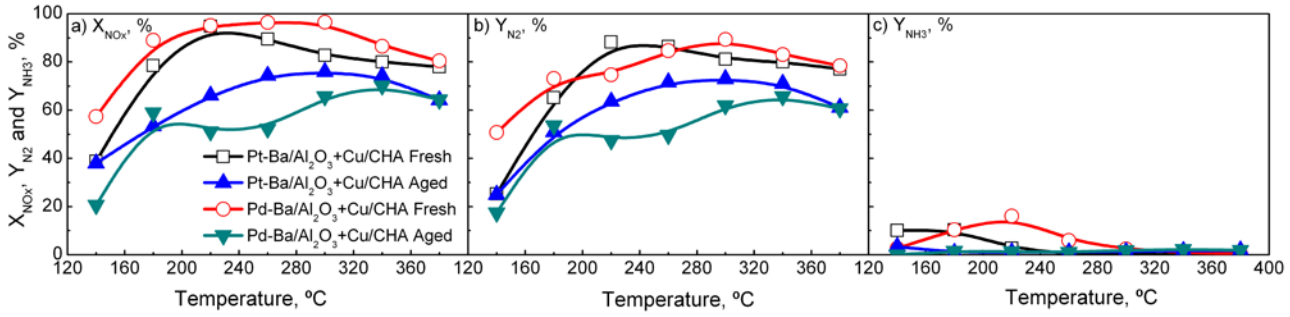

Figure 1. Prepared monoliths' a) NOx conversion, b) N_2 yield and c) NH_3 yield in their fresh and aged form.

4. Conclusions

Due to its higher Pd dispersion, Pd-BaO/Al_2O_3 NSR catalyst shows higher NOx conversion in coupled NSR-SCR configuration compared to Pt-based NSR catalyst. Indeed, except for 220 ºC, higher N_2 yield is observed with Pd-based catalyst. Also, regardless the NSR catalyst, few amount of NH_3 and no NO_2 nor N_2O is observed with coupled NSR-SCR configuration in the whole temperature range. In terms of hydrothermal stability, although Cu/CHA SCR catalysts showed very good resistance, the presence of palladium in the NSR catalyst severely penalized hydrothermal stability of the coupled NSR-SCR system, in line with Pd dispersion decrease.

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[1] B. Pereda-Ayo, D. Divakar, J.R. González-Velasco, Catal. Today 172 (2011) 66–72.
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[3] B. Pereda-Ayo, U. De La Torre, M.P. González-Marcos, J.R. González-Velasco, Catal. Today 241 (2015) 133–142.

Keywords NSR-SCR; Pt/Pd-BaO/Al_2O_3; Cu/CHA; Hydrothermal Stability.

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EDUCATION AND DEGREE AWARDED

PhD	University of the Basque Country, Chemical Engineering Dissertation: "SCR and NSR-SCR systems for DeNOx in diésel exhaust streams: Formulations, kinetics and modeling" Advisor: Prof. Juan Ramón González-Velasco Co-advisor: Prof. Beñar Pereda-Ayo Mark: Sobresaliente Cum Laude (Highest mark)	June 2015
MS	University of the Basque Country, Degree in Chemical Processes and Sustainable Development Thesis: Cu/Zeolite catalysts for NOx elimination with NH_3-SCR technology Advisor: Juan Ramón González-Velasco Mark: 9.9/10	July 2011
BS	University of the Basque Country, Chemical engineering Bachelor work: "Tratamiento de aguas del rio Oka en época de crecidas" Advisor: Estilita Ruiz Romera Mark: 9.5/10	September 2010

CURRENT POSITION

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Chemistry (9.95 ECTS)	2016-2017
Environmental Science and Technology (1.6 ECTS)	2016-2017
Unit Operation Laboratory (1.6 ECTS)	2016-2017
Heat Transfer (0.9 ECTS)	2016-2017
Principles of Environmental Engineering (6 ECTS)	2014-2016
Engineering Economy (2.5 ECTS)	2014-2016
Chemical Reaction Kinetics (3.5 ECTS)	2013-2016

TRAINING PERIODS IN OTHER RESEARCH CENTERS

Spectroscopic techniques for catalyst characterization July 2012
Prof. Agustín Bueno, Department of Inorganic Chemistry and Material Science,
University of Alicante, Spain

Modelling and Simulation Computer Techniques January 2014-May 2014
Prof. Pascal Granger, École Centrale Lille
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RESEARCH TEAMS AND PROJECTS

Title: “Innovaciones en la metanación de CO_2: materiales MDF, cinética, diseño del reactor y estrategias de operación (catalizador y proceso) para un modelo energético renovable”
Codification: CTQ2015-67597-C2-1-R
Financing Entity: Spanish Ministry of Economy and Competitiveness (2015-2018)
PI: Prof. Juan R. González Velasco.

Title: “Sistemas catalíticos combinados NSR-SCR con producción interna de amoniaco para la eliminación selectiva de NOx a N2 de los gases de escape de motores diesel”
Codification: CTQ2012-32899
Financing Entity: Spanish Ministry of Economy and Competitiveness (2013-2015)
PI: Prof. Juan R. González Velasco.

Title: Member of Consolidated Research Group “Chemical Tecnologies for Environmental Sustainability”
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Recognized by: Basque Government (2013-2018)
PI: Prof. Juan R. González Velasco.

Title: Member of Researcher Training Unit “Chemical Process Engineering and SustainableDevelopment”
Codification: UFI-11/39
Financing Entity: University of the Basque Country (2011- 2015)
PI: Prof. Federico Mijangos Antón

Title: “Tecnología combinada NSR-SCR para el control de óxidos de nitrógeno hacia nivel cero de gases de escape de motores diesel y de mezcla pobre”
Codification: S-PE12UN031
Financing Entity: Basque Government (2012- 2013).
PI: Prof. Juan R. González Velasco

Title: Member of Consolidated Research Group “Chemical Tecnologies for Environmental Sustainability”
Codification: GIC 9/UPV 00069 310-13517/200
Recognized by: Basque Government (2011-2012).
PI: Prof. Juan R. González Velasco

Title: “Dinámica de almacenamiento y reducción en un convertidor monolítico para almacenamiento y reducción de NOx de emisiones de mezcla pobre”
Codification: CTQ2009-12517
Financing Entity: Spanish Ministry of Science and Innovation (2011-2012)
PI: Prof. Juan R. González Velasco

AWARDS AND HONOUR

Best PhD Thesis Award 2015 in Engineering, granted by the University of the Basque Country — 2017

OTHER ACADEMIC MERITS

Accreditations for Spanish University Bodies

Profesor Ayudante Doctor (Assistant Lecturer and Researcher) — December 2015
Profesor Contratado Doctor (Lecturer and Research Associate) — June 2016

BS thesis co-advisor:

Student: Yasmina Portilla
Title: "Nuevas formulaciones NSR hidrotérmicamente resistentes para sistemas híbridos NSR-SCR". — July 2017
Mark: 9.2/10

Student: Koro Itsaso Uriarte
Thesis: "Envejecimiento hidrotérmico de sistemas híbridos NSR-SCR para aplicaciones DeNOx". — July 2016
Mark: 9.3/10

LINGUISTIC SKILLS

Mother tongue **Spanish**

Self-assessment of other languages (according to the European levels grid)

	Understanding		**Speaking**		**Writing**
European level (*)	Listening	Reading	Oral interaction	Oral production	
English	C1 Excellent	C1 Excellent	C1 Excellent	C1 Excellent	C1 Excellent
Certificate: **Advance-CAE** (C1)					
Basque	C2 Excellent	C2 Excellent	C2 Excellent	C2 Excellent	C2 Excellent
Certificate: **Euskararen Gaitasun Agiria-EGA** (C1)					
French	A1 Basic	A1 Basic	A1 Basic	A1 Basic	A1 Basic

(*)Common European Framework of Reference for Languages

PUBLICATIONS

Title: Key factors in Sr-doped $LaBO_3$ (B = Co or Mn) perovskites for NO oxidation in efficient diesel exhaust purification
Authors: J.A. Onrubia, B. Pereda-Ayo, U. De la Torre, J.R. González-Velasco
Journal: Applied Catalysis B: Environmental, 213 (2017) 198-210 [FI(WoS)=9.446 Q1(JCR)]

Title: Optimal operating conditions of coupled sequential NOx storage/reduction and Cu/CHA selective catalytic reduction monoliths

Authors: U. De la Torre, B. Pereda-Ayo, J.A. González-Marcos, J.R. González-Velasco
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Title: Steady-state NH_3-SCR global model and kinetic parameter estimation for NOx removal in diesel engine exhaust aftertreatment with Cu/chabazite
Authors: U. De la Torre, B. Pereda-Ayo, M.A. Gutiérrez-Ortiz, J.A. González-Marcos, J.R. González-Velasco
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Título: Performance of Cu-ZSM-5 in a coupled monolith NSR-SCR system for NOx removal in lean-burn engine exhaust
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Journal: Topics in Catalysis. 59 (2016) 259-267 [FI(WoS)=2.486 Q2(JCR)]

Title: Cu-zeolite catalysts for NOx removal by selective catalytic reduction with NH_3 and coupled to NOx storage/reduction monolith in diesel engine exhaust aftertreatment systems
Authors: U. De La Torre, B. Pereda-Ayo, M. Moliner, J.R. González-Velasco, A. Corma
Journal: Applied Catalysis B: Environmental 187 (2016) 419-427 [FI(WoS)=9.446 Q1(JCR)]

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Authors: U. De La Torre, M. Urrutxua, B. Pereda-Ayo, J.R. González-Velasco
Journal: Catalysis Today 273 (2016) 72-82 [FI(WoS)=4.636 Q1(JCR)]

Title: Catalytic properties of CuO/Al_2O_3-based microreactors in SCR of NOx with NH_3
Authors: Z. Boukha, U. De La Torre, J.R. González-Velasco
Journal: Topics in Catalysis, 59 (2016) 1002-1007 [FI(WoS)=2.486 Q2(JCR)]

Title: Influence of ceria loading on the NOx storage and reduction performance of model $Pt–Ba/Al_2O_3$ NSR catalyst
Authors: B. Pereda-Ayo, U. De la Torre, M. Pilar González-Marcos, J.R. González-Velasco
Journal: Catalysis Today 241 (2015) 133-142 [FI(WoS)=4.321 Q1(JCR)]

Title: Role of the different copper species on the activity of Cu/zeolite catalysts for SCR of NOx with NH_3
Authors: B. Pereda-Ayo, U. De la Torre, J.R. González-Velasco, M.J. Illán-Gómez, A. Bueno
Journal: Applied Catalysis B: Environmental 147 (2014) 420-428 [FI(WoS)=7.435 Q1(JCR)]

Title: Coupled ammonia-generating and SCR systems for lean-burn engines exhaust streams aftertreatment
Authors: J.R. González Velasco, U. De La Torre-Larrañaga, B. Pereda-Ayo, M.A. Gutiérrez-Ortiz
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Title: Screening of Fe- Cu-zeolites prepared by different methodology for application in NSR-SCR combined DeNOx system
Authors: U. De La Torre, B. Pereda-Ayo, M. Romero-Sáez, A. Aranzabal, M. P. González-Marcos, J. A. González- Marcos, J. R. González-Velasco
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Title: On the effect of reduction and ageing on the TWC activity of $Pt/Ce_{0.68}Zr_{0.32}O_2$ under simulated automotive exhausts
Authors: M.P. González-Marcos, B. Pereda-Ayo, U. De La Torre, J. R. González-Velasco
Journal: Topics in Catalysis, 56 (2013) 352-357 [FI(WoS)=2.220 Q2(JCR)]

Title: Influence of the washcoat characteristics on NH_3-SCR behaviour of Cu-zeolite monoliths
Authors: B. Pereda-Ayo, U. De La Torre, M. Romero-Sáez, A. Aranzabal, J.A. González-Marcos, J.R. González- Velasco
Journal: Catalysis Today 216 (2013) 82-89 [FI(WoS)=3.309 Q1(JCR)]

Title: Cu-zeolite NH_3-SCR catalysts for NOx removal in the combined NSR–SCR technology
Authors: U. De La Torre, B. Pereda-Ayo, J. R. González-Velasco
Journal: Chemical Engineering Journal, 207–208 (2012), 10-17 [FI(WoS)=3.437 Q1(JCR)]

Title: NOx Remediation in Monolith Channel with NH_3-SCR
Authors: U. De La Torre, B. Pereda-Ayo, J.R. González Velasco
Book chapter: Proceedings of the Iberian COMSOL Multiphysics Conference (2014) 100-107
ISBN: 978-84-617-1737-8

TALKS AND LECTURES

Talks given by the canditate at international congresses

Congress: 10th World Congress on Chemical Engineering (WCCE10)
Title: Optimal control of dual LNT-SCR catalytic converters for high DeNOx efficiency in lean burn automobiles
Authors: U. De La Torre, B. Pereda-Ayo, J.A. González-Marcos, J.R. González-Velasco

Congress: 10th World Congress on Chemical Engineering (WCCE10)
Title: Kinetics of NH3-SCR reaction network over Cu/chabazite
Authors: U. De La Torre, B. Pereda-Ayo, J.A. González-Marcos, J.R. González-Velasco

Congress: 13th European Congress on Catalysis – EuropaCat-XIII
Title: Hydrothermal stability of combined NSR-SCR catalytic converters for NOx removal in lean-burn diesel
Authors: Unai De-La-Torre, Beñat Pereda-Ayo, Juan R. González-Velasco

Congress: 25 Congreso Iberoamericano de Catálisis (CICat2016)
Title: Modelo cinético global de la reacción catalítica selectiva de óxidos de nitrógeno con amoniaco sobre un catalizador Cu/chabacita
Authors: U. De La Torre, B. Pereda-Ayo, J.A González-Marcos, J.R. González-Velasco

Congress: 12th European Congress on Catalysis – EuropaCat-XII
Title: Thermal aging resistance of Cu-zeolite based catalysts on NH_3-SCR for lean burn engines exhaust control
Authors: U. De La Torre, B. Pereda-Ayo, Juan R. González-Velasco, M. Moliner, A. Corma

Congress: XXIV Congreso Iberoamericano de Catálisis (CICAT 2014)
Title: Utilización de Cu-ZSM5 en un sistema doble monolito NSR-SCR para la eliminación de NOx en gases de escape de motores diesel
Authors: U. De La Torre-Larrañaga, M.A. Gutiérrez Ortiz, B. Pereda-Ayo, J.R. González Velasco

Congress: Iberian COMSOL Multiphysics CONFERENCE 2014
Title: NOx Remediation in Monolith Channel with NH_3-SCR
Authors: U. De La Torre-Larrañaga, F. Dhainaut, B. Pereda-Ayo, J.R. González Velasco

Congress: 4th International Conference on Structured Catalysts and Reactors (ICOSCAR-4)
Title: Enhanced NH_3-SCR behavior with Cu-exchanged zeolite monolith vs. Wahscoated ceramic monoliths
Authors: U. De la Torre, B. Pereda-Ayo, M. Romero-Sáez, A. Aranzabal, J.A. González-Marcos, J.R. González-Velasco

Congress: International Congress of Chemical Engineering (ICCE-2012)
Title: Low content Fe/Cu-zeolite NH_3-SCR catalysts for lean-burn engines exhaust control
Authors: U. De La Torre, M. Romero-Sáez, B. Pereda-Ayo, A. Aranzabal, J.A. González-Marcos, J.R. González-Velasco

Congress: V Jornadas de Investigación de la Facultad de Ciencia y Tecnología
Title: Power-to-gas: CO_2 methanation with renewable hydrogen
Authors: U. De La Torre, J. A. González-Marcos, J. R. González-Velasco, J. I. Gutiérrez-Ortiz, J. A. Onrubia

Congress: Congreso de la Sociedad Española de Catálisis (SECAT`16)
Title: Condiciones óptimas de operación en sistema secuencial NSR-SCR con catalizadores monoliticos Cu/CHA y Pt-Ba/Al_2O_3 para eliminación de NOx
Authors: U. De La Torre, B. Pereda-Ayo, J.A González-Marcos, J.R. González-Velasco

Congress: Congreso de la Sociedad Española de Catálisis (SECAT`15)
Title: Determinación de las condiciones de operación de sistemas dobles monolíticos NSR-SCR para la eliminar deslizamientos de NH_3 y NO en la producción de N_2
Authors: U. De La Torre, B. Pereda-Ayo, M. Moliner, J.A. González-Marcos, A. Corma, J.R. González-Velasco

Congress: Congreso de la Sociedad Española de Catálisis (SECAT`13)
Title: Influencia del contenido de Cu en monolitos recubiertos de Cu-zeolita en NOx NH_3-SCR
Authors: U. De la Torre, B. Pereda-Ayo, M.P. González-Marcos, J.R. González-Velasco