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Sparsely loaded Pt/MIL-96(Al) MOFs catalyst with enhanced activity for H_2-SCR in a gas diffusion reactor under 80 °C

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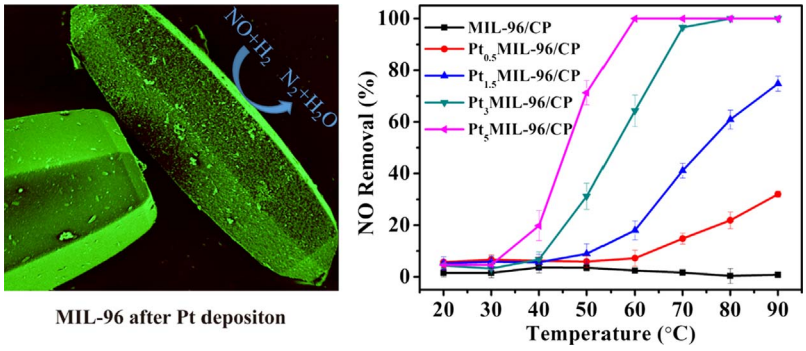
GRAPHICAL ABSTRACT



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ABSTRACT

MOFs (metal-organic frameworks) are stable materials with both organic and inorganic pores, and possess high surface area fascinating structures. Owing to the unique octahedral of aluminum center and strong Al–O bonds, Al-based MOFs show excellent thermal stability. In this paper, MIL-96(Al) is proved to be effective at dispersing Pt particles evenly and sparsely as it is employed as catalyst support. MIL-96(Al) is synthesized via a water based route and different contents of Pt particles are directly deposited on the surface of MIL-96 in one step by hydrothermal method to prepare Pt_XMIL-96 (x represents Pt content) catalysts. The catalyst are sprayed evenly on carbon paper, with Pt content of 0.03%, 0.11%, 0.27% and 0.41%, respectively, and are applied in a gas diffusion reactor with snakelike flow field for low temperature H_2-SCR. For Pt_5MIL-96/CP, the NO removal efficiency can reach up to 100% at 60 °C. Electron transfer between Pt and MIL-96 is observed via X-ray photoelectron spectron (XPS). It reveals that the deposited Pt is in metallic state. Meanwhile, the electronic structure of MIL-96 is kept intact in the process of Pt depositing. The excellent performance of Pt_5MIL-96/CP catalyst strongly suggests its potential application.

1. Introduction

NO_X is considered to be a major pollutant in the atmosphere because of its strong oxidative effect, the contribution to acid rain, photochemical smog, depletion of ozone layer and even global warming [1–3]. In order to meet strict emission laws and regulations, effective NO_X removal techniques are required. In the past few decades, various technologies were being developed and in practice for NO_X reductions. Several promising and reliable techniques including SCR (selective catalytic reduction), SNCR (selective non-catalytic reduction) and NSR

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(NOx storage and reduction) have been adopted for de-nitrification [4–7]. NH_3-SCR was first introduced in 1973 [8] and widely practiced all over the world because of its high efficiency and low cost. But the commonly used commercial catalyst like V_2O_5-WO_3/TiO_2 and V_2O_5-Mo_2O_3/TiO_2 have some disadvantages like high operating temperature, narrow temperature window (300–400 °C) and generation of a large amount of N_2O, besides, the existence of NH_3-slip, air heater fouling, which all limited the feature of NH_3-SCR [8–12]. HC-SCR use hydrocarbons as reducing agent, which requires complete combustion of hydrocarbon. Meanwhile, the producing of CO_2 is unavoidable. Today's emerging needs for SCR are economical, environment-friendly and no greenhouse gas emissions, along without the problems present in NH_3-SCR. Hence, finding an appropriate reducing agent is very urgent. Hydrogen was reported to be very efficient in the process of NO removal in low temperature with or without oxygen [13–17]. Besides, the characteristics of nontoxic, without NH_3-slip and CO_2 emission made H_2-SCR as a highly promising techniques and it still under development [17–19].

NO in flue gas exhausted by coal-fired power plant has the characteristic of high gas flow and low concentration. Actually, most units in China with the capacity of 300 MW and 600 MW, with reports [20,21] showing that the NO_X (NO > 95%) concentration before SCR is between 1.94 g/kg and 8.14 g/kg. Therefore, a catalyst which can effectively remove NO in low concentration, high flow flue gas in a very short time is needed. Pt-based catalyst shows great activity in low temperature H_2-SCR. But Pt nanoparticles are easy to aggregate. Besides, high prices of Pt cannot be ignored as well. Hence, to disperse Pt nanoparticles appropriately, increase the catalytic performance and reduce the Pt usage amount, suitable support is needed. Zeolites [22–25] have been employed as supports for Pt-based catalysts on account of their porosity, high surface area and high adsorption capacities and widely used in the process of NO_X reductions. MOFs (metal-organic frameworks) are the coordination polymers of metal ions and organic ligands [26]. MOFs can be generated with advantages of both organic porous materials and inorganic porous materials, which are stable and possess high surface area fascinating structures. Due to the similarity with zeolites, using MOFs as support for H_2-SCR is feasible.

Using Light-weight metals like magnesium, aluminum and calcium instead of heavy metals as metallic centers draws a lot of attention in recent research [27–30]. Owing to the unique octahedral of aluminum center and strong Al–O bonds [31], Al-based MOFs shows excellent thermal stability. Thermogravimetric analysis shows that Al-MIL species remains stable up to 450 C [31], which provides possibility for Al-MIL species in the application of H_2-SCR. In 2006, Loiseau et al. [32] synthesized MIL-96 which contains infinite chains of $AlO_4(OH)_2$ and $AlO_2(OH)_4$ octahedra. MIL-96 is characterized as honeycomb lattice containing 18-membered rings and reveals three types of different cages. Research shows that it exhibits a hydrogen storage capacity of 1.91 wt% when loaded at 77 K under 3 bar. Wen and coworkers successfully grows Ni-Pt nanoparticles on MIL-96 and applies to hydrogen generation from hydrazine [33]. This demonstrated that the Pt loading in MIL-96 is feasible and the procedure can be used in catalytic reaction.

Carbon paper is a typical carbon-fiber-based porous material, and is chosen as mechanical support layer and gas diffusion layer for catalyst here. It is widely used as gas diffusion layer in electrolyte fuel cells because of the tortuous structure. It can increase the contact area between the catalyst and the flue gas to reduce the Pt usage amount.

2. Experiments

All chemicals used here were commercial and used further purification. Aluminum nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$, 99.0%, Aladdin) and Trimesic acid ($C_6H_3(CO_2H)_3$, 98.0%, Aladdin) are used to synthesize MIL-96 support. Hexachloroplatinic(IV) acid hexahydrate ($H_2PtCl_6{\cdot}6H_2O$, AR, Sinopharm Chemical Reagent Co., Ltd) and N,N-Dimethylformamide (C_7H_3NO, 99.5%, Aladdin) are used on Pt loading. Ethanol absolute (C_2H_5OH, 99.7%, Aladdin) and deionized water are used to wash the samples. Isopropyl Alcohol ($(CH_3)CHOH$, 99.5%, Aladdin) is used as solvent in the process of sample dispersion.

2.1. Synthesis of MIL-96

MIL-96 was hydrothermally synthesized according to the method reported by Loiseau et al. [32–34]. It was hydrothermally synthesized from a mixture of aluminum nitrate and trimesic acid. Aluminium nitrate ($Al(NO_3)_3{\cdot}9H_2O$) (1.314 g) and trimesic acid ($C_6H_3(CO_2H)_3$) (0.140 g) were dissolved in 5 mL deionized water, and the mixture was placed in an ultrasonication bath for 30 min. After that, the solution was transferred into a 25 mL Teflon PTFE vessels and heat at 210 °C for 24 h. When the reaction is completely finished, the Teflon PTFE vessels were naturally cooled to room temperature, and then the product was filtered and washed several times by ethanol and deionized water, and dried in air at 100 °C. Finally, the product was further purified by hydrothermal method in DMF at 150 °C for 300 min. The product was white powder with the formula: $(Al_{12}O(OH)_{18}(H_2O)_3(Al_2(OH)_4)[btc]_6{\cdot}nH_2O)$.

2.2. Preparation of Pt_XMIL-96

The Pt/MIL-96 catalyst was synthesized by a simple hydrothermal method. Firstly, 250 mg of MIL-96 was added into 40 mL DMF solution and then ultrasonic concussion for 30 min. After that, a certain amount of chloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$) was added into the mixture and magnetically stirred for 6 h at 60 °C under 500 rpm. Then, the mixture was transferred into the PTFE vessels and heat at 150 °C for 12 h. After reaction finished, the Teflon PTFE vessels were naturally cooled to room temperature, the product was washed several times by deionized water and dried under vacuum at 60 °C.

2.3. Catalytic activity test

Catalytic activity test was performed by a reactor with snakelike flow field. The experimental setup is shown in Fig. 1. 30 mg catalyst was added into a small vial containing 4 mL isopropanol and 1 mL deionized water. Then the mixture was placed in an ultrasonic bath for 30 min. After that, the turbid liquid was transfered into a spray gun and sprayed on a hydrophobic carbon paper (size 5.5 cm × 5.5 cm, 350 mg) uniformly. Finally, the hydrophobic carbon paper was dried under vacuum at 60 °C for 6 h.

The hydrophobic carbon paper loaded with Pt/MIL-96 was placed between the gas diffusion reactor with a snakelike flow field and a sealplate. The reactant gas composition was 0.1% NO, 2% H_2, 2% O_2 with N_2 as balance gas. The total flow of the inlet gas was set at 120 mL/min and mixed before entering the reactor. Gas residence time is less than 0.09 s in the whole process.

The concentration of NO and NO_2 were analyzed online using a NO-NO_2-NOx Analyzer (Thermo Fisher Scientific, Model 42i), which was connected with computer and the reactor outlet. The result was described in terms of NO removal efficiency, which was calculated on the basis of following equation:

$$NO \text{ Removal efficiency} = \frac{[NO]_{in} - [NO]_{out}}{[NO]_{out}} \quad (1)$$

$[NO]_{in}$, $[NO]_{out}$ represent the inlet and outlet concentration of NO in the reaction, respectively.

2.4. Characterization

Powder X-ray diffraction (XRD) patterns were measured by D/max2550V X-ray diffractometer using a Cu Kα radiation source (40 kV, 100 mA), intensity data were collected in a range of 3–75° at a step size