

Article ID: 0465-7942(2001)01-0123-04

Research Note

# THE HYDROTHERMAL STABILITY OF IN-SITU SYNTHESIZED Cu-ZSM-5/CORDIERITE FOR NO DECOMPOSITION<sup>y</sup>

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## Abstract

The hydrothermal stability and catalytic activities of powdery Cu-ZSM-5 and monolithic Cu-ZSM-5/cordierite synthesized by in situ method for NO decomposition were studied comparatively. After the thermal treatment at 600 ~ 800 °C, the loss of activity on the powdery Cu-ZSM-5 was obvious while the in-situ synthesized monolithic Cu-ZSM-5/cordierite was more stable under the same experimental conditions. From the results of XRD, the loss of zeolite crystallite of the monolithic catalyst was slighter than of pure ZSM-5. It was supposed that the interaction of zeolites and substrate might exist and could improve the hydrothermal durability of the catalyst.

**Key words:** Cu-ZSM-5; cordierite; in-situ synthesis; NO decomposition; hydrothermal stability

**CLC number:** O643.3

**Document code:** A

From the viewpoint of environmental protection, there is a worldwide effort to discover improved solutions for removal of NO<sub>x</sub> emissions. The direct decomposition of NO to its elements has been a significant challenge to scientists for decades<sup>[1]</sup>. Since Iwamoto et al's<sup>[2]</sup> breakthrough discovery of Cu-ZSM-5 efficient for NO decomposition, a storm of interest to study the performance of Cu-ZSM-5 has been generated. Unfortunately, Cu-ZSM-5 is not very stable to even 2% water vapor for extended periods of time<sup>[3]</sup>. So, in practice it must be addressed to make zeolite-based catalysts with good thermal and hydrothermal stability.

The honeycomb structure cordierite ( $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ ) is a traditional automotive catalyst substrate. In recent years, zeolite-ceramic composite membranes become more important. As a monolithic catalyst, zeolites are usually wash-coated on the substrate to provide enough specific surface to carry metallic active component. In our earlier work<sup>[4]</sup>, Cu-ZSM-5/cordierite monolithic catalyst for NO decomposition was prepared by in-situ synthesis. This technology is supposed to superior to the typical "washcoat" method for the well-distributed zeolite layer and possible durability resulted from the interaction between zeolite and support.

In this work, the hydrothermal stability and the catalytic performance of Cu-ZSM-5 and monolithic Cu-ZSM-5/cordierite synthesized by in-situ method for NO decomposition were investigated in order to get a deeper insight into the in-situ synthesized monolithic catalysts.

## In-situ synthesis

A whole honeycomb shaped cordierite substrate obtained from Corning Co. Ltd. with 400cells/

<sup>y</sup> Received date: 2000-03-07

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inch<sup>2</sup> and a diameter of 125mm and thickness of 53mm, was broken into little blocks (2cm × 1cm × 3cm) and one side of them were polished with fine sandpaper before use. In-situ synthesis of ZSM-5/cordierite was performed using a template-free preparation method<sup>[5]</sup>. A reaction mixture of material was put into the autoclave in certain ratio<sup>[6]</sup> and stirred till a well-mixed phase was reached at room temperature. The cordierite blocks were suspended in the mixture. After static crystallization at 453K for 24h, the monolith samples were taken out, washed thoroughly by ultrasonic wave generator, dried at 393K overnight. Identification of the zeolites was achieved by X-ray diffractometer (D/max-2500).

### Catalysts

The as-synthesized samples and powder ZSM-5 were Na<sup>+</sup> form and first converted to the H<sup>+</sup> form by exchanging with HCl ([H<sup>+</sup>] = 0.3mol/L) two times at 363K for 2h alternatively. Then the H<sup>+</sup> form samples were exchanged three times at room temperature with Cu(CH<sub>3</sub>COO)<sub>2</sub> solution ([Cu<sup>2+</sup>] = 0.1 mol/L) to obtain Cu-ZSM-5/cordierite and Cu-ZSM-5 powder, each time for 12h. The products were washed with distilled water and dried at 383K overnight. At last, the honeycomb-type catalyst sample was crushed to 20~30 mesh for use. The powdery catalyst sample was first compressed into a disk and then crushed to 20~30 mesh too.

### Reaction

The catalytic decomposition of NO was carried out with a fixed bed flow reactor. The feed gas was 2.82% NO (balanced with helium) controlled by a mass flow controller. The gas hourly space velocity (GHSV) was 10 000h<sup>-1</sup> based on the density of the monolith catalysts. An on-line gas chromatograph with a thermal conductivity detector (TCD) used for the product analysis, and a molecular sieve 5A+ Porpak P column was used to separate N<sub>2</sub>, O<sub>2</sub>, and NO. The catalytic activity for NO removal was evaluated by the conversion into N<sub>2</sub>.

### Hydrothermal treatment

Hydrothermal aging procedures were performed using a quartz furnace and two boat-shape vessels to contain in-situ synthesized monolithic catalyst and pure zeolite catalyst. They were simultaneously treated at various temperatures (873~1073K) for 2 h with steam flowed through the furnace. The losses in zeolite crystallinity as probed by X-ray diffraction.

### Results

Hydrothermal stability of the catalytic behavior of Cu-ZSM-5 and Cu-ZSM-5/cordierite monolithic catalyst was investigated. Figure 1 shows the comparison of hydrothermal stability between powder Cu-ZSM-5 (Si/Al=50) and in-situ synthesized Cu-ZSM-5/cordierite. Both of them were through 2 hours' hydrothermal treatment at 773, 873, 973 and 1073K. From the

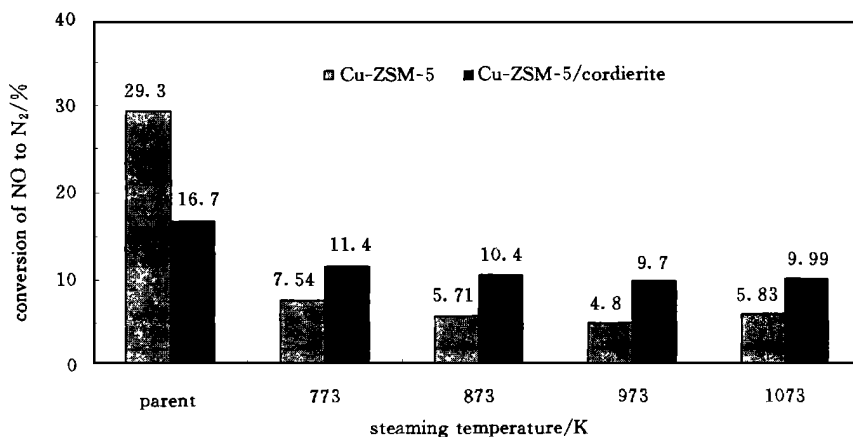


Fig 1 A comparison of hydrothermal stability between two catalysts

figure, we can see that powder Cu-ZSM-5 lose its activity drastically even at 773K. The reason is that water steams cause the dealumination of ZSM-5. It is generally acknowledged that zeolite-based

catalysts used at high temperatures in streams will cause zeolite dealumination. R. A. Grinstead et al reported the relation between deactivation of Cu-ZSM-5 in the selective reduction of NO and dealumination of the zeolite<sup>[8]</sup>. They reported that dealumination will disturb the exchanged Cu ions then result in a deactivation of active centers. The monolithic catalyst exhibited more stable catalytic behavior than the powder zeolite catalyst. Its activity lost more mildly and slightly than the powder Cu-ZSM-5 relatively. It can be assumed that the interaction exists between zeolite and substrate inhibited the dealumination of ZSM-5 in some extent. Another reason for this kind of inhibition is the loading Cu ions. The monolithic catalyst can be loaded more Cu ions than the powder Cu-ZSM-5<sup>[4]</sup>, and the loading Cu ions in Cu-ZSM-5 can inhibit the dealumination substantially<sup>[7]</sup>. Something must be explained is that the powder Cu-ZSM-5 has higher NO conversion in single run, this is mainly due to the less zeolite amount on the monolithic catalysts.

Another essentially qualitative measure of degraded zeolite crystallinity is to scale the intensity of strongly diffracting reflections of aged samples to the fresh material. Data are gathered into Table 1. It can be concluded that the structure of ZSM-5 was not disturbed under the hydrothermal treatment conditions, but the crystallinity degree of zeolite was decreased. The crystallinity of pure ZSM-5 decreased about 30% after hydrothermal treatment at 1073K, whereas the monolithic catalyst seemed not to be changed. This means the monolithic catalyst has a good durability after hydrothermal treatment. However, by the comparison of Figure 1 and Table 1, it can be concluded that there is not a strictly quantitative relation between the decrease of crystallinity and the NO conversion. That may be due to the crystallinity lose is not the only reason for catalyst deactivation.

**Table 1 Effect of hydrothermal treatment on relative crystallinity of zeolite**

hydrothermal treatment temperature	relative crystallinity of ZSM-5/ %	
	Cu-ZSM-5	Cu-ZSM-5/ cordierite
parent	100	100
773K for 2h	97.7	99.3
873K for 2h	95.4	98.7
973K for 2h	87.7	97.2
1073K for 2h	69.3	94.9

It was found that ZSM-5 obtained in such a way has a better hydrothermal stability of the structure<sup>[8]</sup>. This important result makes zeolite-based catalysts useful in practice automotive exhaust purification.

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## 原位合成 Cu-ZSM-5/ 堇青石用于 NO 分解的水热稳定性研究

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### 摘 要

对比研究了 Cu-ZSM-5 粉末和原位合成的 Cu-ZSM-5/堇青石的水热稳定性与相应的分解 NO 的催化活性。发现经过 600 ~ 800 °C 水蒸气处理后, 纯 Cu-ZSM-5 粉末发生了明显的失活, 而经过相同条件处理的 Cu-ZSM-5/堇青石活性变化不大。XRD 结果显示, 整体式催化剂经水热处理后结晶度下降程度小于纯 Cu-ZSM-5 粉末。推测认为, 原位合成样品中分子筛与堇青石载体的相互作用提高了催化剂结构的水热稳定性。

关键词: Cu-ZSM-5; 堇青石; 原位合成; NO 分解; 水热稳定性

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## STUDIES ON THE SYNERGISM OF INTERMOLECULAR INTERACTION OF XANTHAN NK-01 AND GALACTOMANNAN

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### Abstract

Xanthan NK-01 and galactomannan are two natural biopolysaccharides. When two polysaccharides were mixed by suitable ratio, the viscosity of mixing polysaccharides solution is higher than viscosity of a single polysaccharide at same concentration. If solution concentration of mixing polysaccharides is around 0.2%, the gel was formed, but solution of a single polysaccharide does not form gels. These researches indicated that the synergism was appeared by intermolecular interaction of xanthan NK-01 and galactomannan, but this synergism was influenced by pH, inorganic salts and temperature.

**Key words:** xanthan; galactomannan; synergism