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In-situ Synthesis of ZSM-5 with Different Si/Al Ratios on Honeycomb-shaped Cordierite and their Behavior on NO Decomposition

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Abstract: Zeolites ZSM-5 with different Si/Al ratios were *in-situ* synthesized on the surface of honeycomb-shaped cordierite support for the first time. Characterizations of XRD and SEM were performed and it has been proved that the zeolite ZSM-5 was grown on the surface of the cordierite homogeneously. NO decomposition on the Cu exchanged ZSM-5/cordierite monolith catalysts was also studied. It was found that the monolith catalysts have a fine initial activity at 673K and GHSV of 10,000h^{-1}. Such method should be a good way to make auto exhaust converter with monolith catalyst for NOx removal.

Keywords: Cordierite, ZSM-5, *in-situ* synthesis, NO decomposition.

The cleaning techniques to reduce air pollution produced by the exhaust gases from vehicles' engine are focused by research workers in recent years [1-2]. Among them, the catalytic conversion of the poisonous substances, such as CO, HC and NOx into non- or less poisonous ones may be the most effective. The catalyst that is called "monolithic catalyst" was composed of three parts: substrate, active coating and active components [3]. The substrate in common use was the honeycomb-shaped cordierite, whose main component was: $2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$. The active coatings (γ -Al_2O_3, zeolites, *etc.*)were usually "washcoated" on the surface of the cordierite in order to provide larger specific surface to carry the metallic active components. However, the zeolite coatings easy peeled off the substrates under high GHSV, because of their low adherence. And this method yields crystal layers that have a low continuity and a limited accessibility [4]. The main objective of this work is to develop a new method, by which the crystals are directly grown on the surface of the honeycomb shaped cordierite from a sol under zeolite synthesis conditions. In this way, coatings may be grown that have a high continuity and attrition resistant and chemically stable from the interaction between zeolite and support. Furthermore, the effect of *in-situ* synthesized monolith Cu/ZSM-5 catalyst with different Si/Al ratios on the decomposition of NO has been investigated. It has been found that the monolith catalysts have pretty good activities to the reaction of $2NO \rightarrow N_2+O_2$.

Experimental

1. In-situ synthesis and monolithic catalysts preparation

A whole honeycomb-shaped cordierite substrate (400cells/inch^2) was broken into pieces (2cm×1cm×0.5cm), and placed paralleled in autoclave without Teflon sleeves. A material mixture composed of sodium aluminate (self-prepared), silica sol (industrial grade), tetrapropyl ammonium bromide (TPABr, self-prepared), sodium hydroxide (analytically pure), and distilled water in a certain ratio was put into the autoclave and stirred till a well-mixed phase was reached at room temperature. Then the autoclave was put into the oven at 448K for static crystallization. After the crystallization, the products were cooled down rapidly. The as-synthesized samples were washed out with ultrasonic wave generator and dried at 383K for 12 hours. Then the samples calcined carefully at 823K for 6 hours in order to remove amine. The Na form samples was first exchanged to H form by NH_4Cl solution, then further ion-exchanged into cupriferous catalysts by cupric-acetate solution.

2. Characterization

The products from *in-situ* synthesis were characterized on an X-ray diffractometer (Rigacu D/max 2500), using CuK α radiation, graphite monochromatic and continuous scanning registration. The morphological structure was determined on a SEM micrographs (HITACHI X-650 Scanning Electron Microscope). The Si/Al ratios and the amount of zeolite on the support were calculated with help of ^{29}Si solid MAS-NMR. The Cu content of the monolithic catalyst was determined on an American ICP9000 (N+M) Plasma-atom Emission Spectrum.

3. Evaluation of catalyst

The reaction was carried out in a continuous flow stainless reactor. The composition of feed gas was 2.82% NO (balanced by He gas), the total GHSV was 10,000h^{-1}, and the reaction temperature was 673K. A SP-502 gas chromatography with a TCD detector used to monitor catalytic activity.

Results and discussions

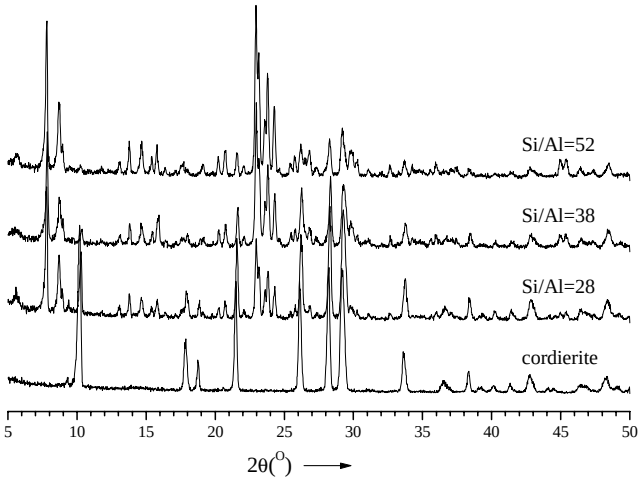
There are three samples *in-situ* synthesized from sols with variation of the aluminum content. **Table 1** summarizes data of characterization results together with

Table 1. Some parameters of the catalysts

Samples number	Si/Al(mol)	Zeolite wt%	Cu wt%	Cu exchange level(%)
1#	28	15.31	0.89	162
2#	38	28.66	0.93	121
3#	52	31.08	0.61	99

synthesis conditions. **Figure 1** shows the XRD patterns both of *in-situ* synthesized samples and cordierite. Compared with the spectrum of blank cordierite (0#), the samples (1#—3#) after *in-situ* synthesis showed the characteristic peaks of ZSM-5 between 8-9° and 22-25° , which proved that ZSM-5 zeolite layers had "grown" on the substrates. Besides, with increasing of Si/Al ratios, the relative peak-intensity of ZSM-5 to those of cordierite became more dominant. The SEM micrographs of the cordierite and as-synthesized samples were given in **Figure 2**. A large difference in the surface morphology of cordierite was found between before and after *in-situ* synthesis. And a continuous polycrystalline zeolite layer covered the surface of cordierite substrate after *in-situ* synthesis. The change observed in the average crystal size increases with the SiO_2/Al_2O_3 and the crystals of zeolite became well shaped. This indicates that the synthesis mixture with higher Si/Al ratios was favorable to ZSM-5 crystals grow on the cordierite.

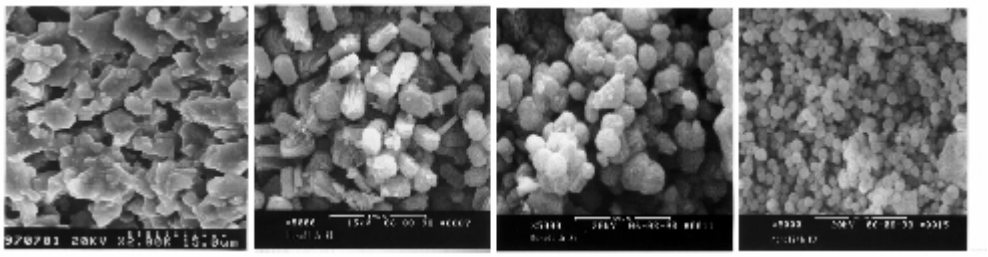
Figure 1. X-ray diffraction patterns of as-synthesized samples with different Si/Al ratios



In order to analyze the effect of the Si/Al ratio on NO decomposition, experiments over these monolithic catalysts varied with different temperature were performed. The results of this test are depicted in **Figure 3**. It can be seen that the catalytic activity of blank cordierite to decomposition of NO was very weak and can be ignored, while the synthesized monolithic catalysts showed much higher activities for NO decomposition. And all catalysts (1#-3#) show a maximum of NO conversion into N_2 at 673K. And the catalyst with higher Si/Al ratio is more active at higher temperatures. Because the sample 2# and 3# has the similar zeolite content and Cu content but different Si/Al ratio, a conclusion could be drown that larger Si/Al ratios facilitates the activity of NO decomposition. In order to check if the effect of catalyst copper loading on NO conversion is not important under our reaction conditions, we measure the catalytic activity on sample 2# at 673K with different copper loading. From the analysis of **Figure 4**, we can say that the effect of zeolite copper loading is exerted major influence on the conversion of NO especially at lower copper exchange level. But we can also observe that the influence is softening at higher copper exchange level. So the catalytic activity

depends on both: the zeolite Si/Al ratio and the copper loading. And when the copper exchange level is higher than 80%, the former is predominant.

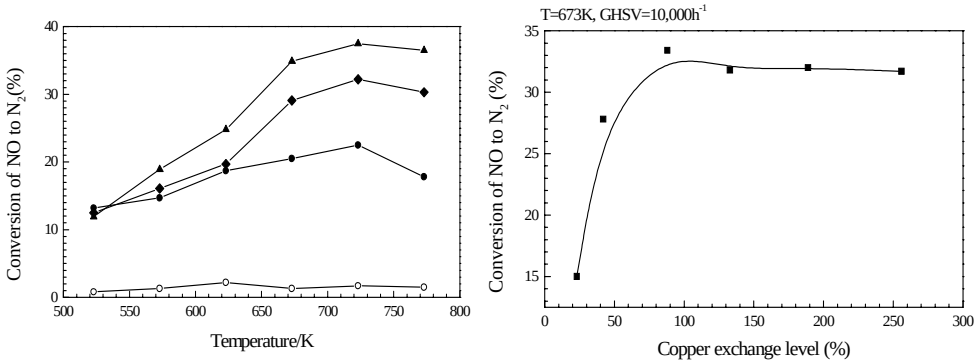
Figure 2. SEM pictures of as-synthesized samples with different Si/Al ratios



Cordierite (A) Si/Al=52 (B) Si/Al=38 (C) Si/Al=28

Figure 3. NO conversion on CuMFI/cordierite catalysts with different Si/Al ratio as a function of temperature

Figure 4. NO conversion over catalyst 2# as a function of copper loading



(○) Cordierite; (●)Si/Al=28; (♦) Si/Al=38; (▲)

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