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A novel Pt/zeolite-based honeycomb catalyst for selective CO oxidation in a H_2-rich mixture

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ABSTRACT

In this paper a study aimed to develop a Pt catalyst supported on a novel zeolite-based material (Z-PM) prepared from mine waste pumice is reported. A detailed physico-chemical characterization of the powder Pt/Z-PM catalyst has been carried out by means of XRD, TPR, SEM, TEM, BET surface area and XPS measurements in order to investigate its morphological, structural and electronic aspects.

The catalytic properties of Pt/Z-PM were investigated in the preferential reaction oxidation (PROX) of CO in a H_2-rich mixture. A comparison with a conventional Pt/SiO_2 catalyst in the CO-removal efficiency over a broad temperature range is presented. Preliminary results are also reported on the development of a washcoated Pt/Z-PM catalyst on a cordierite honeycomb, that is currently under investigation with aim to provide a guidance to the design and operation of a monolith PROX reactor at an industrial scale.

1. Introduction

Purification of hydrogen reformed from hydrocarbon-fuels is a key-process in the fuel cells technology [1]. Removal of ca. 1% CO remaining in the reformates to a trace-level is essential to avoid a serious poisoning of anode-catalysts. Since the importance of the preferential reaction oxidation (PROX) of CO in a H_2-rich mixture, a great amount of research has been conducted to improve catalyst activity and selectivity by optimizing catalyst compositions and structures [2–4]. Catalysts supported on zeolite have been also proposed [5–7]. Pt metal loaded on mordenite exhibited fairly high conversion with a high selectivity of ca. 90% over a wide fuel-flow rate condition even at relatively low temperature of 150 °C [8]. Superior performances have been recently obtained by using Pt–Fe/mordenite systems both as powders and honeycomb catalysts where the active catalytic material is applied as a coating on an inert honeycomb carrier [9].

In addition to catalyst formulation improvement, the catalyst structure (powders, pellets or honeycomb) also contributes to the catalyst performance [10]. Catalyst coating onto porous, ceramic monolith structures is a proven material technology demonstrated in automotive catalytic converters for a few decades. In principle, the ceramic monolith support structures enable elimination or manipulation of any external and internal mass transfer steps to enhance the reaction activity and selectivity using appropriate material structures and flow conditions. Low-pressure drop is another unique feature of the monolith structure. Therefore, monolith structured catalysts are highly considered for industrial scale.

In this paper a study aimed to the development of a Pt catalyst, supported on a novel zeolite-based material, named Z-PM, for the PROX process is reported. This material, obtained from a mine waste pumice by extraction of most of the silica contained through a patented process [11], display a porosity and surface area (about 30–40 m^2/g) greater than the starting reactant and a high content (around 60%) of crystalline zeolite P. These features make the Z-PM material highly promising as a catalytic support, as we have recently demonstrated by using Pt/Z-PM catalysts for selective hydrogenation reactions in liquid phase [12,13]. Here, we investigate the catalytic behaviour of a Pt/Z-PM catalyst in the removal of CO in a H_2-rich mixture by selective oxidation. The present study addresses moreover a preliminary basic issue about testing of the Pt/Z-PM catalyst on a honeycomb support. Such an understanding will provide a guidance to the design and operation of a monolith PROX reactor at an industrial scale.

2. Experimental

2.1. Catalyst preparation

Powder Pt/Z-PM catalyst has been prepared by impregnation, by using the incipient wetness technique, of the Z-PM support (BET surface area 33 m^2/g) with the suitable amount of solution of $Pt(acac)_2$ (platinum acetylacetonate, $Pt(C_5H_7O_2)_2$ 99.9%, Aldrich) in acetone in order to have a Pt content of 2 wt%. After impregnation,

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Table 1
Chemical composition, surface and micropore area of the zeolitized-pumice (Z-PM) material obtained after the silica extraction process from mine waste pumice.

Composition (wt%)							SA (m^2/g)	Micropore area (m^2/g)
SiO_2	Al_2O_3	FeO	CaO	MgO	Na_2O	K_2O		
50.68	25.65	4.36	2.11	0.90	15.35	1.85	34.4	3.6

the catalyst was dried at 120 °C in air for 10 h and then reduced under H_2 flowing at 350 °C for 2 h. The reference Pt/SiO_2 was also prepared in the same way, by using a commercial silica support (SiO_2 Grace, BET surface area 276 m^2/g).

For the preparation of the monolith catalyst, a cordierite honeycomb with a cell density of 225 cpsi (cells per square inch) of about 1 mm square channels, was used. The cordierite monolith was then dipped several times into an aqueous slurry of the Z-PM catalyst containing 10 wt% of sodium metasilicate ($Na_2SiO_3 \times 5H_2O$) as a binder, followed by drying and calcination at 500 °C for 4 h.

2.2. Catalyst characterization

BET surface area and porosity data were determined by adsorption–desorption of dinitrogen at 77 K using a Micromeritics ASAP 2010 instrument. XRD spectra were recorded on an Ital Structure mod. APD 2000 X-ray diffractometer using the Cu Kα radiation and mounting powder samples on a Plexiglass holder. Diffraction peaks of crystalline phases were compared with those of standard compounds reported in the JCPDS Data File.

Scanning electron microscopy (SEM) analyses were carried out with a JEOL 5600LV electron microscope. The samples were coated with a thin layer of gold to prevent charging of the samples. Micrographs of the samples were recorded with a 10–20 kV accelerating voltage. X-ray photoelectron spectroscopy (XPS) measurements were performed by using a Physi-cal Electronics (PHI) 5800-01 spectrometer by using a monochromatic Al Kα X-ray source at a power of 350 W. An Ag foil was taken, after argon sputtering, for checking the initial calibration of the binding energy (B.E.) scale. Further calibration was made with respect to the C 1s peak of the adventitious carbon at B.E. 284.6 eV.

2.3. Catalytic activity

Activity tests were carried out in the temperature range between 50 and 300 °C. Reactant gases, containing 1.0% CO, 1.5% O_2, balance H_2, were prepared by mixing each of the pure gases by use of mass flow controllers. The total flow rate was 500 cm^3/min (evaluated at 25 °C and 1 atm). An on-line gas chromatograph (GC) with a thermal conductivity detector was used to measure inlet and outlet gas compositions. On powdered catalysts, 0.1–0.15 g of sample was placed in a "U"-type quartz glass reactor. To test the catalytic activity of Pt/Z-PM-coated monolith, a quartz reactor specifically designed to contain the monolith honeycomb (0.5 cm × 5 cm in size), was employed. The temperature of the catalyst bed or the monolith was monitored and controlled by a PID controller equipped with K-type thermocouple.

The CO conversion was calculated from the variation of the detected CO concentration: CO conversion (%) = $[(CO_{in} - CO_{out})/CO_{in}]100$, where CO_{in} and CO_{out} indicate the inlet and outlet CO concentration, respectively. The selectivity to CO_2 (S) was calculated as follows: $S = [0.5CO_2/(O_{2in} - O_{2out})]\ 100$, where CO_2 indicate the concentration of CO_2 produced, O_{2in} and O_{2out} the inlet and outlet O_2 concentration, respectively.

3. Results

3.1. Catalysts preparation and characterization

3.1.1. Pt/Z-PM powder

The Z-PM support used in this study has been prepared according to a patented method from mine waste pumice. Briefly, a silica extraction has been carried out twice with an aqueous solution of NaOH under hydrothermal conditions [11]. Therefore, compared to starting pumice the resulting material contains much less silica and consequently a Si/Al atomic ratio strongly reduced. The main characteristics (chemical composition, surface area and porosity) of the Z-PM support are summarized in Table 1. Particularly important for the reaction under study is the presence of a remarkable amount of iron(II) and iron(III) remaining in the amorphous phase. Z-PM shows also a degree of microporosity (micropore area 3.6 m^2/g) and BET surface area (33 m^2/g) higher compared to traditional pumice supports previous reported in literature [14,15]. In the same time, the most of the amorphous structures rearranges into the crystal structure of zeolite P. SEM analysis micrograph shown in Fig. 1a illustrates the typical

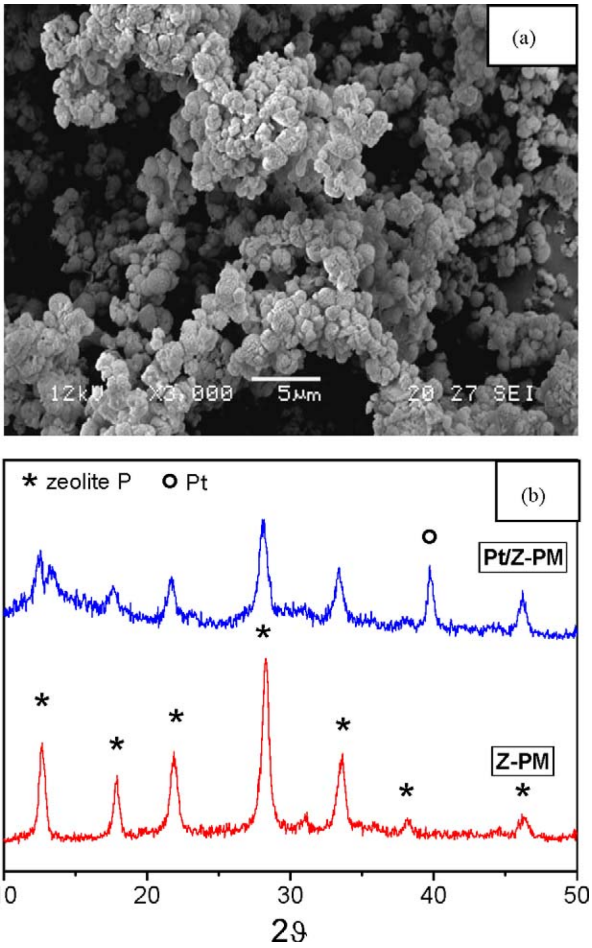

Fig. 1. (a) SEM micrograph showing the typical morphology of the Z-PM support; (b) XRD patterns of the Z-PM support and of reduced Pt/Z-PM catalyst.

morphology of the Z-PM support. The particle size distribution of the Z-PM grains is almost homogeneous, with an average value of 2 μm. XRD data (Fig. 1b) indicated that the crystalline fraction of the material is composed only of zeolite P.

Powder Pt/Z-PM catalyst has been prepared by impregnation, by using the incipient wetness technique, of the Z-PM support. A detailed characterization of the Pt/Z-PM catalytic system has been reported in previous papers [12,13]. Here, we summarize the main results. XRD pattern of the catalyst reduced in hydrogen (Fig. 1b), shows that the structure of zeolite P has been maintained also after reduction at high temperature (350 °C). The peak at a Bragg angle of 39.82 two-theta indicates the presence of metallic Pt with a mean particle size of 26.7 nm, as calculated from line broadening analysis of the diffraction peak. TEM analysis has further specified that both large Pt particles, having size of 50 nm or higher, and Pt particles of only few nanometers are presents.

Temperature programmed reduction analysis has revealed that reduction of Pt ions into metallic platinum occurs at low temperature, in the range 80–230 °C. It is likely that the contemporary reduction of someone (e.g., iron(II) and iron(III)) of the reducible components of the support occurs as well, catalyzed by hydrogen spillover from Pt onto support [16], favouring a strong interaction between Pt and the Z-PM support. Results from a XPS investigation have confirmed this, showing a slight increase of the Pt-d band vacancies, as typically occurs in bimetallic Pt-alloys [17]. Moreover, XPS also exhibited a clear shift to lower B.E. for the Fe 2p3/2 peak in the presence of Pt, indicating an electron transfer from Pt to the surface Fe species [13].

3.1.2. *Pt/Z-PM-based honeycomb*

Cordierite was the monolith substrate material chosen because, from a practical use, is capable of withstanding rapid thermal gradients and constant vibrations for extended periods of time. Zeolite washcoating of cordierite honeycomb has been already investigated for the development of monolith reactors [17–19]. However, at best of our knowledge, this is the first report on the washcoating of a zeolitized-pumiceous material up on a cordierite monolith support.

A picture of the monolith honeycomb is shown in Fig. 2. The preparation of the Pt/Z-PM-based monolith was accomplished by impregnation of the monolith with an aqueous slurry solution containing the Z-PM catalyst. In order to keep tightly the catalyst on the surface, the washcoat layer must adhere strongly to the substrate maintaining a relatively high surface area. It has been reported that the use of a binder is not essential for the washcoating of zeolite powder at small particle size [19]. However, in order to improve the adherence of the Pt/Z-PM catalyst, an aqueous solution of sodium metasilicate has been used as a binder. For the same reason, a high temperature treatment (500 °C) was also performed.

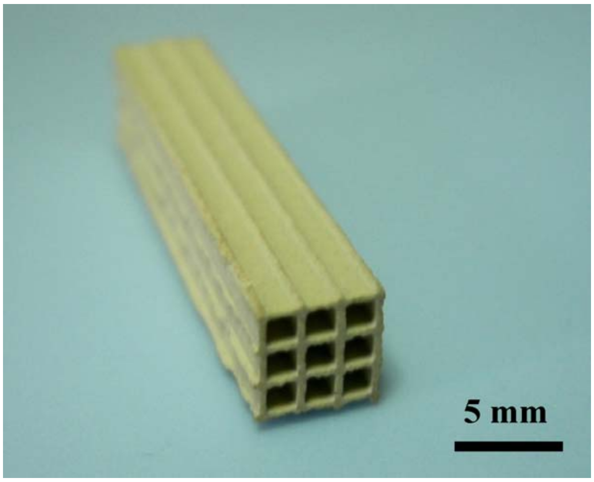

Fig. 2. Picture of the Pt/Z-PM-based honeycomb used for the kinetic study.

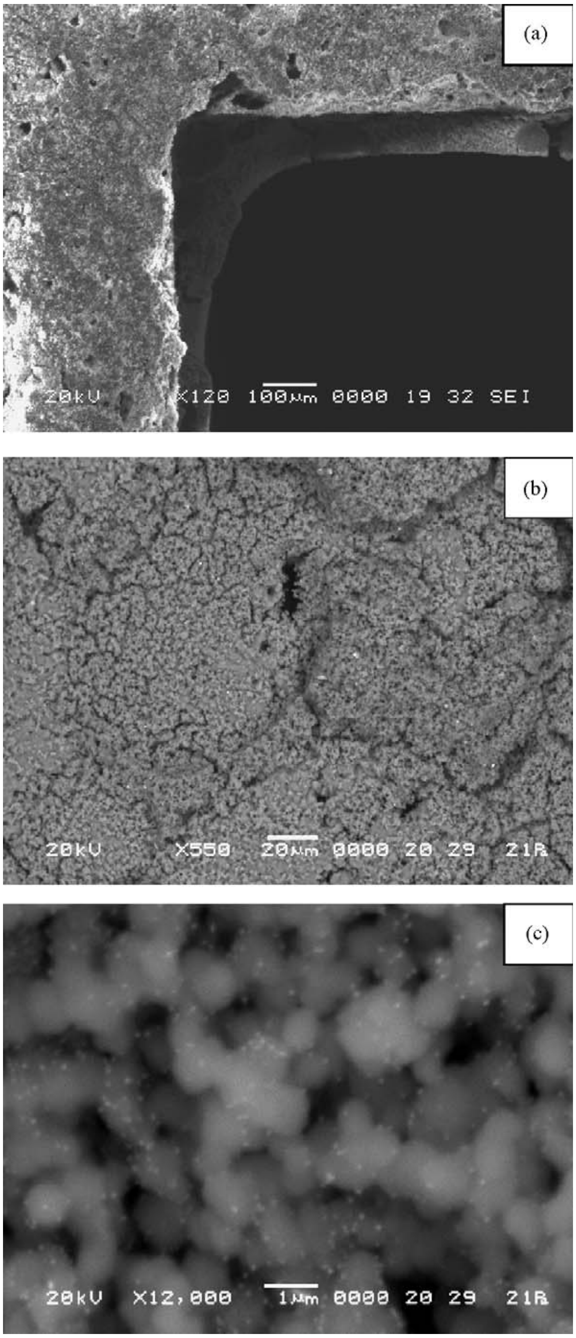

Fig. 3. (a) Cross-section; (b) and (c) surface characteristics of the Z-PM washcoating on the cordierite monolith.

SEM micrographs reported in Fig. 3a and b show, respectively, the cross-section and surface of the Pt/Z-PM washcoating layer (about 5.6 wt%). At higher magnification (Fig. 3c) of the washcoating layer, the platinum particles are imaged as white spots homogeneously distributed on the surface of the Z-PM support grains.

3.2. *Kinetic tests*

Preliminary kinetic tests for the selective oxidation of CO (space velocity, GHSV = 225×10^3 h^{-1}, O_2/CO molar ratio = 1.5) in the

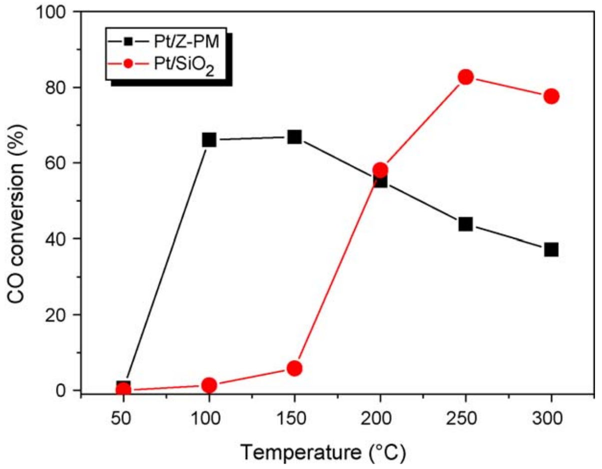

Fig. 4. CO conversion–temperature curves obtained in the oxidation of CO with oxygen in the presence of a high excess of hydrogen on both Pt/Z-PM and reference Pt/SiO_2 powder. Experimental conditions: 1% CO, 1.5% O_2, balance H_2; GHSV = 225 × 10^3 h^{-1}.

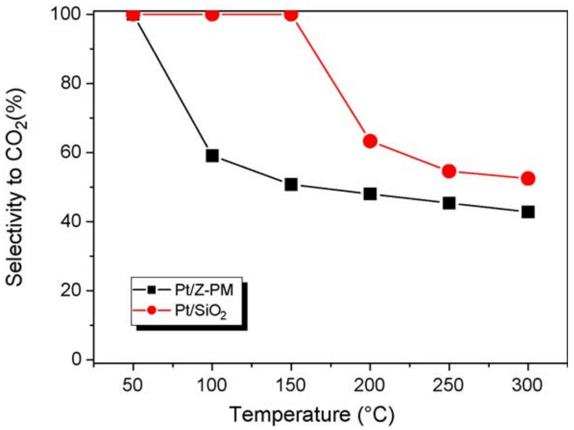

Fig. 5. CO selectivity as a function of the temperature in the oxidation of CO with oxygen in the presence of a high excess of hydrogen on both Pt/Z-PM and reference Pt/SiO_2 powder. Experimental conditions: 1% CO, 1.5% O_2, balance H_2; GHSV = 225 × 10^3 h^{-1}.

presence of a high excess of hydrogen on both Pt/Z-PM and reference Pt/SiO_2 powder catalysts have shown that their behaviour is strongly dependent on the reaction temperature. Results indicated that the Pt/Z-PM sample was more active than Pt/SiO_2 sample at low temperature (50–150 °C). Indeed, oxygen conversion (not shown) reached 100% already at 100 °C on the Pt/Z-PM catalyst, whereas a temperature of almost 200 °C was necessary on the reference catalyst. CO conversion–temperature curves, shown in Fig. 4, confirm this behaviour. At higher temperature, CO conversion start to decrease, due to the increased rate of the competing H_2 oxidation reaction and the possible onset of the reverse water–gas shift reaction, which generates CO. The selectivity to CO_2 is reported in Fig. 5. In the low range of temperature the selectivity to CO_2 on the Pt/Z-PM catalyst lies in the range 50–60%.

Previous studies by Watanabe et al. have already highlighted the positive effect of zeolite supports and Fe promoter on platinum active sites in the PROX reaction [9,20]. The enhancement of the catalytic properties of Pt in the presence of Fe has been attributed to a non competitive dual site adsorption pathway proceeding through the interaction of CO adsorbed on Pt with oxygen species adsorbed on the adjacent Fe sites [9,20–22].

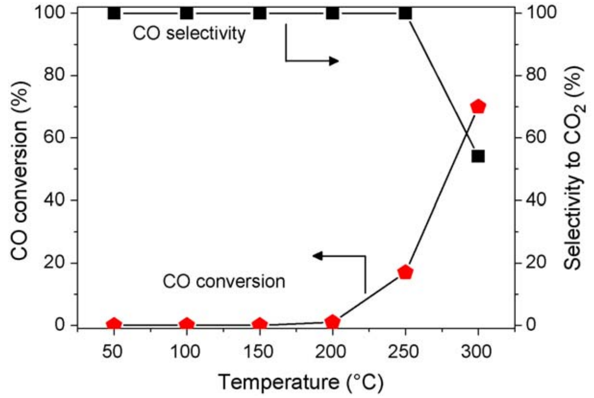

Fig. 6. CO conversion–temperature curves obtained in the oxidation of CO with oxygen in the presence of a high excess of hydrogen on the Pt/Z-PM-based monolith reactor. Experimental conditions: 1% CO, 1.5% O_2, balance H_2; GHSV > 1.5 × 10^6 h^{-1}.

On the basis of the characterization data above reported on the Pt/Z-PM catalyst, indicating the presence of bimetallic Pt–Fe sites in which Fe species in close proximity to Pt alter its electronic state, it can be proposed that the enhanced catalytic properties of the Pt supported on Z-PM are due to the strong interaction occurring between the active Pt phase and the Fe component of the support.

Current PROX reactors use pellet or monolith-based substrates [10,23]. The PROX reaction was then performed on a Pt/Z-PM catalyst washcoated on a cordierite honeycomb support. In Fig. 6 the CO conversion and selectivity to CO_2 on the monolith catalyst is reported as a function of the temperature. The reaction starts at the temperature of 250 °C where CO conversion is about 17% with a 100% selectivity to CO_2. No deactivation activity was observed during the time on stream (6 h) of the catalyst, suggesting that there is no sintering or coke formation on the catalyst surface in the course of the reaction. Further, no mechanical degradation of the deposited catalytic layer was observed after reaction, indicating its strong adherence to the monolith.

With respect to powdered Pt/Z-PM catalyst, a shift towards high temperature was observed. However, a direct comparison with the powdered catalyst cannot be made considering the much higher space velocity (GHSV > 1.5 × 10^6 h^{-1}) for the monolith catalyst due to the low catalyst washcoating loading. It is expected in fact that the light off temperature increases and maximum conversion decreases with increasing space velocity. Moreover, it cannot be excluded that other parameters (e.g., the higher temperature treatment of the monolith, the presence of a certain amount of inert binder in the washcoating catalyst formulation) can play a role in this regard. Anyway, on the basis of the preliminary features demonstrated by the Pt/Z-PM catalyst, further work is underway to optimize the catalyst formulation and/or microstructure (Pt loading, Pt/Fe ratio, Pt particle size distribution, etc.) and washcoating characteristics (washcoating loading, binder/catalyst ratio, treatment temperature, etc.) in order to accomplish the properties required for a PROX monolith catalyst.

4. Conclusions

In summary, the results reported on a novel Pt-based catalyst supported on a zeolited-pumice support demonstrate its promising performance in the selective CO oxidation in a H_2-rich mixture. Details of a wide characterization study of the developed Pt/Z-PM catalyst are indicative of the presence of Fe species of the support in close proximity to Pt. This alter the Pt electronic state, making it more prone to activate CO oxidation at lower temperature in comparison to a Pt/SiO_2 catalyst.

Preliminary results obtained in the development of a washcoated Pt/Z-PM catalyst on a cordierite honeycomb are promising and future work is planned in order to enhance the performance of the PROX monolith catalyst through an optimized catalyst formulation and washcoating characteristics.

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