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Direct synthesis of zeolite coatings on cordierite supports by in situ hydrothermal method

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Abstract

A simple and green in situ hydrothermal method, free of organic templates or zeolite seeds, was examined and introduced by depositing several typical microporous aluminosilicate zeolites (Linde A, Linde Y, mordenite and ZSM-5) on cordierite supports. Such preparative factors as crystallization time, crystallization temperature and basic strength were systematically investigated to discuss their effect on the growth of zeolites on cordierite supports. The as-prepared zeolite/cordierite samples were characterized by various techniques and a supposed in situ growth mechanism of zeolites on supports was given. The aluminium atoms on cordierite supports were activated by OH^- and these activated atoms subsequently built a zeolite framework together with the silicon atoms and aluminium atoms of the synthesis gel. Based on this, the in situ deposition of zeolites can be easily extended to other aluminium-containing supports. With respect to pure zeolite powders, the in situ coated zeolites on supports exhibited much better stability and accessibility, which were thought essential for industrial applications. Copper ion-exchanged ZSM-5/cordierite was studied as catalyst for the direct decomposition of NO and selective catalytic reduction of NO by propane in excess oxygen. Cu-ZSM-5/cordierite was found to exhibit an obviously enhanced turnover frequency compared to Cu-ZSM-5 powders, which made it a potential deNO_x catalyst for future applications.

Keywords: Zeolite coatings; In situ synthesis; Cordierite; Stability; Accessibility; TOF

1. Introduction

Crystalline molecular sieves with microporous structure have been extremely successful as catalysts for oil refining, petrochemistry and organitic synthesis in producing fine and speciality chemicals, particularly when dealing with molecules having kinetic diameters below 10 Å [1]. In most cases, these materials are synthesized by hydrothermal method and the particle size obtained by this method is generally small [2]. The direct use of materials with small particle size may cause many problems, such as high pressure drops and difficulty in separation and operation. A simple way to solve these problems is to make use of zeolite crystals coated on structured support materials [3]. Ceramic, especially honeycomb cordierite ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$), is the support in common use because of its superior mechanical stability and hydrothermal stability as well as its plasticity. The usual coating techniques are dip-coating, slip-coating and slurry-coating [4]. However, it is well known that crystalline zeolite materials are difficult to washcoat, and that the use of binder may increase the diffusion problem and reduce the accessible porosity. Then, it has been proposed to prepare the zeolite component from crystallites grown on support surfaces, so-called in situ synthesis [5]. The main advantage of in situ synthesis over other coating techniques is that the support is used as a base for nucleation and that a chemical bonding between crystals and outer support layer is formed [6]. This results in a natural transition from support to zeolite layer and consequently a high thermal, chemical and mechanical stability of the zeolite/support monolith.

Various zeolites such as ZSM-5 [7–11], TS-1 [12] and mordenite [13] have been successfully coated on supports by the in situ hydrothermal synthesis method. Moreover, in situ

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synthesized monolithic zeolite/support and modified zeolite/support have been proved to be successful catalysts for many important reactions [14–20]. Currently, the study of in situ synthesis focused on the optimized preparation of zeolite coatings (mainly ZSM-5) on various supports, such as honeycomb cordierite [10,11], ceramic foam [7], stainless steel [21], and carbon materials [8]. The synthesis process usually involves the use of organic templates or zeolite seeds, which makes the growth of zeolite crystals on a support rather complicated.

In the present study, a series of zeolites (Linde A, Linde Y, mordenite and ZSM-5) were synthesized on honeycomb cordierite supports by an in situ hydrothermal method in the absence of organic templates or zeolite seeds. Such a simple synthesis system would provide us a better understanding of the growth of zeolites on supports. Based on the synthesis and characterization results, we demonstrated how zeolite crystals could grow on a cordierite support in this work. The advantages of in situ synthesis were also discussed and modified zeolite/cordierites were tested as catalysts for the direct decomposition and selective reduction of nitric oxide.

2. Experimental

2.1. Synthesis

Cordierites manufactured by Corning Incorporated (60 cells/cm^2, 0.3 mm average wall thickness) were used as support materials. Before being used as supports, the commercial cordierites were cleaned in HCl (0.1 M) by ultrasonic for 20 min, washed by deionized water and then dried at 373 K.

For the synthesis of zeolites, tetraethylorthosilicate (TEOS, AR) was used as silicon source and aluminium sulfate (AR) as aluminium source. No template was needed throughout the synthesis processes. TEOS, sodium hydroxide, aluminium sulfate and water were mixed at certain proportions. After 3 h vigorous stirring, the gained transparent liquid and bulk cordierites were put into a Teflon-lined stainless steel autoclave together for static crystallization at certain fixed temperatures for a period of time. Then the samples were taken out, washed in deionized water by ultrasonic waves to remove the unstable adherends on the cordierite, and then dried at 373 K overnight. The specific synthesis conditions of different zeolites were displayed in Table 1.

For the synthesis of ZSM-5/Al, tetraethylorthosilicate was used as the silicon source and the aluminium source was from the aluminium support. No template was needed throughout the synthesis process. Tetraethylorthosilicate, sodium hydroxide and water were mixed in the proportions of $80SiO_2$:15NaOH:$3000H_2O$. After 2 h of vigorous stirring, the gained transparent liquid and the aluminium plate (pretreated in 0.5 mol/L HCl for 2 h to remove the aluminium oxide on the surface) were put into Teflon-lined stainless steel autoclaves for static crystallization at 453 K for 24 h. Then the samples were taken out, washed in deionized water by ultrasonic, and then dried at 373 K overnight.

Cu-ZSM-5/cordierite was prepared from synthesized ZSM-5/cordierite by the solution ion-exchange with 0.1 M $Cu(CH_3COO)_2$ at room temperature under slow stirring four times, 48 h each time, to ensure an ion-exchange level of 100%. The ion-exchanged sample was washed four times in an ultrasonic generator, 15 min each time, to remove the metal ions adhering on the surface to a large extent, and then calcined at 823 K for 4 h in air.

2.2. Characterization

X-ray diffraction (XRD) analysis of the as-synthesized zeolite/cordierite samples was performed on a Rigaku D/max 2500 diffractometer, equipped with a graphite monochromator and using Cu Kα radiation. The zeolite/cordierite monoliths were cut into small thin pieces (8 mm × 8 mm) for analysis.

A HITACHI S-3500N scanning electron microscope (SEM) was used for studies of external and internal surface morphology of zeolite/cordierites. SEM images were recorded on the samples covered with a thin layer of gold deposited by sputtering.

Surface areas and pore diameters were determined by nitrogen adsorption on the ASAP 2010M facility (Micromeritics).

Zeolite loading in zeolite/cordierite was obtained by calculating the weight increase of cordierite after hydrothermal synthesis. The Si/Al ratio of zeolite on cordierite support was calculated from the contents of Si and Al, which were determined by ICP (IRIS Advantage, TJA solution).

Table 1
Hydrothermal synthesis conditions for the synthesis of zeolites [22]

Sample zeolite/structure	Batch molecular composition[a]				Synthesis conditions	
	SiO_2	Al_2O_3	Na_2O	H_2O	Temperature (K)	Time (h)
Linde A/LTA	2	1	3	120	373	4
Linde Y/FAU[b]	10	1	5	200	373	8
Mordenite/MOR	30	1	5	750	453	24
ZSM-5/MFI	80	1	10	1500	453	24

[a] Cordierite supports excluded.

[b] A little seed gel ($10Na_2O:Al_2O_3:10SiO_2:200H_2O$) was used.