

Direct NO decomposition over conventional and mesoporous Cu-ZSM-5 and Cu-ZSM-11 catalysts: Improved performance with hierarchical zeolites

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Abstract

Conventional Cu-ZSM-5 has for many years been recognized as a unique catalyst for direct NO decomposition. Zeolite-based catalysts have a crystallographically well-defined microporous structure. In such microporous catalysts, the creation and accessibility of the active sites is often influenced by the geometry of the pore system. To improve these catalysts, secondary mesoporous systems can beneficially be introduced into the structure of conventional zeolites. Here, this approach was used with Cu-containing ZSM-5 and ZSM-11 type mesoporous zeolite catalysts, which were used as catalysts for direct NO decomposition. It was discovered that introducing mesoporosity into the conventional materials leads to a significant improvement of the catalytic activity. Additionally, mesoporous Cu-ZSM-11 catalyst was found to be about twice as active as mesoporous Cu-ZSM-5. This difference is attributed to the fact that ZSM-11 has only straight microporous channels, while ZSM-5 has both straight and sinusoidal channels. Apparently, there is a preferential formation of active sites and/or improved accessibility in the straight channels compared to the sinusoidal channels, which make the ZSM-11 material a better catalyst than ZSM-5. All samples were characterized by XRPD, SEM, TPD-NH₃, in situ EPR and N₂ physisorption measurements. Thus, this confirms our previous observation that the special pore structure of Cu-ZSM-5 is not a decisive factor for the catalytic activity in NO decomposition.

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1. Introduction

Nitrogen oxides in the exhaust gases from combustion of fossil fuels remain a major source of air pollution. It contributes to photochemical smog, acid rain, ozone depletion, and greenhouse effects [1]. The current technology for reducing nitrogen oxide emissions in exhaust gases is selective catalytic reduction (SCR). One major disadvantage of this technology is that it requires addition of reductants such as hydrocarbons, CO, H₂ or NH₃, which can lead to production of secondary

pollutants [1,2]. The direct catalytic NO decomposition represent the simplest and most attractive solution for NO abatement, since it does not require addition of any reducing agent and only N₂ and O₂ are formed [2]. Except at very high temperatures, the catalytic decomposition of NO into N₂ and O₂ is thermodynamically favorable [3], but due to the electronic distribution within the orbitals of the NO molecule this reaction is spin-forbidden, and thus NO is kinetically stable. Therefore the use of a catalyst is required to achieve reasonable reaction rates. However, so far no catalyst with sufficiently high activity and stability for commercial applications is known.

In 1986, Iwamoto et al. [4] discovered the remarkable activity of Cu-ZSM-5 catalysts in NO decomposition. After that, significant efforts have been devoted to understand why this system is unique in comparison with other copper-containing systems or transition metal ions exchanged in

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ZSM-5 [5]. Compared to other previously studied zeolite materials, the over-exchanged Cu-ZSM-5 exhibits a significant enhancement both in terms of the conversion rate and selectivity [6–8]. Studies of zeolite X, zeolite Y, mordenite and ZSM-5 supports with the same copper content performed by Iwamoto et al. [9] showed that the activity order was always the same: ZSM-5 \gg zeolite Y \sim mordenite \gg zeolite X. Thus, it is a common notion that ZSM-5 has some special properties that makes it particularly useful in the direct NO decomposition reaction. The structure of the active site and the reaction mechanism has been discussed in literature numerous times [2,10–14]. Obviously, information about the nature of active sites in Cu-ZSM-5 catalysts may contribute to the design of new and more active catalysts. Previously, we have shown that the Cu-ZSM-11 and Cu-ZSM-12 (both with only straight pores) are more active catalysts for direct NO decomposition than the well-known Cu-ZSM-5 catalysts (with both straight and sinusoidal pores) [15]. This difference in catalytic activity was attributed to the accessible active sites being located almost exclusively in the straight zeolite pores.

Much of the success of zeolite catalysts can be explained by the presence of micropores with well-defined structures. The exact shape and size of the micropores may result in various kinds of shape selectivity [16–18]. Nevertheless, the sole presence of micropores may in many cases also limit the catalytic performance of zeolite catalysts, particularly when diffusion in the micropores becomes significantly slower than the catalytic reaction [19]. Several different preparative strategies have been attempted to circumvent this problem. One of these is to introduce mesopores into each individual zeolite crystal. This is usually done by suitable post-treatments such as dealumination [20] or desilication [21], which lead to partial disintegration of the zeolite crystals. However, during the last few years, it has proven possible to introduce a very high degree of mesoporosity into zeolite crystals in a more controlled manner. This new family of crystalline zeolitic materials, the so-called mesoporous zeolite single crystals, is prepared by nucleating zeolite crystals inside a carbon material so that the zeolite crystals grow and partially encapsulate the carbon. After complete crystallization, the carbon is removed by combustion. The resulting zeolite material has been shown conclusively to consist of relatively large mesoporous single crystals [18,22,23]. Compared to other known approaches for introducing mesopores into the structure of zeolites, this method does not lead to the partial destruction of the zeolite crystal. So far, mesoporous zeolite single crystals have been reported for zeolite structures MFI [22–25], MEL [26], and MTW [27]. Other synthesis schemes have been presented as well, such as assembling zeolite seeds with organic structure directors present [28], by resin macrotemplating [29], by using carbon aerogels [30], or by recrystallization [31].

Here, a comparative study of conventional and mesoporous (synthesized by carbon-templating method) copper-exchanged ZSM-5- and ZSM-11-type zeolite catalysts in direct NO decomposition is presented.

2. Experimental

2.1. Materials

For synthesis of mesoporous zeolites, carbon black particles (BP-2000) having an average particle diameter of 12 nm (ASTM D-3249), obtained from Carbot Corporation, were used as inert matrices. Carbon black was dried at 110 °C for 24 h prior to use. All other reagents were of reagent grade and used without further purifications: tetraethylorthosilicate (TEOS, 98 wt.%, Aldrich), tetrapropylammonium hydroxide (TPAOH, 40 wt.%, Fluka), tetrabutylammonium hydroxide (TBAOH, 40 wt.%, Fluka), ethanol (EtOH, 99 wt.%, Aldrich), sodium hydroxide (NaOH, 97 wt.%, Riedel-de Haen), sodium aluminate (NaAlO₂, 54 wt.% Al₂O₃ and 41 wt.% Na₂O, Riedel-de Haen), ammonium nitrate (NH₄NO₃, 99.5 wt.%, Merck), copper(II) nitrate—trihydrate (Cu(NO₃)₂·3H₂O, 99.5 wt.%, Merck), and distilled water.

2.2. Catalysts preparation

2.2.1. Synthesis of conventional ZSM-5-type zeolite

The zeolite Na-ZSM-5 was prepared by the following procedure. A clear solution of 0.3 g of sodium aluminate and 0.3 g of sodium hydroxide in 9.8 g of water was added to 19.4 g of tetrapropylammonium hydroxide (TPAOH, 40 wt.%). Then, 19.7 g of tetraethylorthosilicate (TEOS) was slowly added, and the mixture was left with stirring for 2 h to obtain a homogeneous gel. The composition of the resulting synthesis gel was 1 Al₂O₃–100 SiO₂–20 TPA₂O–4 Na₂O–200 H₂O. After aging for 2 h at room temperature, the gel was introduced into a stainless steel autoclave, heated to 443 K and kept there for 72 h. Then, the autoclave was cooled to room temperature, the product was suspended in water, filtered by suction, resuspended in water, and filtered again. Finally, the product was dried at 383 K for 10 h and the organic template was removed by controlled combustion in air in a muffle furnace at 823 K for 20 h.

2.2.2. Synthesis of conventional ZSM-11-type zeolite

The zeolite Na-ZSM-11 was prepared by the followed procedure. A clear solution of 0.3 g of sodium aluminate and 0.3 g of sodium hydroxide in 9.8 g of water was added to 12.4 g of tetrabutylammonium hydroxide (TBAOH, 40 wt.%). Then, 19.7 g of tetraethylorthosilicate (TEOS) was slowly added, and the mixture was left with stirring for 2 h to obtain a homogeneous gel. The composition of the resulting synthesis gel was 1 Al₂O₃–100 SiO₂–20 TBA₂O–4 Na₂O–200 H₂O. After aging for 2 h at room temperature, the gel was introduced into a stainless steel autoclave, heated to 443 K and kept there for 72 h. Then, the autoclave was cooled to room temperature, the product was suspended in water, filtered by suction, resuspended in water, and filtered again. Finally, the product was dried at 383 K for 10 h and the organic template was removed by controlled combustion in air in a muffle furnace at 823 K for 20 h.

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