

Preparation of Pt/beta zeolite–Al₂O₃/cordierite monolith for automobile exhaust purification

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Abstract

A two-step route was developed to prepare zeolite beta coatings on structured monolith. Al₂O₃ layer was deposited on cordierite substrate by slurry dip-coating in the first step and beta zeolite layer was then coated on Al₂O₃/cordierite by direct dynamic hydrothermal synthesis in the second step. The as-prepared beta zeolite–Al₂O₃/cordierite was characterized by means of XRD and SEM techniques and the stability of beta coatings was studied. Based on these results, the advantages of the two-step method were discussed. After the introduction of Pt to beta zeolite–Al₂O₃/cordierite, the obtained Pt/beta zeolite–Al₂O₃/cordierite monolith was tested as promising catalyst for the purification of automobile exhaust from real lean-burn engine.

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1. Introduction

Nitrogen oxides (NO_x), generally referred to NO and NO₂, are major air pollutants that contribute a lot to the formation of photochemical smog and acid rain. Due to the increasingly stringent regulations on NO_x emissions, various post-treatment methods have been attempted for the elimination of NO_x emissions from stationary and mobile sources [1]. Selective catalytic reduction of NO_x by hydrocarbons (HC-SCR, HC: hydrocarbon) is a potential approach to remove NO_x from automobile exhaust under lean-burn conditions [2]. In the past years, zeolite-based materials have been extensively studied as possible HC-SCR catalysts. Noble metal modified zeolites, *e.g.* Pt/beta zeolite [3–5], exhibit remarkably deNO_x performance and are regarded promising catalysts for future application. For practical application, catalyst powders are generally fixed on structured substrate to achieve lower pressure drop and shorter diffusion distances, as the case of three-way catalyst (TWC). Therefore, the coating techniques are important issues that show great influence on the performance of monolithic catalyst.

Honeycomb cordierite (2MgO–2Al₂O₃–5SiO₂) is the substrate in common use, especially for monolithic automobile

catalysts, due to its superior hydrothermal stability and plasticity. There are two general ways to obtain zeolite coatings on cordierite substrate, *i.e.* deposition from slurry of zeolite particles followed by thermal stabilization and direct hydrothermal synthesis [6]. For the former method, it is known that crystalline zeolite materials are difficult to deposit on cordierite and the use of binders are necessary to obtain stable zeolite coatings. The excessive use of binders probably leads to the low utilization ratio of zeolite and corresponding decrease in catalytic activity [7]. The latter method, *i.e.* direct hydrothermal synthesis technique, is a newly developed method to make zeolite coatings on cordierite. ZSM-5/cordierite [8,9] and mordenite/cordierite [10,11] with high zeolite loading and good stability have been obtained. However, the results of direct hydrothermal synthesis are very much related to the synthesis parameters of zeolite powders. As for beta zeolite, it is rather difficult to coat on cordierite substrate by common direct hydrothermal synthesis method [12].

In this work, a two-step method, with the combination of slurry deposition and direct hydrothermal synthesis, to prepare beta zeolite–Al₂O₃/cordierite monolith is reported. The advantages of this two-step method over single slurry deposition method or direct hydrothermal synthesis method are discussed. After the introduction of Pt to beta zeolite–Al₂O₃/cordierite, the as-prepared Pt/beta zeolite–Al₂O₃/cor-

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dierite is tested as promising catalyst monolith for the purification of automobile exhaust from real lean-burn engine.

2. Experimental

2.1. Sample preparation

2.1.1. Preparation of $\text{Al}_2\text{O}_3/\text{cordierite}$

Cordierite honeycomb monoliths (Corning, 400 cpi, 0.1 mm average wall thickness) were used as substrate. $\text{Al}_2\text{O}_3/\text{cordierite}$ was prepared by traditional dip-coating method. Briefly, γ -alumina (Sinopec, BET surface area $125.2 \text{ m}^2/\text{g}$) and H_2O were mixed at the ratio of 1:2 and vigorously stirred for 2 h to form slurry. The pH value of the slurry was carefully adjusted to 5 ± 0.2 by addition of CH_3COOH . The pretreated cordierite was immersed in the slurry for 1 min, taken out and blown with hot air to remove the excess slurry. After dried at 120°C over night, the monolith was calcined at 600°C in flowing air for 4 h and labeled as $\text{Al}_2\text{O}_3/\text{cordierite}$.

2.1.2. Preparation of beta zeolite- $\text{Al}_2\text{O}_3/\text{cordierite}$

Firstly, $\text{Al}_2\text{O}_3/\text{cordierite}$ was pre-treated in 0.5 M NH_4NO_3 in an ultrasonic bath for 20 min and then dried at 120°C over night. Then, beta zeolite precursor gel was prepared. Briefly, sodium hydroxide (NaOH), potassium hydroxide (KOH), tetraethylammonium hydroxide (TEAOH), silica powder (SiO_2) and water were mixed under vigorous stirring at the proportion of $28\text{SiO}_2:2\text{NaOH}:1\text{KOH}:14\text{TPAOH}:400\text{H}_2\text{O}$. The resulting homogeneous gel was aged at 40°C for 48 h. Finally, the pre-treated $\text{Al}_2\text{O}_3/\text{cordierite}$ and aged gel were put into teflon lined stainless steel autoclave for crystallization under rotation at 160°C for 72 h. After crystallization, the monolithic sample was taken out, washed with distilled water ultrasonically, dried at 120°C over night and then calcined at 600°C in air for 4 h.

2.1.3. Preparation of beta zeolite/cordierite

For reference, beta zeolite/cordierite was also prepared via two different routes, *i.e.* slurry dip-coating and direct hydrothermal synthesis. For dip-coating, zeolite beta and H_2O were mixed at the ratio of 1:2 and vigorously stirred for 2 h to form slurry. The pH value of the slurry was adjusted to 5 ± 0.2 by addition of CH_3COOH carefully. The pretreated cordierite was immersed in the slurry for 1 min, taken out and blown with hot air to remove the excess slurry. After dried at 120°C over night, the monolith was calcined at 600°C in flowing air for 4 h and labeled as beta zeolite/cordierite-dip. For direct hydrothermal synthesis, aged beta zeolite precursor gel and pretreated cordierite were put into teflon lined stainless steel autoclave for crystallization under rotation at 160°C for 72 h. After crystallization, the monolithic sample was washed, dried, calcined and labeled as beta zeolite/cordierite-hyd. The route is as essential as that employed for the synthesis of beta zeolite- $\text{Al}_2\text{O}_3/\text{cordierite}$. The only difference is the cordierite is used as substrate for the preparation of beta zeolite/cordierite-hyd while $\text{Al}_2\text{O}_3/\text{cordierite}$ is used as substrate for the preparation of beta zeolite- $\text{Al}_2\text{O}_3/\text{cordierite}$.

2.1.4. Preparation of Pt/beta zeolite- $\text{Al}_2\text{O}_3/\text{cordierite}$

Pt/beta zeolite- $\text{Al}_2\text{O}_3/\text{cordierite}$ monolithic catalyst was prepared by impregnating the as-prepared beta zeolite- $\text{Al}_2\text{O}_3/\text{cordierite}$ with aqueous solution of $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ at the constant temperature. In a typical preparation process of Pt/beta zeolite- $\text{Al}_2\text{O}_3/\text{cordierite}$, 50 mL $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ aqueous solution (Pt concentration: 4.0 mg/mL) was added to 100 g beta zeolite- $\text{Al}_2\text{O}_3/\text{cordierite}$ to achieve Pt loading of *ca.* 0.2%. The as-prepared Pt/beta zeolite- $\text{Al}_2\text{O}_3/\text{cordierite}$ sample were carefully washed by distilled water, dried at 120°C over night and calcined at 500°C in flowing air for 4 h.

2.2. Characterization methods

The X-ray diffraction (XRD) analysis of all samples was carried out on a Rigaku powder diffractometer (D/MAX - RB). The scanning rate was 4°min^{-1} and Cu $\text{K}\alpha$ radiation ($\lambda = 0.1542 \text{ nm}$) was used.

The surface morphology of samples was examined by scanning electron microscopy (SEM, JEOL JSM 6400) operated at 20 kV. The samples were covered with a thin layer of gold film by sputtering before observation.

The specific surface areas of the samples were determined by nitrogen adsorption at 77 K on Micromeritics ASAP 2010 analyzer.

The loadings of beta zeolite in monoliths prepared by different methods were calculated based on the weight increase before and after preparation.

The stability of beta zeolite- $\text{Al}_2\text{O}_3/\text{cordierite}$ monolith and beta zeolite/cordierite sample was tested by means of ultrasonic vibration on a KQ-800KDE-mode ultrasonic apparatus. After each 15 min, the sample was taken out from ultrasonic, dried and then the weight loss was measured.

2.3. Automobile exhaust purification on Pt/beta zeolite- $\text{Al}_2\text{O}_3/\text{cordierite}$

The Pt/beta zeolite- $\text{Al}_2\text{O}_3/\text{cordierite}$ was tested as monolithic catalyst for the purification of lean-burn automobile exhaust from real four-valve S. I. engine (1.34 L). The controllable quasi-homogeneous mixture inside the cylinder made by the controllable injection on this engine realized the fast quasi-homogeneous mixture combustion. The air fuel ratio (A/F) was controlled at 20 ± 0.5 . The monolithic catalyst (*ca.* 100 g) was fixed inside the vent-pipe of the engine, heated by an electrical heater. The temperature was measured by NiCr-NiAl thermojunction and controlled by relay and temperature controller. The products after catalytic reaction were online analyzed by a five-component exhaust analyzer (MW56-AVL DIGAS 4000 LIGHT).

3. Results and discussion

3.1. Characterization of beta zeolite- $\text{Al}_2\text{O}_3/\text{cordierite}$

XRD analysis provides us with an easy judgment on the coating results of zeolites on cordierite substrate. Fig. 1

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