Fe-mordenite/cordierite monolith for the catalytic decomposition of nitrous oxide

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Abstract

Mordenite zeolites were coated on cordierite support by in situ hydrothermal method or dip-coating method. The mordenite/cordierite was characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM) techniques and their stability was studied. The mordenite/cordierite monolith prepared by in situ synthesis showed much better stability than that prepared by dip-coating. Iron was introduced into mordenite/cordierite by ion exchange and Fe-mordenite/cordierite catalyst was prepared. Fe-mordenite/cordierite prepared from in situ synthesis exhibited good activity and stability for N_2O catalytic decomposition, with great potential for future application.
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1. Introduction

N_2O has been recognized as strong greenhouse gas with very long atmospheric lifetime up to $\sim$120 years, and its global warming potential of N_2O is about 310 times that of CO_2 [1]. Moreover, N_2O constitutes as the main stratospheric source of pollutant NO and severely destructs the ozone layer [2]. Many efforts have been made to develop end-of-pipe technologies to mitigate N_2O emission from anthropogenic sources, such as adipic acid production and nitric acid manufacture. An effective way to minimize the impact of N_2O on the environment is to catalytically decompose N_2O to environment-friendly N_2 and O_2 [3–7].

Currently, iron-containing zeolites (such as Fe-ZSM-5) have attracted much attention due to their good catalytic performance under simulated industrial conditions. For practical application, catalysts have to be fixed on structured substrate to form monoliths, thus methods for monolith preparation are very important [8]. Ceramic, especially honeycomb cordierite ($2MgO–2Al_2O_3–5SiO_2$), is the substrate in common use because of its superior mechanical stability and hydrothermal stability as

well as its plasticity. Various coating techniques, e.g. dip-coating and slurry-coating [9], have been developed to deposit catalysts on structured ceramic surfaces. Moreover, for zeolite catalyst, it has been proposed to grow the zeolite directly on ceramic surfaces, so-called in situ hydrothermal synthesis. Up to now, in situ hydrothermal synthesis is proven as suitable technique for making zeolite/ceramic monolith [10,11] and zeolite monolithic catalysts have been employed in several important gas phase reactions, such as the selective catalytic reduction of NOx [12].

In this work, mordenite/cordierite monolith is prepared by in situ hydrothermal synthesis method and by common dip-coating method, respectively. Then active phase of iron is introduced into mordenite/cordierite by ion exchange and Fe-mordenite/cordierite is studied as monolithic catalyst for the decomposition of N_2O. The research aim of this work is to give some hints on the preparation of monolithic Fe-mordenite/cordierite, with potential application for N_2O decomposition.

2. Experimental

2.1. Sample preparation

2.1.1. Synthesis of mordenite

For the synthesis of mordenite, tetraethylorthosilicate (TEOS, AR) was used as silicon source and aluminum sulfate

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(AR) as aluminum source. No template was added throughout the synthesis processes. TEOS, sodium hydroxide, aluminum sulfate and water were mixed at the molar ratio of $30SiO_2:1Al_2O_3:5Na_2O:750H_2O$. After 3-h vigorous stirring, the gained transparent liquids were put into a Teflon-lined stainless steel autoclave for static crystallization at 180 °C for 12 h. Then the samples were taken out, washed with deionized water in ultrasonic waves to remove the unstable adherends on the cordierite, and then dried at 100 °C overnight.

2.1.2. In situ synthesis of mordenite/cordierite

Cordierites (Corning Incorporated, 60 cells/cm²) were pretreated by ultrasonic with diluted HCl solution. For mordenite to grow on cordierite substrate, the transparent liquid (the same as that for the synthesis of mordenite) and bulk cordierites were put into a Teflon-lined stainless steel autoclave together for static crystallization at 180 °C for 12 h. The obtained monolithic sample were taken out, washed with deionized water and then dried at 100 °C overnight.

2.1.3. Dip-coating of mordenite onto cordierite

For the dip-coating process, a suspension of 30% (wt.) mordenite in deionized water (pH 6) was used to impregnate the cordierite substrate. The suspension was carefully crushed before dip-coating. Four successive immersions were performed to achieve the zeolite loading of ca. 20% (wt.), and after each immersion the obtained monolith was blown by hot air and then dried at 150 °C.

2.1.4. Ion exchange process

Iron-containing zeolite catalysts were prepared from mordenite/cordierite monolith or mordenite powder by wet ion exchange using ferrous salt at room temperature. For example, 5.0 g of parent sample was exchanged with 500 mL 0.05 mol/L $FeSO_4$ (pH ~3.0) for 48 h under vigorous stirring in the flowing N_2 stream. The as-exchanged samples were then filtered, thoroughly washed, dried at 100 °C and calcined at 600 °C for 4 h in air.

2.2. Characterization techniques

The XRD patterns of all samples were measured on a Rigaku powder diffractometer (D/MAX-RB) using Cu Kα radiation ($\lambda = 0.1542$ nm) at a scanning rate of 4°/min in $2\theta = 5$–40°.

SEM images were acquired on a HITACHI S-3500N scanning electron microscope. The samples were covered with a thin layer of gold deposited by sputtering before observation.

The temperature-programmed reduction experiments of samples were carried out on a chemisorption analyzer (Chemisorb 2720, Micromeritics) with 5 vol.% H_2/Ar at a heating rate of 10 °C/min from 40 to 800 °C. Prior to reduction, the sample was treated in He at 450 °C for 1 h.

2.3. Stability of mordenite/cordierite monolith

The stability test of mordenite/cordierite monolith samples were carried out on a KQ-800KDE-mode ultrasonic apparatus.

The samples were put into deionized water and treated by ultrasonic for a certain period of time at the power rating of 0.8 kW.

2.4. Catalytic performance test

N_2O decomposition experiments were performed in a fixed-bed microreactor at atmospheric pressure. Typically, 0.1 g powder sample or 0.5 g monolith sample was placed in a quartz reactor and pretreated in He at 600 °C for 1 h. After cooling to 300 °C, the reactant gas mixture (N_2O, or O_2 or H_2O, He balance) was fed into the reactor. The total flow rate of gas mixture was kept at 60 mL min^{-1}, i.e. GHSV = 30,000 h^{-1} (referred to Fe-mordenite). The steady-state tests were conducted isothermally every 25 °C from 300 to 600 °C or at a constant reaction temperature of 600 °C. The gas products (after 1-h reaction) were analyzed on-line using a gas chromatograph (Agilent 6820 series) equipped with a TCD detector and two serial columns (a Porapak Q column served for the separation of N_2O and N_2/O_2, and a molecular sieve 5 Å column for the separation of N_2 and O_2).

3. Results and discussions

3.1. Characterization of mordenite/cordierite monolith

Fig. 1 shows the XRD patterns of blank cordierite, mordenite powder and mordenite/cordierite monolith. As seen in the figure, typical diffraction peaks at 10.4°, 18.03°, 19.0°, 21.6°, 26.4°, 28.4°, 29.4° and 33.9° are observed in the XRD pattern of blank cordierite, corresponding to the structure of ceramic ($2MgO$–$2Al_2O_3$–$5SiO_2$). In the XRD pattern of mordenite powders, diffraction peaks corresponding to the typical structure of mordenite are observed [13]. While in XRD patterns of mordenite/cordierite, diffraction peaks of both blank cordierite and mordenite can be observed, suggesting that
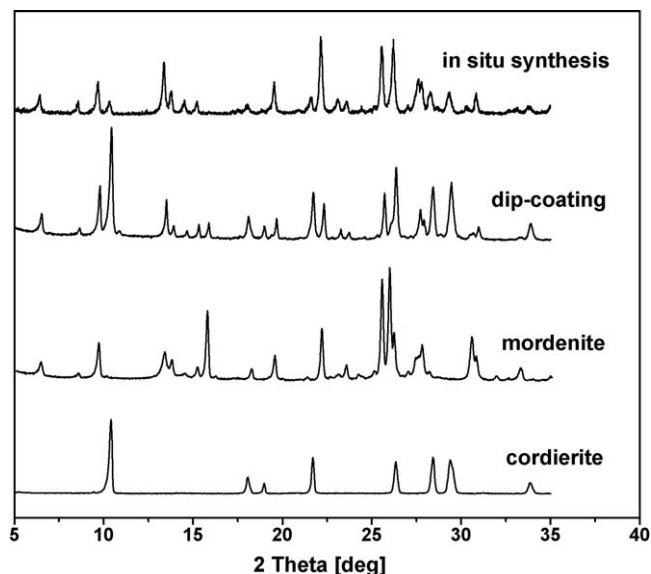

Fig. 1. XRD patterns of blank cordierite, mordenite powder and mordenite/cordierite monolith prepared by different methods.

mordenite is successfully coated on the surface of cordierite either by in situ synthesis method or by dip-coating method.

The SEM images of blank cordierite, mordenite and mordenite/cordierite are shown in Fig. 2. The irregular ceramic structure is observed for cordierite support and prisms of about 20 μm are observed for mordenite powders. In the images of in situ synthesized mordenite/cordierite, bulk mordenite prisms of about 20 μm are observed to coat on external surface of cordierite, while mordenite prisms together with small clubs are observed on the internal surface. It is seen that mordenite tends to form small crystals (i.e. clubs) on the internal surfaces than on the external surfaces. During the process of in situ synthesis, cordierite is the substrate for crystal nucleation and the crystals orientation is thus affected [10]. Besides, the growth of mordenite is also dimensionally restricted by the structure of cordierite when growing on the internal surface. For dip-coated mordenite/cordierite, crushed mordenite prisms are observed to compactly coat on the external surface of cordierite while few mordenite prisms are observed on the internal surface. Obviously, mordenite tends to be coated on the external of cordierite support rather than on internal surface.

3.2. Stability of mordenite/cordierite monolith

The stability of mordenite/cordierite monolith is tested by means of ultrasonic treatment and the results are shown in Fig. 3. It is seen that no obvious weight loss can be observed after 1-h treatment for in situ synthesized sample, indicating the good stability of the tested sample. In contrast, nearly 50% coatings fall off from mordenite/cordierite prepared by dip-coating method after 1-h treatment. The lack of stability for dip-coated sample may be fatal defect for industrial application.
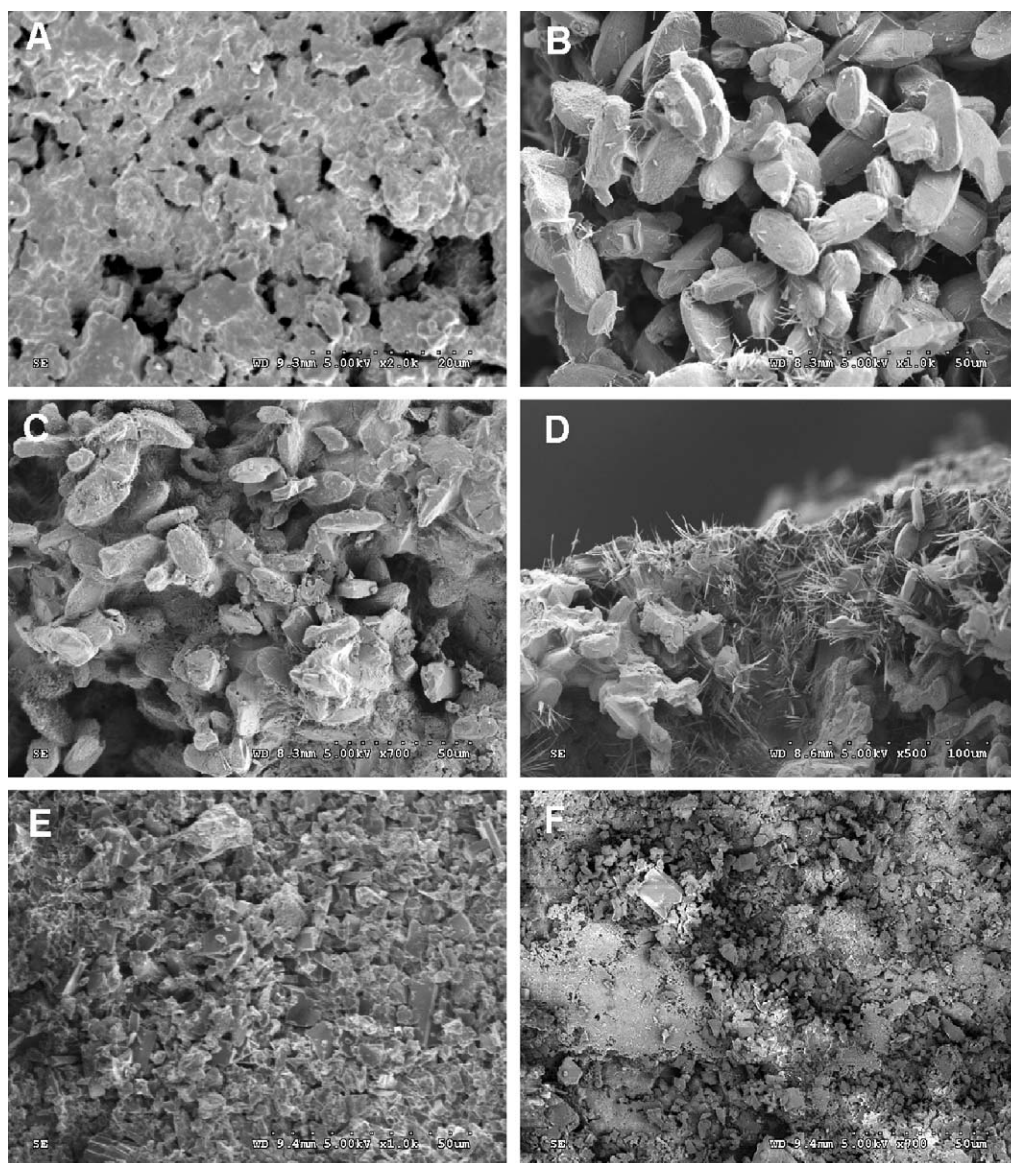

Fig. 2. SEM images of cordierite, mordenite and mordenite/cordierite monolith prepared by different methods: (A) blank cordierite; (B) mordenite powder; (C) external surface of in situ synthesized monolith; (D) internal surface of in situ synthesized monolith; (E) external surface dip-coated monolith; (F) internal surface of dip-coated sample.
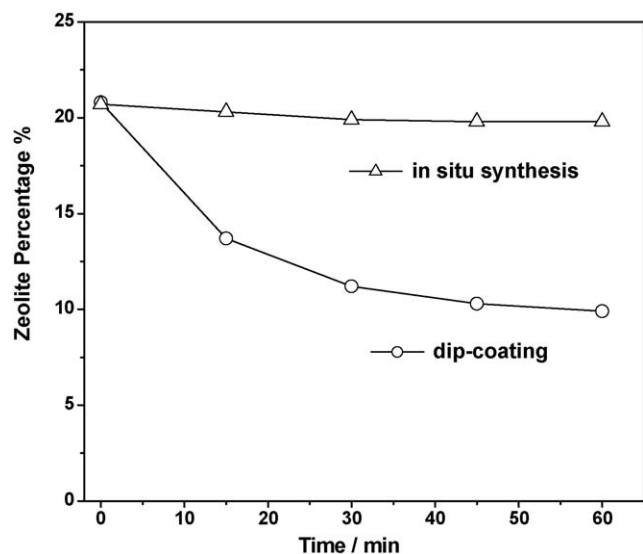
Fig. 3. Stability test of mordenite/cordierite monolith prepared by different methods.

3.3. Catalytic performance for N_2O decomposition

The catalytic activities for N_2O decomposition over Fe-mordenite powders and Fe-mordenite/cordierite monolith prepared by different methods are shown in Fig. 4. As for Fe-mordenite, N_2O decomposition starts at about 450 °C and the 50% N_2O conversion occur at 560 °C. The dip-coated Fe-mordenite/cordierite exhibits nearly identical activity for N_2O decomposition to Fe-mordenite powder with similar mordenite loadings. Based on the preparation process, dip-coated Fe-mordenite/cordierite monolith can be even thought as a mechanical mixture of Fe-mordenite powder and cordierite support. While for in situ synthesized Fe-mordenite/cordierite, an improved activity for N_2O decomposition is observed when
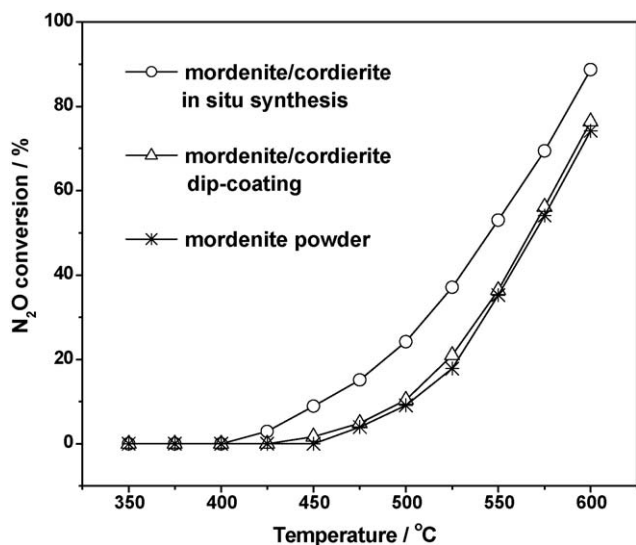

Fig. 4. N_2O catalytic decomposition on Fe-mordenite powder and Fe-mordenite/cordierite monolith. Reaction conditions: 0.1 g powder or 0.5 g monolith, 0.5% N_2O, 5% O_2, balance He, GHSV = 30,000 h^{-1} (referred to zeolite loadings).

compared to Fe-mordenite powder and nearly 90% N_2O conversion can be obtained at 600 °C. The improved activity may be attributed to the better accessibility of zeolite coating derived from in situ synthesis method [14]. By in situ synthesis, the zeolite crystals directly nucleate on cordierite support and mainly grow along certain direction. The order in crystal growth and the highly dispersion of zeolite crystals greatly improves the accessibility of zeolites and which effectively avoided the "dead volume" caused by the random packing of zeolites. When iron is introduced to mordenite/cordierite, the agglomeration of iron to bulk iron oxides induced by calcination can be prevented to some extend. Bulk iron oxides are known to play a negative role for N_2O decomposition [15], and thus in situ synthesized Fe-mordenite/cordierite shows better activity for N_2O decomposition.

The formation of iron oxides in Fe-mordenite and Fe-mordenite/cordierite is analyzed by means of H_2-TPR. As seen in Fig. 5, the reduction of Fe species starts at 200 °C and continues to over 750 °C. Based on previous investigations, the reduction peaks in the range of 250–450 °C are attributed to the reduction of ion-exchanged Fe species in tetrahedral or octahedral coordination, while the reduction peaks at 550–750 °C are attributed to the reduction of bulk iron oxides [16,17]. It is seen that a large proportion of bulk iron oxides exist in Fe-mordenite and dip-coated Fe-mordenite/cordierite while the iron oxides in in situ synthesized Fe-mordenite/cordierite can nearly be ignored. The formation of bulk iron oxides is greatly suppressed in Fe-mordenite/cordierite due to the orientation of crystal growth during in situ synthesis [18] and the catalytic activity for N_2O decomposition is greatly improved in such a way.

The durability of Fe-mordenite/cordierite catalyst prepared by in situ method in the absence or presence of H_2O was further investigated. Time-on-stream profiles in Fig. 6 show that the N_2O conversion is about 88% at 600 °C and remained almost unchanged for 60 h, indicating that the catalyst is highly durable under these conditions. The presence of 2.5% H_2O
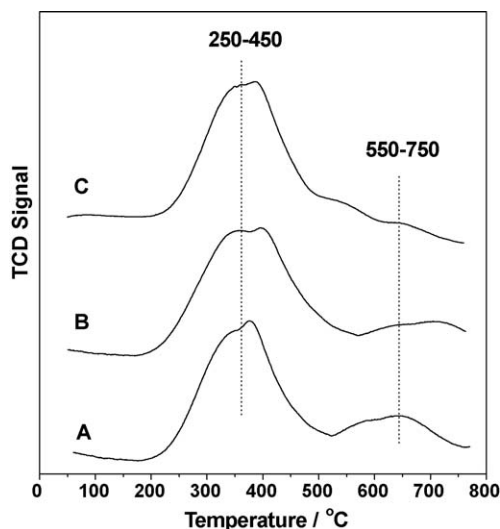

Fig. 5. H_2-TPR profiles of Fe-mordenite powder (A), Fe-mordenite/cordierite monolith prepare by dip-coating method (B) and in situ synthesis (C).
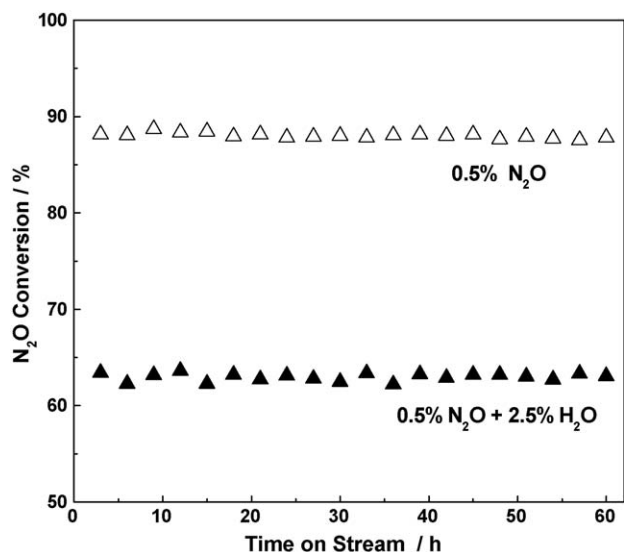
Fig. 6. Time-on-stream behavior of Fe-mordenite/cordierite for N_2O decomposition at 600 °C. Reaction conditions: 0.5 g catalyst, 0.5% N_2O, 5% O_2, 0 or 2.5% H_2O, balance He, GHSV = 30,000 h^{-1}.

shows obvious negative effect on N_2O decomposition and the N_2O conversion decreases from about 88% to about 63%. Good durability of Fe-mordenite/cordierite is also achieved in the presence of H_2O, which demonstrates its potential for future application.

4. Conclusion

Mordenite/cordierite monolith is prepared by in situ hydrothermal synthesis method or by common dip-coating method. The as-prepared monoliths are characterized by means of XRD and SEM techniques. The monolithic sample prepared by in situ method exhibits much better stability than the sample prepared by dip-coating. Fe-mordenite/cordierite monolith exhibits good activity and stability for N_2O decomposition, which demonstrates its potential for application.

Acknowledgements

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