Catalysis Communications 103 (2018) 69–73

Contents lists available at ScienceDirect

Catalysis Communications

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

Short communication

Regulating the catalytic properties of Pt/Al_2O_3 through nanoscale inkjet printing

Vasiliki K. Chatziiona[a], Barbara K. Constantinou[a], Petros G. Savva[a], Georgios G. Olympiou[a], Konstantinos Kapnisis[b], Andreas Anayiotos[b], Costas N. Costa[a,*]

[a] Department of Environmental Science and Technology, Laboratory of Environmental Catalysis, Cyprus University of Technology, P.O. Box 50329, CY 3603 Limassol, Cyprus

[b] Department of Mechanical Engineering and Materials Science and Engineering, Cyprus University of Technology, P.O. Box 50329, CY 3603 Limassol, Cyprus

ARTICLE INFO

Keywords:
Inkjet printing
Supported Pt catalysts
H_2-SCR
TPSR
NO reduction

ABSTRACT

For the first time ever, a 0.1 wt% Pt/Al_2O_3 catalyst was prepared by novel inkjet printing and compared against two catalysts prepared by a standard and modified wet impregnation method. The printed catalyst was found to present excellent activity and wide operating temperature window on the selective catalytic reduction of NO by H_2 under strongly oxidizing conditions (H_2-SCR) in the very low-temperature range of 100–200 °C. The transient studies performed in the present work indicated that the printing process followed led to a unique surface structure of the printed catalyst that probably favors the formation of different active intermediate NO_x species, which are active at very low reaction temperatures. Moreover, it was found that the inkjet printing protocol followed resulted in a relatively uniform nano-spherical structure of the developed catalyst.

1. Introduction

The reduction of NO emissions has become one of the greatest challenges in environment protection and that is why it is being intensely studied for the last four decades [1–5]. In order to reduce the environmental footprint of marine and land diesel engines, new technological solutions are needed to overcome intrinsic drawbacks of existing emission control technologies (NH_3-SCR, HC-SCR) [1–4]. Therefore, the development of innovative environmental catalysts is of outmost importance. Up to now the majority of supported catalysts are prepared by conventional methods (impregnation, sol gel, etc.) [6,7], which are complex and lack high-degree control over composition and structure [8].

An attractive and alternative approach to the development of catalysts, is the utilization of an inkjet type material printer in order to synthesize solid catalysts at a nanoscale level. Inkjet printing has been a promising tool for high-throughput inorganic-catalyst synthesis, even though the references are limited in literature [9–11]. Catalyst Multilayer Printing as compared to the other methods proves to be more advantageous as it provides a homogeneous mix at the molecular level in the liquid state [12]. Furthermore, it provides picolitre precision and control of the deposition of each layer and allows for a uniform distribution of catalyst material onto the surface of substrate.

The present research utilizes the previous work of Liu et al. (2012) who proposed an inkjet printing assisted cooperative-assembly (IJP-A) method for ultrafast exploration of multi-component mesoporous metal oxides catalysts [10]. Their ink formula, was composed of an amphoteric non-aqueous solvent, metal species, and block-copolymers to optimize the performance of the printing process [10,13,14].

This work provides a starting point for the development of a new catalysts' development technology through multilayer catalyst printing, which can be used to address air pollution control (De-NO_x). Successful development and application of this technique is expected to revolutionize the way of catalyst synthesis used in industry. Subsequently, in the present work much effort has been devoted to synthesize 0.1 wt% Pt/Al_2O_3 catalysts, with innovative methods, and study the catalytic reaction of the low temperature H_2-SCR of NO under strongly oxidizing conditions. In addition, transient studies were also performed on the catalysts prepared by different preparation methods. The current work strives to achieve catalyst design through printing, which is essentially the connection of the catalyst preparation techniques with the final characteristics of a catalyst, i.e., excellent catalytic performance in the very low temperature range of 100–200 °C.

* Corresponding author.
E-mail address: costas.costa@cut.ac.cy (C.N. Costa).

http://dx.doi.org/10.1016/j.catcom.2017.09.016
Received 26 June 2017; Received in revised form 29 August 2017; Accepted 19 September 2017
Available online 21 September 2017

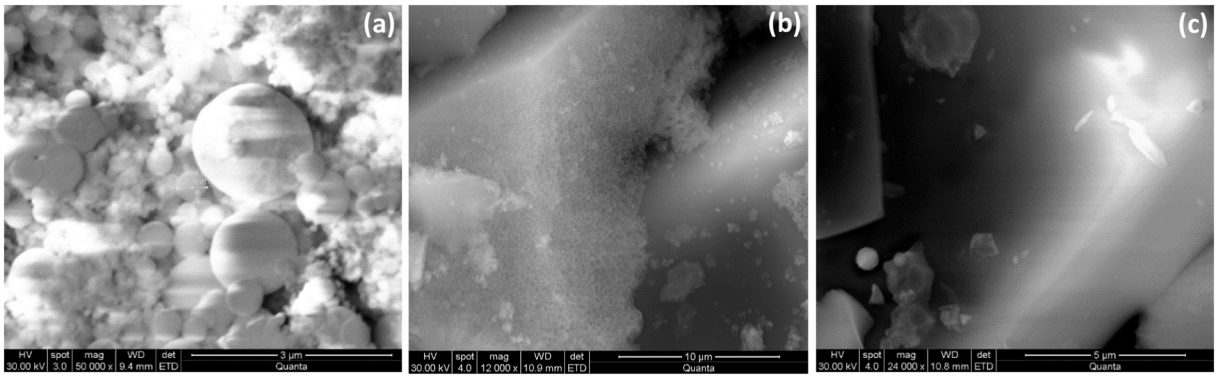

Fig. 1. SEM images of 0.1 wt% Pt/Al_2O_3 catalysts prepared by (a) novel inkjet printing, (b) the wet impregnation (WI) method using "ink formula" and (c) the wet impregnation (WI) method using de-ionized water.

2. Experimental

2.1. Catalysts preparation

The three Pt-supported catalysts (0.1 wt% Pt/Al_2O_3) studied in the present work were prepared by novel inkjet printing and by the wet impregnation (W.I.) method using $Pt(C_5H_7O_2)_2$ (Aldrich) as the metal precursor of Pt. The precursor of Al_2O_3 ($Al(NO_3)_3.9H_2O$) was supplied by BDH Chemicals. For the preparation of the first catalyst, the support (Al_2O_3) was impregnated at 55 °C in a solution containing the appropriate amount of the metal precursor in de-ionized water. The development of the second catalyst involved the use of an "ink formula" as suggested by Liu et al. [10,13]. In particular, the latter formula included the metal precursors, isopropanol, acetic acid, nitric acid and F127 polymer. The preparation of the third catalyst included the formulation of two different "material inks" [10,13], one containing the precursor of the support and the other the precursor of the metal, in such a concentration that could lead to the desired Pt loading (0.1 wt %). The ink formulas were stirred for 2–3 h before they were inserted into the ink cartridges of a modified EPSON-L800 printer. The printer was mainly comprised by an actuator, three sensors and a controller. "CATAprint®" software was specially designed to continuously monitor the printing process and allowing maximum control of any occurring errors [15]. The printer ejected 1.5pl droplets onto a stainless steel tray. The catalyst's layers were printed alternatively in order to achieve uniform topography and larger interface between the support and the metal. After preparation, all catalysts were dried at 120 °C and then calcined in air at 500 °C for 2 h, before storage. All catalyst samples were also in situ pre-treated with 20% O_2/He at 500 °C for 2 h and pure hydrogen at 300 °C for 2 h prior the catalytic/transient experiments.

2.2. Catalysts characterization

The surface morphology of the catalysts was examined through a Quanta 200 scanning electron microscope (SEM). Powdered specimens were deposited on the SEM stubs and then inserted in the specimen chamber, using a voltage of 30 kV. The dispersion of Pt was determined by Temperature Programmed Desorption of H_2 (H_2-TPD) following the experimental protocol described elsewhere [16,17,20].

2.3. Catalytic and transient studies

The flow system used for conducting catalytic and transient experiments, consisted of a custom made flow measuring control system and a fixed bed quartz micro-reactor which is described in detail elsewhere [16]. The amount of catalyst loaded into the reactor was 0.15 g (W.I. solids) and 0.1 g (printed sample), in powder form, and the total gas flow rate was 100 cm^3/min and 66.5 cm^3/min, respectively, leading to the same W/F and GHSV for all catalysts examined. The feed stream of the catalytic experiment consisted of 0.05 vol% NO, 5 vol% O_2, 1 vol % H_2 and He as balance gas. The conversion of NO (X_{NO}, %) of the H_2-SCR and the N_2 (S_{N2}, %) and N_2O (S_{N2O}, %) reaction selectivities were estimated based on the equations reported by Olympiou and Efstathiou [17].

Transient experiments were conducted on all Pt-supported catalysts, using Temperature-Programmed Surface Reaction (TPSR). After pretreatment of the catalysts, the feed was switched to He and the temperature was increased to 350 °C for 30 min and then the reactor was cooled down to 200 °C (temperature of maximum NO conversion). The feed was then switched to NO/H_2/O_2, where the reaction took place for 45 min (establishment of steady-state), before the reactor was cool down quickly to 25 °C under the same gas mixture. After that, the feed was changed back to He and kept at 25 °C for 5 min. Finally, the temperature of the catalyst was gradually increased to 500 °C, using a rate of 30 °C/min, while a constant flow of He (50 cm^3/min) was maintained over the sample to carry out the TPSR experiment. The final step was recorded by an on line quadrupole mass spectrometer (Hiden Analytical).

For the catalytic experiments, the analysis of the effluent gas stream was performed using an on line Gas Chromatograph-Mass Spectrometer (GC–MS, Agilent 5975C – 7890A). Calibration of the gaseous responses obtained was achieved using standard gas mixtures. The mass numbers (m/z) 2, 15, 28, 30, 44 and 46 were used for H_2, NH_3, N_2, NO, N_2O and NO_2, respectively.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. SEM studies

Fig. 1 presents the HR-SEM images obtain on the three catalysts examined in the present work. As shown in Fig. 1, the catalysts prepared using the ink formula (Fig 1a and b), indicate a distinct honeycomb, spongy-like structure which does not appear in the case of the catalyst that was prepared by standard W.I., using water as a solvent (Fig. 1c). It is suggested that this unique structure is a consequence of the decomposition of the polymer's micelles, after catalyst's calcination. According to the images presented in Fig. 1, the most significant difference between the three catalysts, is the distinct spherical particles morphology (nano-spheres) of the printed catalyst (Fig. 1a). In particular, as shown in Fig. 1a, the particles consisting the printed catalyst, vary in the area of 100–800 nm, with the majority of the particles appearing in the range of 100–300 nm. The average size of the latter catalyst's particles was calculated to be around 150 nm. On the contrary, the catalysts prepared by the wet impregnation method present rather large grains (particles) of undefined structure with rather smooth external surface morphology. The above results indicate that the nano-spherical shape of the printed catalyst's particles is produced only