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Catalytic combustion of toluene on Pt zeolite coated cordierite foams

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ABSTRACT

The catalytic properties of Pt based cordierite foam catalysts have been evaluated in catalytic combustion of toluene (800 ppm in air). The catalysts contain identical Pt content (0.1%) which was introduced by three different ways: Pt ion exchange on MFI zeolite and then coating on the foam; Pt ion exchange after zeolite coating and finally Pt directly wet impregnated on the cordierite foam. The catalytic behaviour of Pt foam based catalysts was compared with that of PtMFI zeolite under powder form. Pt exchanged MFI supported on the cordierite foams present an improvement of activity for toluene combustion of about 50 °C on the light off temperature ($T_{50\%}$).

The enhanced performance of the structured catalysts is due not only to the open structure of foams and homogeneous thin layers catalyst deposited on their cell walls, but also to the fact that the size and location of Pt particles present in MFI zeolite are changed during the dipping step. Indeed, as prepared Pt samples and those used in the preparation of the slurry were observed by transmission electron microscopy revealing that the chemical interaction of PtMFI zeolite with the binder and detergent, both present in the slurry, leads to an increase of Pt particles size which were found to migrate from internal pores to the external surface of zeolite crystallites thereby increasing catalytic activity.

1. Introduction

Volatile organic compounds (VOCs) are emitted from a large variety of sources, such as transports and industry (outdoor sources) as well as from household products (indoor sources). The implementation of more stringent environmental regulation to control VOCs emissions has led to the development of new effective methods for their abatement. Among those techniques, are thermal and catalytic combustion, the latter becoming most suitable and economical especially for low concentrations of organic emissions [1]. The selection of catalysts for VOCs combustion has been the subject of many studies, being noble metals based catalysts (Pt, Pd, Rh) the preferred ones due to their high specific activity, resistance to deactivation and ability to be regenerated [2]. Usually, the metals are supported on high surface area materials such as alumina, silica or zeolite. For industrial abatement of VOCs, which involve exothermic reactions and high flow rates, the catalyst substrate is commonly a monolithic or a honeycomb material (ceramic or metallic) where the active phase is deposited. Such substrate structure offers great advantage of low pressure drop and is widely preferred to more traditional pellet shaped or powder catalysts. However, these monoliths or honeycombs that are made of longitudinal parallel channels have some limitations concerning the laminar flow occurring inside the channels, the mass transfer from the gas phase to the catalytic layer on the walls and difficulties to control temperature for many exothermic or endothermic reactions [3,4]. Some of these disadvantages can be overcome by using special designs in metallic monoliths [5] or foams of open porosity (85–90%) which allow increasing the turbulence and the radial mixing [6]. Foams can be either ceramic or metallic. The ceramic foams were first used as filters for molten metals, but recently have received a great deal of interest and are being applied to different catalytic processes [6]. As in the case of monoliths, the ceramic foams are also usually coated with a catalyst support layer to increase BET surface area and to provide a support material that has a better interaction with the active catalyst material [7,8]. Zeolites can be applied for coating ceramic honeycomb monoliths or foams. The zeolite crystals can be hydrothermally synthesized in situ on the cell walls of the ceramic carrier [7,9] or they can be applied by washcoating using a slurry of zeolite particles followed by a stabilising thermal treatment [10]. The characteristics of the final coating are a complex function of support

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characteristics, slurry properties and preparation conditions [8]. Recently, we have developed a washcoating method to support homogeneous and well-adherent layers of MFI zeolite onto cordierite foams [11]. The catalytic performances of those MFI structured catalysts were evaluated in the combustion of representative VOCs, such as isopropanol and toluene, and it was observed that they showed higher catalytic activity than the powder zeolite, mainly in the case of foams containing Pt on MFI [12]. Pt supported on zeolites have already demonstrated efficiency for the catalytic combustion of a variety of VOCs at relatively low temperatures in conventional reactors [13,14] or using microstructured catalysts or microreactors [15]. It is well known that the preparation method, the support porosity and metal content as well as particle size can affect the catalyst properties [2].

In this work, we studied the catalytic properties of Pt based foam catalysts in which Pt was introduced in three different ways and we provide an explanation for the improvement in activities observed in the case of toluene combustion with Pt exchanged MFI supported on cordierite foams.

2. Experimental

2.1. Catalysts preparation

The cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$) foams, were produced by a polymeric replication method [16]. A flexible polyurethane foam was impregnated with a ceramic cordierite precursor slurry, optimized through the addition of a surfactant (Targon 1128, BK Ladenburg, F.R. Germany) and a thickening agent (sodium bentonite, MO34, Chemicer, Spain), in order to obtain adequate rheological behaviour.

Three types of Pt catalysts containing identical Pt loading 0.1 (wt.%) were prepared: (1) PtMFI_CF prepared by coating PtMFI zeolite onto the foam structure; (2) Pt_MFICF in which Pt was introduced after zeolite coating and finally (3) PtCF with Pt directly wet impregnated on the cordierite foam.

PtMFI catalyst was prepared by ionic exchange in MFI zeolite (Si/Al = 15, Zeolyst Corp.), in order to introduce 0.1 wt.% of platinum. A given volume of $Pt(NH_3)_4Cl_2$ (Sigma Aldrich) precursor solution (5×10^{-3} M), was added drop wise in a MFI suspension (1 g/100 mL of water) at room temperature, remaining under stirring for 12 h. The resulting sample was then collected by centrifugation and dried overnight at 100 °C. Finally, the Pt based-catalyst was calcined at 300 °C for 8 h (1 °C min^{-1}) under an air flow of 4 L h^{-1} g^{-1} catalyst.

The PtMFI zeolite was then supported on cordierite foams by a washcoating method. This method consists of the immersion of the ceramic foams, pre-treated with a cationic polymer, within a catalyst suspension containing 13 wt.% of catalyst, 0.14 wt.% of binder (colloidal silica), and 0.4 wt.% of surfactant (Teepol). Afterwards the excess of suspension is removed by centrifugation. In a final step, the sample was calcined at 450 °C for 3 h at static air (heating rate of 5 °C min^{-1}). This coated foam sample was named as PtMFI_CF. The remaining PtMFI zeolite (PtMFI$_s$ sample) was removed by centrifugation from the slurry used for dipping foams and then it was dried and calcined under conditions described above. A sample PtMFIs/CF was obtained by mechanical mixing of PtMFIs with crushed foam.

Sample Pt_MFICF was prepared from a MFI zeolite coated foam in which Pt was introduced by ion exchange following the procedure described above. Finally the sample PtCF, without zeolite, was obtained by impregnation of the cordierite foam with $Pt(NH_3)_4Cl_2$ solution.

2.2. Structural and catalyst characterization

The morphology of the cordierite foams was evaluated by scanning electron microscopy (SEM), using a Hitachi S-2400 equipment, with a 15 kV beam. Based on SEM images and using an image analysis software (SigmaScan Pro5), the cell mean diameter of the ceramic foam structure was determined. The porosity of the foams is estimated by the formula: $\varepsilon = 1 - (\rho/\rho s)$, where ρ is the density of the foam (weight-to-volume ratio), and ρs is the density of the solid (2.6 g cm^{-3}). The coatings loadings in the samples were determined gravimetrically. The dispersion and thickness of these coatings were evaluated by optical microscopy (Olympus CK 40 M microscope) using the SigmaScan Pro5 software. The adherence of the catalysts coatings onto the foam's surface was also evaluated by determining the weight loss, after exposing them to ultrasounds for 1 h at room temperature. The platinum (Pt) content of samples was determined by inductively coupled plasma (ICP) spectrometry. The evaluation of Pt dispersion and metal size particles was determined by H_2 chemisorption (H_2/Ar, 5 vol.%) using a Micromeritics Autochem II–2920 analyser at 308 K. The samples were first reduced under H_2 flow (25 mL min^{-1}) at 773 K and subsequently evacuated under Ar at 623 K overnight. Transmission electron microscopy (TEM) using a Hitachi – 8100 microscope was used to evaluate the metal size particles on the surface of zeolite crystals.

2.3. Catalytic tests

The catalytic behaviour of samples was evaluated for the toluene combustion. The catalytic tests were performed at atmospheric pressure in a fixed-bed flow reactor under temperature programmed surface reaction conditions (TPSR) with an heating rate

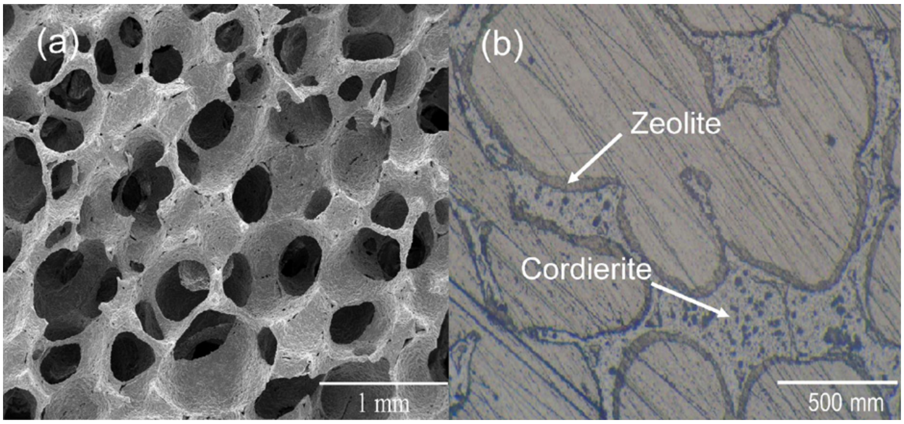

Fig. 1. SEM micrograph of a cordierite foam produced by replication (a) and an optical image (b) of a typical polished cross-section of MFI-coated foam.

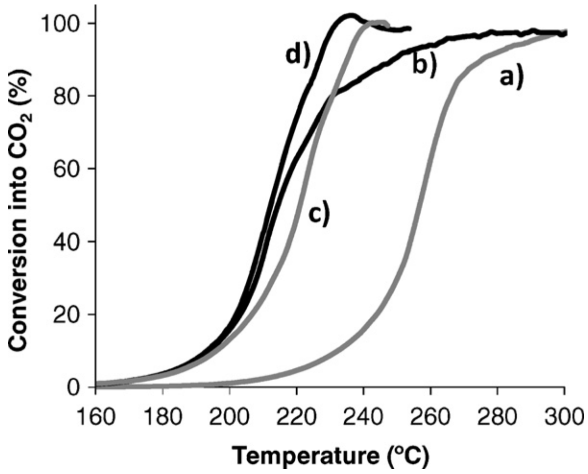

Fig. 2. Conversion of toluene into CO_2 as a function of the temperature for PtMFI (a), PtMFIs (b), PtMFIs/CF (c) and PtMFI_CF (d) catalysts.

of 1 °C min^{-1} and an air flow of 15 L h^{-1} containing 800 ppm of toluene. In order to be comparable, all tested catalysts contained the same amount of zeolithe (about 92 mg).

The feed and the reaction products were analyzed by on-line gas chromatography (HP 5890 gas chromatograph equipped with a Poraplot Q column) for hydrocarbons and IR Siemens Ultramat 23 analyzer for CO_2 and CO. Before the reaction, the catalysts were pretreated under a 15 L h^{-1} air flow at 450 °C for 1 h. The catalytic activity was evaluated in terms of conversion to CO_2 by measuring its concentration each 2 min.

3. Results and discussion

The morphology of cordierite foams consists of a three-dimensional array of struts forming open cells with more or less circular or ellipsoidal shape (Fig. 1a) leading to large channels of about 575 ± 55 μm in diameter, although some cells had closed windows. The strut thickness is between 60 and 70 μm and the porosity is about 85%.

Cylindrical cordierite foams (length ~1.2 cm; diameter ~1.8 cm) were dip coated using the conditions previously described in Section 2.1. At a glance zeolite coatings are homogenously distributed throughout the cordierite foam structure with thicknesses as low as 27 μm (Fig. 1b). Apparently, neither dimensional changes nor blockage of the large channels of the ceramic foams is observed.

Fig. 2 shows the catalytic behaviour of Pt based catalysts for toluene total oxidation (800 ppm in air) observed for samples with about the same zeolite content (92 mg). The catalyst PtMFI under powder form presents the lowest activity with a light-off temperature (temperature at which 50% of toluene conversion into CO_2 is attained) of about 260 °C, while the structured catalyst PtMFI_CF (curve d) is the most active evidencing a decrease of about 50 °C in the light-off temperature. This increase of activity could be due to the effect of foam 3D tortuous structure providing at same time an enhanced of mixing and turbulence, leading to better mass and heat transfers. However as this effect was not verified so intensely for CuMFI based catalysts (results not shown) it was decided to investigate the origin of activity increase for Pt studied catalysts. In order to evaluate whether there was an effect of the foam structure on toluene conversion or not it was decided to compare the light off curve of PtMFI_CF catalyst with the ones observed for three powder samples: the initial PtMFI sample; PtMFI$_s$ removed from the slurry used for dipping foams and PtMFI$_s$/CF prepared by mechanical mixing of PtMFI$_s$ with crushed foam (Fig. 2 curves b and c, respectively). In fact, the catalysts containing PtMFI$_s$ which had previously contacted the other slurry components (detergent and binder) are more active than the initial PtMFI powder zeolite.

Table 1
Metal dispersion and Pt particle sizes determined by H_2 chemisorption on powder PtMFI$_i$ sample and on PtMFI_CF foam (after grinding).

Sample	Metal dispersion (%)	Particle size (nm)
PtMFI$_i$	66	1.5 ± 0.2
PtMFI_CF	49	2.3 ± 0.2

To explain these observations the Pt particles present in the different catalysts samples were characterized by TEM and by H_2 chemisorption. Fig. 3 clearly shows great differences between as prepared Pt samples and those used in the preparation of the slurry. In PtMFI micrographs (Fig. 3a) the Pt particles are not detected at the surface, meaning that the metal is inside the zeolite pores. On the contrary, the presence of large metal particles on the surface of zeolite crystals were observed on samples PtMFI$_s$ removed from the slurry which were probably formed by sintering of Pt particles initially present inside the zeolite pores (Fig. 3b). The values shown in Table 1 for Pt dispersion and particle size determined by H_2 chemisorption also confirm that the Pt dispersion decreased after contact of PtMFI zeolite with the components (binder and detergent) of the slurry used to perform the washcoating of the foams. This increase of metal particle sizes explains the higher activity for toluene combustion observed with all catalysts containing PtMFI$_s$ zeolite deposed on the ceramic foam structure or even when the foam is crushed (PtMFI$_s$/CF). Actually, it is known that Pt dispersion is a major factor affecting the intrinsic activity of VOCs catalytic oxidation [2] and there are a few works dealing with the structure sensitivity of aromatics hydrocarbons combustion on Pt based catalysts showing that oxidation rates increase with increasing metal particle size [17,18]. For example the toluene oxidation rate over Pt/Al_2O_3 catalysts was found to be about 10 times higher for Pt crystallites size of 15.5 nm compared to one of 1.0 nm [17].

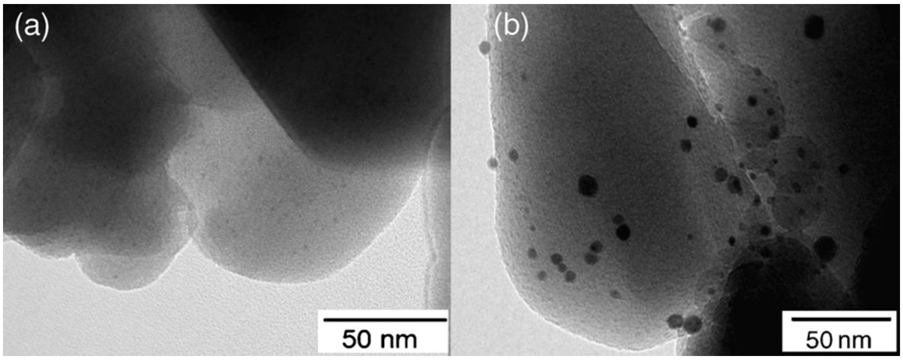

Fig. 3. TEM micrographs for samples PtMFI (a) and PtMFI$_s$ (b).

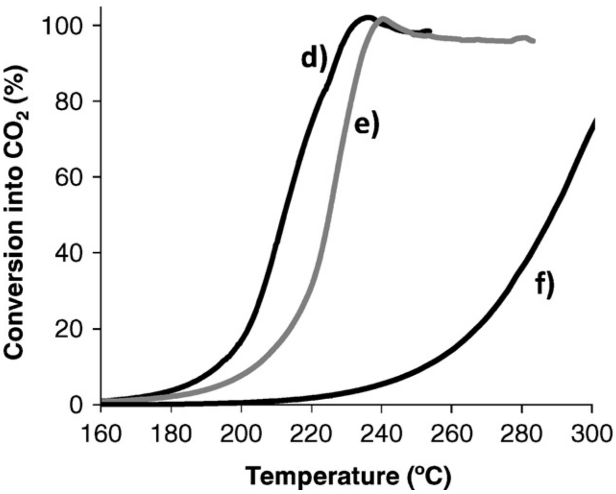

Fig. 4. Conversion of toluene into CO_2 as a function of the temperature for PtMFI_CF (d), Pt_MFICF (e) and PtCF (f) catalysts.

Finally, the influence of the preparation method used to introduce Pt on the cordierite foams was analysed by comparison of light off curves shown in Fig. 4. As it can be observed, the structured PtMFI_CF catalyst prepared by washcoating PtMFI on the foam is slightly more active than Pt_MFICF catalyst in which Pt was introduced after zeolite coating. Indeed, a decrease of about 10 °C in the light-off temperature ($T_{50\%}$) was attained. The Pt catalyst directly impregnated on the cordierite foams (PtCF) has a light-off temperature $T_{50\%}$ higher (~50 °C) than PtMFI coated ones which attests the improving effect of zeolite on the catalytic active phase. The small difference of activity between PtMFI_CF and Pt_MFICF catalysts is also probably related to differences in Pt dispersion, but it was not possible to confirm it because the analysis of the metal dispersion would involve the foam grinding.

4. Conclusions

The enhanced performances of the structured catalysts for toluene catalytic combustion is due not only to open structure of foams and homogeneous thin zeolite layers deposited on their wall cells, but also to the fact that the size and location of Pt particles present in MFI zeolite are changed during the dipping step.

The initial Pt dispersion of the PtMFI zeolite is not representative of the state after coating on the cordierite foam. The chemical interaction of PtMFI zeolite with the binder and detergent, both present in the slurry, leads to an increase of Pt particles size which were found to migrate from internal pores to the external surface of zeolite crystallites thereby increasing catalytic activity for toluene combustion.

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