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Facile synthesis of uniform FeZSM-5 crystals with controlled size and their application to N_2O decomposition

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Dedicated to Prof. Carmine Colella on the occasion of his 70th birthday.

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ABSTRACT

FeZSM-5 zeolites with crystal sizes ranging from 70 nm to 20 μm were synthesized by adjusting the alkalinity of the synthesis system and optimizing the crystallization conditions. After steam-activated treatment, these zeolites were used as catalysts in the direct decomposition of N_2O, showing that the larger the zeolite crystal size, the higher the reaction temperature required for the complete decomposition of N_2O. Moreover, N_2O decomposition over the FeZSM-5 catalysts with crystal sizes larger than 5 μm at high temperatures shows that the conversion of N_2O decreases with increasing the zeolite crystal size, implying that the internal mass transfer limitations are available. However, under the applied conditions, the diffusion limitations are absent and the observed reaction rates are controlled by the intrinsic kinetics of N_2O decomposition over the FeZSM-5 catalysts with crystal sizes smaller than 2 μm.

1. Introduction

Industrial emissions of nitrous oxide (N_2O) have received a global attention due to its significant impact on the destruction of the ozone layer, besides its greenhouse effect [1]. Two ways are considered to be alternatives to dispose N_2O. One is the conversion of N_2O with low concentration, including direct decomposition and selective catalytic reduction, into environmentally friendly N_2 [2]. Another is the use of high concentration N_2O as an active oxygen donor, *i.e.*, one-step oxidation of benzene to phenol with N_2O [3,4].

FeZSM-5, especial steam-activated one, is reported to be a potential catalyst for the direct decomposition of N_2O and the hydroxylation of benzene with N_2O [5–8]. Plenty of work has been devoted to elucidating the mechanism of these reactions over FeZSM-5 [9–15]. It is generally accepted that the extra-framework dinuclear iron species in the zeolite are the active sites, which readily react with N_2O to generate anion radical oxygen species, the so-called α-oxygen [7,10,11,16–18].

For a catalytic reaction over zeolites, internal mass transfer limitations are common phenomena. The oxidation of benzene to phenol by N_2O over FeZSM-5 catalysts is apparently limited by the internal mass transfer of benzene because of the molecular size of benzene being similar to the channel opening sizes of the zeolite. Additionally, this reaction encounters a rapid catalyst deactivation due to the diffusion limitations of benzene and phenol in and out of the zeolite crystals and thus the accumulation of these components inside the crystals, leading to the formation of coke. A lot of work, involving the introduction of mesopores in FeZSM-5 crystals [19–24] and the reduction of the crystal size of the synthesized zeolites [25], has been carried out to improve the internal mass transfer limitations and overcome the catalyst deactivation.

However, in the direct decomposition of N_2O over FeZSM-5, because the molecular size of N_2O (0.33 nm) is much smaller than the channel opening sizes of MFI-type zeolite (0.51 nm × 0.55 nm and 0.56 nm × 0.53 nm), the mass transfer of N_2O inside zeolite is believed to be very fast and thus little work has been conducted to investigate the diffusion limitations of N_2O in FeZSM-5 crystals. However, for the complete decomposition of N_2O over FeZSM-5 catalysts, an operation at high temperatures is generally required, and under such a high temperature condition the intrinsic reaction rate on the active species for N_2O decomposition could be very fast and the mass transfer limitations of N_2O inside the zeolite crystals might be present.

From an engineering viewpoint, to judge whether a catalytic reaction is controlled by the mass transport limitations, one often investigates the relationship between reaction rate and catalyst particle size. If the observed rate decreases with increasing catalyst particle size, the internal mass transfer limitations are considered to be present. Generally, the commercially available zeolites and thereafter the post-treated zeolites are not uniform in size and shape, leading to some uncertainty in the determination of intrinsic catalytic kinetics. Therefore, uniform zeolite crystals with different sizes are desirable to investigate the intrinsic catalytic kinetics. Unfortunately, the facile synthesis of uniform FeZSM-5 crystals with controlled size has not been reported yet, although

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some work on the tailoring synthesis of ZSM-5 has been conducted [26].

The current study deals with the controllable synthesis of FeZSM-5 crystals with different sizes by altering the alkalinity in the synthesis system as well as by optimizing the crystallization conditions. These synthesized FeZSM-5 samples are first activated by steam and then used in the direct decomposition of N_2O to investigate the crystal size-dependence decomposition conversion, which is of utmost importance for judging whether the internal mass transfer limitations of N_2O decomposition over FeZSM-5 catalysts are present.

2. Experimental

2.1. Chemicals

Tetrapropyl ammonium bromide (TPABr, Analysis Grade, A.R.), water glass (26.5 wt.% SiO_2 and 10.6 wt.% Na_2O), and colloidal silica sol (LUDOX® AS-40, 40 wt.% SiO_2) were purchased from Sigma–Aldrich Co. Ltd. Aluminum sulfate [$Al_2(SO_4)_3 \cdot 18H_2O$, A.R.], aluminum hydroxide [$Al(OH)_3$, A.R.], sodium bicarbonate ($NaHCO_3$, $\geqslant$99.5 wt.%), and ferric nitrate [$Fe(NO_3)_3 \cdot 9H_2O$, A.R.] were purchased from Sinopharm Chemical Reagent Co. Ltd., China. All chemicals were used as received. The deionized water was obtained from Millipore Milli-Q® ultrapure water purification systems with the resistivity larger than 18.2 MΩ.

2.2. Zeolite synthesis

In a typical synthesis of nanosized FeZSM-5, 5 ml of $Al_2(SO_4)_3$ solution (0.2 M) and 2.1 g of TPABr were dissolved into 5.9 g of deionized water. After vigorous stirring for 30 min, 2.0 ml of H_2SO_4 solution (4.84 M), 0.2 ml of $Fe(NO_3)_3$ solution (0.2 M), and 9 g of water glass were added into the above-prepared solution in order. After stirring for another 2 h, the mixture was transferred into a Teflon-lined autoclave and heated at 110 °C for 2 d and then 180 °C for 1 d. Afterwards the product was filtered, washed with deionized water for three times, and dried at 120 °C overnight. The sample is referred to as NS-1. For other nanosized FeZSM-5 samples, the synthesis recipes were slightly different, e.g. the alkalinity of the synthesis system was changed for the synthesis of samples NS-2 and NS-3 while both alkalinity of the synthesis system and dosage of $Fe(NO_3)_3$ were changed for the synthesis of sample NS-4.

The synthesis recipe and procedure of FeZSM-5 crystals with a size of about 2 μm were very similar to those of nanosized FeZSM-5, except for that the alkalinity of the synthesis system and the crystallization conditions were different. These synthesized samples are referred to as MS-1 to MS-4.

In the synthesis of FeZSM-5 crystals with sizes larger than 10 μm, colloidal silica sol, $Al(OH)_3$, and NaOH combined with $NaHCO_3$ were used as silica, alumina, and alkali sources, respectively. In a typical synthesis, 0.22 g of NaOH and 0.13 g of $NaHCO_3$ were firstly dissolved into 13.6 g of deionized water, the mixture was then vigorously stirred for 30 min, and finally 1.26 g of TPABr was added, followed by stirring for another 30 min. Afterwards 0.18 g of $Al(OH)_3$ and 7.2 g of colloidal silica sol were added into the above-prepared solution to form a highly viscous hydrogel, followed by adding 1.2 ml of $Fe(NO_3)_3$ solution (0.2 M) into the prepared hydrogel. After vigorously stirring for 2 h, the synthesis was carried out hydrothermally without agitation in a Teflon-lined autoclave placed in an oven at 190 °C. The autoclave was removed after 2 d from the oven and quenched in cold water to stop the reactions. Afterwards, the product was filtered and the solid was washed with deionized water. The washed solid was then dried at 120 °C overnight prior to a further analysis. The synthesized sample is referred to as MC-1. By changing the ratio of NaOH to $NaHCO_3$ used in the synthesis system, other three samples MC-2, MC-3, and MC-4 were prepared.

The gel composition (molar ratio) and hydrothermal conditions for the syntheses of all the Fe-ZSM-5 samples are summarized in Table 1.

The as-synthesized samples were calcined at 550 °C for 5 h to remove the template and ion exchanged with a 0.2 M NH_4NO_3 solution (liquid-to-solid ratio = 30:1 ml/g) for three times at 60 °C. Then the samples were washed, filtered, and dried at 120 °C overnight. Finally the samples were calcined at 550 °C for 4 h in order to get their H-form FeZSM-5 zeolites.

The H-form FeZSM-5 zeolites were activated in a mixture flow of nitrogen (30 ml/min) and steam (a partial pressure of 30 mbar) at ambient pressure and 600 °C for 5 h in order to get the catalysts for the decomposition of N_2O.

2.3. Characterization

The X-ray diffraction patterns were recorded on a Philips PW3040/60 diffractometer using CuKα radiation ($\lambda = 1.54$ Å). N_2 adsorption/desorption isotherms were measured at −196 °C. The SEM images were obtained using a HITACHI S-4800 microscope equipped with a field emission gun. The acceleration voltage was set to 5 kV. The samples were stuck on the observation platform and sprayed with gold vapor under high vacuum for about 20 s. The UV–vis spectra were recorded by a Nicolet Evolution 500 UV–vis spectrometer against $BaSO_4$ under ambient conditions.

Table 1
Gel compositions and crystallization conditions for synthesizing FeZSM-5 crystals with different sizes.

Sample code	Composition (molar ratio)							Crystallization conditions
	Na_2O	$NaHCO_3$	Al_2O_3	SiO_2	TPABr	$Fe(NO_3)_3$	H_2O	
NS-1	0.04[a]	0	0.025	1	0.2	0.001	25	110 °C 2 d, 180 °C 1 d
NS-2	0.06[a]	0	0.025	1	0.2	0.001	25	110 °C 2 d, 180 °C 1 d
NS-3	0.08[a]	0	0.025	1	0.2	0.001	25	110 °C 2 d, 180 °C 1 d
NS-4	0.12[a]	0	0.025	1	0.2	0.005	25	110 °C 2 d, 180 °C 1 d
MS-1	0.12[a]	0	0.025	1	0.2	0.001	25	170 °C 2 d
MS-2	0.16[a]	0	0.025	1	0.2	0.001	25	170 °C 2 d
MS-3	0.18[a]	0	0.025	1	0.2	0.005	25	170 °C 2 d
MS-4	0.18[a]	0	0.025	1	0.2	0.007	25	170 °C 2 d
MC-1	0.05775[b]	0.0345	0.025	1	0.1	0.005	21	190 °C 2 d
MC-2	0.0525[b]	0.045	0.025	1	0.1	0.005	21	190 °C 2 d
MC-3	0.04725[b]	0.0555	0.025	1	0.1	0.005	21	190 °C 2 d
MC-4	0.0315[b]	0.087	0.025	1	0.1	0.005	21	190 °C 2 d

[a] From water glass.
[b] From NaOH.