Intermetallics 94 (2018) 179–185

Contents lists available at ScienceDirect

Intermetallics

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

Ordered intermetallic Pt-Fe nano-catalysts for carbon monoxide and benzene oxidation

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ARTICLE INFO

Keywords:
A. Nanocrystalline metals
B. Oxidation
C. Electron microscopy
Transmission
D. Catalysis

ABSTRACT

Conversion of toxic, indoor pollutants into innocuous products through catalytic reaction is one of the promising among other permanent solutions. γ-Al_2O_3 supported, Pt-based intermetallic nanoparticles (NPs) using abundantly available metal e.g., Fe (Pt-Fe; Pt_3Fe and $PtFe_3$) as catalysts are successfully prepared through a wet-impregnation method followed by calcination in the presence of H_2 at 800 °C. Although the intermetallic Pt-Fe NPs are prepared at elevated temperatures, they are, however, not agglomerated and are finely dispersed on the γ-Al_2O_3 support with the average particle size between 4 and 6 nm. No other intermetallic or alloy phases of Pt-Fe were not observed under the set synthesis conditions. Despite the same Pt-mass loading in the both Pt-Fe catalysts, intermetallic $PtFe_3$ catalysts showed much improved carbon monoxide (CO) oxidation activity by at least 8-fold compared to that of the intermetallic Pt_3Fe catalysts. The intermetallic $PtFe_3$ catalysts showed the enhanced activity for CO oxidation compared to that of the intermetallic Pt_3Fe catalysts, however, both the intermetallic Pt-Fe catalysts showed virtually the same catalytic activity for benzene oxidation. Both the intermetallic Pt-Fe catalysts showed the stable, multi-cycle catalytic performance for the catalytic CO and benzene oxidation and retain their structure and morphology even after catalytic reaction.

1. Introduction

The continuous exposure of indoor *cocktail* emissions (e.g., carbon monoxide (CO), volatile organic compounds, etc.) which are present inside of the homes, office buildings and other enclosed locations (e.g., parking places, vehicles, spacecraft, etc.) even at very low concentration ranges, induces severe health risks which are comparable to that of outdoor emissions. World Health Organization reports that these emissions at indoor, where the people spend more than 90% of their time, are the main attributes for increased mortality and global disease which are 4.3 million and 3%, respectively, per annum [1]. Construction materials (e.g., building articles, wood-composites, adhesive agents, etc.) [2] household products [3], combustion of biomass (firewood, cow-dung cake, crop residues, etc.) [4] or fossil fuels (e.g., coal, gasoline, etc.) [5] for cooking, heating, bathing, etc. are the possible major sources for indoor emissions. It has been monitored that CO is one of the major among other indoor pollutants in the developing countries due to the combustion of solid fuels. Adequate ventilation is one of the viable solutions to minimize the health risks of indoor emissions, however, they pollute outdoor environment at community level which becomes an additional problem. Therefore, catalytic conversion of the indoor emissions into innocuous products is one of the promising among other permanent solutions.

Intermetallic catalysts of platinum group metals (PGM) (e.g., Pt, Pd, etc.) have been considered as alternative to the traditional PGM catalysts due to their proven, favourable catalytic properties in terms of enhanced catalytic activity with same or a lower mass-loading of PGM [6–8]. On the other hand, the traditional PGM catalysts have obvious limitations in terms of catalytic activity at desired temperature range, long-term performance, durability [9] as well as resistance against poisonous moieties, etc. [10] and importantly, the cost of PGM associated with market fluctuation, scarce resources at localized regions, etc. [11]. Non-PGM catalysts (e.g., oxide-based) have later been explored as alternative to the traditional PGM catalysts and found that they possess promising activity at an initial stage, however, long-term and durable performance and stability against poisoning moieties remain the major challenges again to use them as practical catalysts [12–18]. The ever-developed PGM-based intermetallic catalysts showed

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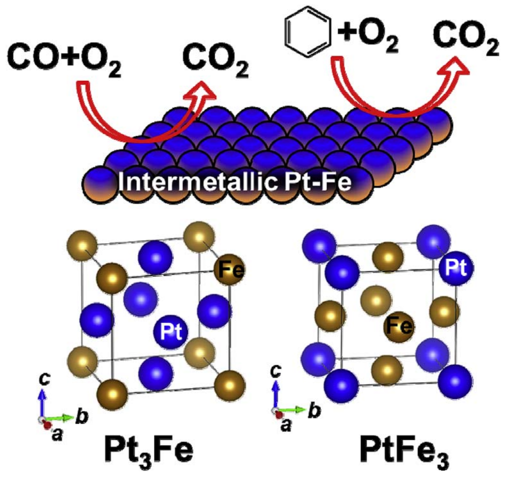
https://doi.org/10.1016/j.intermet.2018.01.008
Received 20 October 2017; Received in revised form 16 December 2017; Accepted 9 January 2018
0966-9795/

enhanced durable activity for electro-catalytic application [19–25], automobile exhaust purification [26–28], photocatalytic applications [29,30], hydrogenation [31–34] etc. due to the changes in the *d*-band center, bi-functional activity, electronic structures, etc. [35,36]. Although several intermetallic catalytic systems have been reported, however, they have been mostly for energy-related applications (e.g., fuel cells) and a few for combustion-related applications (e.g., automobiles [37,38]). It should be noted that there are scarce studies on PGM-based intermetallic catalysts on indoor air treatment.

Intermetallic phase of Pt with a low-cost metal (e.g. Fe) seems to be promising for several catalytic applications, however, mostly reported as cathode- (reduction reaction, e.g., oxygen) and anode-catalysts (oxidation reaction e.g., methanol, ethanol, etc.) for fuel cell applications [39–48]. In addition, intermetallic phases of Pt-Fe have also been prepared for hydrogenation reaction [49], electro-oxidation of CO/H_2 [50] and data storage applications [51]. It should be noted that most of the reported intermetallic Pt-Fe nanoparticles with the particle size smaller than 10 nm have been prepared through wet-chemical methods at a room or moderate temperatures [52–56]. They have been used mostly for room temperature-based catalytic applications and their use has been carefully avoided for high temperature catalytic applications due to the sintering effect of particles which would have the adverse effects on long-term catalytic applications. Efforts have been made to prepare the catalyst particles with the desired smaller size at high temperature, however, they were found to be sintered at the high temperatures [57,58]. Moreover, Pt-Fe systems have been realized, however they have mostly disordered structure due to the temperature conditions adopted for the synthesis. More importantly, the surface of the synthesized intermetallic nanoparticles has impurities (e.g., organic moieties) due to the use of organic ligands, solvents, shape-directing agents, etc. for the synthesis, which likely affect the catalytic activity [59–61]. Therefore, ordered intermetallic nanoparticles with cleaned surface and preferably the size smaller than 10 nm are required for high temperature catalytic applications, however, it remains a major challenge. Recently, the researchers have reported the ordered intermetallic Pt-Cu nanoparticles (Pt_3Cu, PtCu and $PtCu_3$) with the average size of 4–6 nm at 500 and 800 °C for catalytic oxidation of CO [26].

In this work, we have successfully synthesized platinum (Pt)-based intermetallic catalysts using abundantly available Fe on the γ-Al_2O_3 support through a simple, wet-impregnation method followed by calcination under H_2 environment and used them for indoor air-treatment applications. CO and benzene (C_6H_6) as model indoor air pollutants were selected to demonstrate the catalytic activity of the synthesized intermetallic Pt-Fe (Pt_3Fe and $PtFe_3$) catalysts as shown in Scheme 1. It was also successfully demonstrated that the developed intermetallic Pt-Fe catalysts showed the stable, multi-cycle catalytic performance for CO and C_6H_6 oxidation reaction. It should be noted that Pt and Fe forms three types of intermetallic systems for instance Pt_3Fe, PtFe and $PtFe_3$. Both Pt_3Fe and $PtFe_3$ have cubic structure and PtFe has tetragonal structure. The cubic structure of Pt_3Fe and $PtFe_3$ were selected intentionally to access the suitable intermetallic phase for the CO and C_6H_6 oxidation.



Scheme 1. Schematic illustration of oxidation reaction of CO and C_6H_6 on the surface of intermetallic Pt-Fe systems. The unit cell of intermetallic Pt_3Fe and $PtFe_3$ system is shown at the bottom.

2. Experimental section

2.1. Materials and methods

Chloroplatinic acid hexahydrate (H_2PtCl_6. $6H_2O$) (Pt assay: ≥ 37.50%) (Sigma Aldrich) and Iron (III) 2,4-pentanedoinate ($C_{15}H_{21}FeO_6$), (Alfa Aeser) were used as precursors for the synthesis of intermetallic Pt-Fe catalysts. γ-Al_2O_3 beads (Sasol, Germany) were crushed using a domestic mixer followed by a mortar and pestle for 10 and 30 min respectively, and they were used as support for the synthesis of intermetallic Pt-Fe catalysts. HCl (37%) and HNO_3 (69%) (Emparta, ACS Merck) were used for Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) studies. ICP multi-element standard solution IV (Centripur, Merck, 1000 mg l^{-1} in dilute HNO_3) was used to quantify Pt- and Fe-contents in the intermetallic catalysts. Methanol (Merck Ltd.) was used as solvent for the synthesis of intermetallic Pt-Fe catalysts. N_2-balanced H_2 (5%), CO (5%), O_2 (99.99%) and He (99.998%) were purchased from Alchemie Gases and Chemicals Pvt. Ltd. The water used for washing was purified using a Millipore system.

2.2. Synthesis of intermetallic Pt-Fe catalysts

γ-Al_2O_3-supported, ordered intermetallic Pt-Fe catalysts (Pt_3Fe and $PtFe_3$) were synthesized by calcination of the Pt- and Fe-precursors coated γ-Al_2O_3 under H_2 environment (N_2-balanced H_2, 5%) at set conditions. The Pt- and Fe-precursors coated γ-Al_2O_3 powder was prepared using a wet-impregnation method. 50 ml of methanol solutions containing stoichiometric Pt- and Fe-precursors and 1 g of γ-Al_2O_3 were mixed for 30 min at a room temperature and they were further stirred at 60 °C till the complete evaporation of methanol. The resultant powder was ground using a mortar and pestle followed by calcination at 800 °C for 8 h. It should be noted that 0.5 wt% of Pt-loading was maintained for both intermetallic Pt-Fe catalysts. 0.1327 g of Pt-precursor and 0.0301 and 0.2712 g of Fe-precursors were used for the synthesis of intermetallic Pt_3Fe and $PtFe_3$ catalysts, respectively.

2.3. Characterization

The intermetallic Pt-Fe catalysts were characterized by pXRD using a X-ray diffractometer (Rigaku: Miniflex-II-DD34863) to examine the intermetallic phase formation of Pt-Fe by performing of 2θ scanning with 0.02° increment for 3 s between 20 and 90°. The XRD instrument was operated at 30 kV and 15 mA using a CuKα radiation (λ = 0.15418 nm). The particle size distribution and shape of the intermetallic Pt-Fe nanoparticles on the γ-Al_2O_3 support were obtained using a Transmission Electron Microscopy (TEM) instrument (JEM-2100 F, Acceleration voltage: 200 kV). The suspensions of the intermetallic Pt-Fe catalysts were prepared by mixing of the catalysts in ethanol by sonication for 15 min and they were dropped gently on a Cu-grid (Electron Microscopy Sciences, CF200-CU, 200 Mesh) followed by drying using a hot plate at 40 °C. The formation of the ordered, intermetallic Pt-Fe phase of the synthesized catalysts was further confirmed by performing of the SAED studies on the selected area of the catalysts during TEM observation. The above mentioned characterization studies (pXRD, TEM, SAED, etc.) were repeated over the intermetallic Pt-Fe catalysts after the catalytic evaluations to examine the stability of the catalysts, so-called post-mortem analysis, under set catalytic conditions.