Ion-beam Sputtering for the surface modification of heterogeneous nanodispersed Catalysts

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Introduction

Interface science is crucial for the development of new technologically advanced materials [1]. In particular, this study shows that ion beam sputtering can be used as an effective technique for the controlled surface modification of solid heterogeneous catalysts. The surface properties of these nano materials can be tailored to enhance their catalytic performance leading to better resistance to aging and a reduction of the PGM loading [2]. The technique has been applied on catalysts of relevant interest like the ones applied in the emission control (e.g. $Pt/Ce_{0.7}Zr_{0.3}O_2$ catalyst) [3][4]. The effect of the different parameters of ion bombardment (type of ions, energy, doses) on the catalytic activity has been investigated. Modeling of the treatment has also been introduced to the describe erosion of the surface through ion sputtering and deeply understand the correlations between the parameters of the bombardment and the observed enhanced catalytic activity.

Materials and Methods

A sample of Pt (1% w/w) $Ce_{0.7}Zr_{0.3}O_2$ was prepared by impregnating commercially sourced $Ce_{0.7}Zr_{0.3}O_2$. The catalyst was then bombarded with N^+ ion beams. One sample, *Pt(1.2keV)* was treated with an ion energy of 1.2keV and an ion current 10mA, receiving 4 doses. The other sample *Pt(1.5keV)* was treated using an ion energy of 1.5keV and an ion current of 20mA, receiving 16 doses. The incident angle of the ion beam was 28˚ to the catalyst surface. The treated samples were compared with an untreated sample, Pt fresh.

To investigate the effect of the ion bombardment on the catalytic activity, TPR (Temperature Programmed Reduction) experiments have been carried out in the presence of 4000ppm of H_2. The temperature was ramped from 313K to 773K at a rate of 5K/min. Catalytic testing was carried out on all samples by using a reaction mixture composed of 10% O_2, 4.5% H_2O, 2000ppm CO, 2000ppm CH_4, 2000ppm C_3H_6, and 200ppm NO with a total flow of 100ml/min. The temperature was increased from 303K to 773K at a rate of 5K/min. The outlet gases from the reactor were analysed using a Pfeiffer Vacuum quadrupole mass spectrometer.

Results and Discussion

The reducibility of the samples after bombardment has been assed in TPR experiments reported in Fig.1. The peaks of H_2 consumption for the treated samples were observed at lower temperature with respect to the fresh catalyst: at 427K and 405K for *Pt(1.2keV)* and *Pt(1.5keV)* respectively, whilst 445K corresponds to the maximum of H_2 uptake for the fresh catalyst. The total H_2 consumption observed from reduction of *Pt(1.5keV)* is lower than the one observed in *Pt(1.2keV)*. This can be attributed to the higher number of ion doses used on the *Pt(1.5keV)* sample. The catalytic activity on bombarded catalysts was assessed in oxidation tests in the presence of gas mixture representative of the exhaust gas composition.

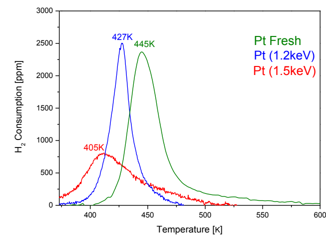

Figure 1. H_2 consumption as a function of temperature determined from TPR experiments using 4000ppm H_2, on untreated Pt 1w/w% $Ce_{0.7}Zr_{0.3}O_2$ (Ptfresh), and treated samples; Pt(1.2keV) – 10mA/15min dose x4, Pt(1.5keV) 20mA/15min dose x16.

The results are reported in terms of CO and C_3H_6 conversion as a function of temperature in Fig. 2. It is observed that the catalyst showed an enhanced catalytic activity after ion bombardment in the oxidation of both CO and C_3H_6. The temperature at which 50% conversion was achieved (T_{50}) for CO oxidation were 513K and 500K for *Pt(1.2keV)* and *Pt(1.5keV)* respectively, 10 to 20K lower than the T_{50} value of the fresh sample. The T_{50} values for C_3H_6 oxidation over *Pt(1.2keV)* and *Pt(1.5keV)* were 522K and 511K respectively, which show improved catalytic activity of the treated catalysts at low temperature compared with Pt fresh (T_{50} 526K). The results are in line with HRTEM analysis which revealed that the samples, after ion bombardment, are characterized by an uniform distribution of nanoparticles on the catalytic surface, as well as by the formation of atom vacancies and incomplete terraces. Analogous results have been obtained from the study of alternative catalytic systems such as Pd/ $Ce_{0.7}Zr_{0.3}O_2$ treated with the same ion bombardment protocol, which provokes a remarkable change in the particle morphology.

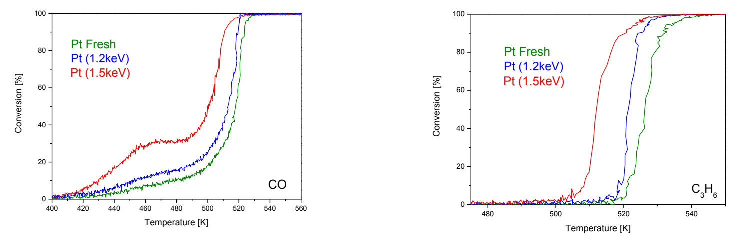

Figure 2. CO conversion and C_3H_6 conversion as a function of temperature. Feed composition 10% O_2, 4.5% H_2O, 2000ppm CO, 2000ppm CH_4, 2000ppm C_3H_6 and 200ppm NO.

Significance

Ion beam irradiation has been used as a post synthesis technique for the controlled surface modification of heterogeneous emission control catalysts. The study, carried out using $Pt/Ce_{0.7}Zr_{0.3}O_2$, proves that this method enhance the catalytic activity and the stability of the catalyst and opens up to the application of this method to several catalytic materials.

References

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O01	Asymmetric Group 4 Metallocenes for Ethylene Polymerisation	Jessica Lamb, Jean-Charles Buffet, Zoë Turner and Dermot O'Hare

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O14	One-step plasma-catalytic activation of CO2 and CH4 into value-added liquid fuels and chemicals at room temperature	Li Wang, Yaolin Wang and Xin Tu
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O17	Tailoring Platinum Bimetallic Catalyst Surface Structures to Specific Reactants	Elizabeth Raine, Paul Collier, Mark Feaviour and Edman Tsang
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O20	Continuous production of bio-renewable, polymer-grade lactone monomers through Sn-β catalysed Baeyer-Villiger oxidation with H2O2	Keiko Yakabi, Ceri Hammond and Antoine Buchard
O21	Microwave assisted catalytic hydrolysis of fibrous cellulose over framework catalysts	Songshan Jiang, Xiaolei Fan and Christopher Hardacre
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O24	Tandem dehydration-MPV reduction of Al-SBA15 with pentoses from hemicelullose	Rafael Perez, Helen Daly, Marco Fraga and Christopher Hardacre
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O27	Effect of Flue Gas Impurities on the Electroreduction of CO2 in Superbase Ionic Liquids	Adam Greer, Rebecca Taylor, Johan Jacquemin, Christopher Hardacre and Peter Robertson
O28	Catalytic Activity of Electrodeposited MoS2 Films for Hydrogen Evolution	Jo Humphrey, Michael O'Connell and Andrew Wain
O29	Electrochemically assisted CO2 hydrogenation on alkali-modified Ru/YSZ	Tan Sze Yen, Matthew West, Efstratios Stavrakakis, Danai Poulidi and Naimah Ibrahim
O30	Ag-Bi-W complex oxide: a promising photocathode for CO2 reduction	Claudia Longo, Miguel Tayar Galante, Krishnan Rajeshwar, Norma Tacconi, Jeotikanta Mohapatra, J. Ping Liu, Bob C Fitzmorris, Jin Z Zhang, Nathan Hollingsworth, Nora H. de Leeuw, S.F. Rebecca Taylor and Chris Hardacre
O31	Catalytic films on Aluminium supports generated by plasma electrolytic oxidation	Chaozhou Li, Arthur Garforth, Aneta Nemcova, Aleksey Rogov and Aleksey Yerokhin
O32	Gold-Palladium Bimetallic Catalyst Stability in Electrochemical ORR: Consequences for Hydrogen Peroxide Selectivity	Enrico Pizzutilo, Simon Freakley, Serhiy Cherevko, Sriram Venkatesan, Graham Hutchings, Christian Liebscher, Gerhard Dehm and Karl Mayrhofer
O33	Selective hydrogenation of alkynes and conjugated alcohols over Pd and Pt-based catalysts coated on the tube reactor walls	Nikolay Cherkasov, Yang Bai, Antonio Exposito and Evgeny Rebrov
O34	Selective hydrogenation of aromatic carboxylic acids over Pt-Sn catalysts	Xiaohan Chen, Helen Daly, Ziyun Wang, Haresh Manyar, Peijun Hu and Christopher Hardacre
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O37	New Insights into the Activation and Deactivation of Au/CeZrO4 in the Low-Temperature Water-Gas Shift Reaction	James Carter, Xi Liu, Qian He, Sultan Althahban, Ewa Nowicka, Simon Freakley, Liwei Niu, David Morgan, Yongwang Li, Hans Niemantsverdriet, Stanislaw Golunski, Christopher Kiely and Graham Hutchings
O38	Time-resolved 3D XRD-CT of low-temperature water-gas shift catalysts during activation; effects of catalyst and gas composition on crystalline phase and possible deactivation processes.	Daniela Farmer, David Waller, Gopinathan Sankar and Andrew Beale
O39	Photo-switchability of Au-Co Alloy Nanoparticles in Green Chemical Syntheses	Erandi Prangige, Zhu Huaiyong and Sarina Sarina
O40	Ceria supported Copper Single Site Catalyst for CO Oxidation	Liqun Kang, Ruoyu Xu, Qiming Wang and Ryan Wang
O41	CO2 conversion to dimethyl ether and methanol using PdZn/ZSM-5 catalysts	Hasliza Bahruji, Michael Bowker and Jonathan Ruiz Esquius
O42	Towards Understanding the Nature of the Hydrocarbon Pool formed during Primary Olefin formation from Methanol and Dimethyl Ether: influence of CO and H2	Toyin Omojola, Nikolay Cherkasov, Dmitry Lukyanov, Evgeny Rebrov and Andre van Veen
O43	Colloidal Cu/ZnO nanocatalysts for the hydrogenation of CO2 to methanol: The influence of the synthetic route	Alice Leung, Andres Garcia-Trenco, Sebastian D. Pike, Edward R. White, Milo S. P. Shaffer, Charlotte K. Williams and Jonathan Weiner
O44	Spatiotemporal Investigation into the role of the Oxygen Storage Component in Three Way Catalysts	Alexandre Goguet and Ciaran Coney
O45	Ion-beam Sputtering for the surface modification of heterogeneous nanodispersed Catalysts	Ruairi O'donnell, Salvatore Scaglione, Danilo Zola and Nancy Artioli
O46	Investigating the effect of reduction conditions on CO oxidation over Pt-based NSR catalyst	Sarayute Chansai, Robbie Burch and Chris Hardacre
O47	Following the Evolution of Supported PdO Nanoparticles using a Combined XAFS/DRIFTS method	Ellie Dann, Emma Gibson, Richard Catlow, Paul Collier, Tugce Eralp, Diego Gianolio, Christopher Hardacre, Anna Kroner, Agnes Raj, Alexandre Goguet and Peter Wells
O48	Photocatalytic organic synthesis: from fundamental to applications	Ren Su, Yitao Dai, Chao Li, Nina Lock, Hans Niemantsverdriet, Yongwang Li and Flemming Besenbacher
O49	Cinnamyl alcohol oxidation: an investigation of the autoxidation and catalytic pathways with the use of bimetallic Au-Pd supported nanoparticles.	Emilia Rucinska
O50	Identification of active species in graphitic oxide for the initiator and metal free epoxidation of dec-1-ene.	Samuel Pattison, Liam Thomas, David Willock and Graham Hutchings
O51	Graphitic oxide supported Iron catalysts for the solvent and initiator free aerobic epoxidation of dec-1-ene	Joseph Macginley, Samuel Pattisson, Robert Jenkins, Jennifer Edwards and Graham Hutchings
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O53	The low temperature solvent-free oxidation of cyclohexene to cyclohexanediol using molecular oxygen as oxidant	Owen Rogers, Sam Pattisson, Joseph Macginley, Keith Whiston, Graham Hutchings and Stuart Taylor

O54	Combined Neutron Scattering and NMR Spectroscopy Studies Examining Benzene Hydrogenation in Porous Media	Terri-Louise Hughes, Chris Hardacre, Marta Falkowska, Markus Leutzsch, Andy Sederman, Mick Mantle, Tristan Youngs and Daniel Bowron
O55	Combined QENS and MD studies of the dynamics of cyclic C6 hydrocarbons confined in MCM-41	Daniel Dervin, Chris Hardacre and Richard Catlow
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O59	Computational QM/MM studies of the Methanol to Hydrocarbons process on zeolites H-Y and H-ZSM-5	Stefan Nastase, Alexander O'Malley, Andrew Logsdail and Richard Catlow
O60	Reactivity of SO2 on Pt (001), (011) and (111) surfaces	Marietjie J. Ungerer, David Santos-Carballal, Abdelaziz Cadi-Essadek, Cornie G.C.E. van Sittert and Nora H. de Leeuw
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