

The role of pore size on the thermal stability of zeolite supported Cu SCR catalysts



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ABSTRACT

A comparison study on the hydrothermal stability of Cu SCR catalysts supported on an 8-ring small pore chabazite and a 12-ring large pore beta zeolite was performed to understand why small pore zeolite supported Cu catalysts are in general hydrothermally more stable than medium pore or large pore zeolite supported Cu catalysts and how different pore sizes affect the hydrothermal stability of the catalysts. In situ XRD hydrothermal experiments show that, even though the parent chabazite and beta zeolites have comparable hydrothermal stability and both can maintain their zeolite framework structure after a 900 °C hydrothermal exposure, the presence of Cu in the Cu/beta catalyst accelerates the collapse of the BEA framework structure at temperatures above 800 °C whereas Cu in the Cu/chabazite catalyst has little effect on the CHA framework structure. The loss of beta zeolite framework structure is due to a detrimental Cu/Al₂O₃ interaction. It is proposed that the constricting dimensions of the small openings in a small pore zeolite can hinder the destructive Cu/Al₂O₃ interaction as well as the zeolite dealumination process, hence significantly improving the hydrothermal stability of the small pore zeolite supported Cu catalyst.

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1. Introduction

Zeolite supported Cu catalysts are highly active in the selective catalytic reduction (SCR) of NO_x (NO and NO₂) from lean-burn exhaust emissions when NH₃ is available as a reductant. Under typical reaction conditions, the catalysts can convert a very low concentration of NO_x (~100 ppm) with the stoichiometric amount of NH₃ at >90% efficiency in the presence of nearly 1000 times of excess of O₂ (~10%). This makes the catalysts highly attractive for diesel engine powered vehicles to meet the stringent emission regulations [1–6]. In addition, the presence of ordered crystalline lattice structures with defined exchangeable sites of Cu ions in the zeolite supports makes it feasible to study the fundamental details about the nature of active sites and how those sites are influenced by the framework structure. Therefore, extensive studies have been devoted to Cu/zeolite SCR catalysts in the past several decades [7,8].

Both the zeolite support and the exchanged Cu ions in a Cu/zeolite SCR play important roles in SCR reactions. The intracrystalline pores in a zeolite support generate a large surface area for low concentrations of NO_x and NH₃ to adsorb and to concentrate

on the surface. The pore structure also provides spatial confinement for the molecules to react. More importantly, the Brønsted acid sites originated from the tetrahedral aluminum centers in the zeolite support activate the adsorbed NH₃ forming NH₄⁺ ions, which is believed to be a key step in the SCR reaction mechanism [8,9]. The tetrahedral aluminum centers can also anchor Cu cations so that they are atomically dispersed inside the pores of the zeolite structure. It is generally accepted that the highly dispersed Cu ions activate NO through a redox cycle and that the oxidation of NO and the subsequent formation of NO_x surface adsorption complexes on the catalyst is another key step in the SCR reaction mechanism [10,11]. The presence of both exchanged Cu sites and the Brønsted acid sites in a Cu/zeolite catalyst enables adsorbed NO_x surface complexes to further react with adsorbed NH₄⁺ producing N₂ at a very high selectivity [8,12,13].

Since a Cu/zeolite SCR catalyst is a bi-functional catalyst which provides both acidic and redox functions for SCR reactions, it is vital that the two functions are well balanced for the catalyst to achieve the optimum SCR activity and selectivity. For practical applications, such as mobile diesel NO_x emission control, the catalyst also must maintain both functions during the useful life of the vehicle in order for the vehicle to meet the emission regulations. Typically, this would require the Cu/zeolite catalyst to be durable after hydrothermal exposure at a high temperature (for example 670 °C) for

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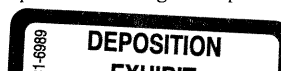


Table 1

Examples of Cu/zeolite SCR catalysts and their NO_x conversion (%) at 250 °C before and after different hydrothermal treatment [23].

Catalysts	Structure	Pore size	Fresh	750 °C/24 h	900 °C/1 h
Cu/Beta	BEA	Large pore 12-ring	98%	69%	58%
Cu/ZSM-5	MFI	Medium pore 10-ring	98%	19%	28%
Cu/SAPO-34	CHA	Small pore 8-ring	95%	99%	97%
Cu/Chabazite	CHA	8-ring	100%	99%	99%
Cu/Nu-3	LEV	8-ring	97%	90%	98%
Cu/ZSM-34	ERI	8-ring	100%	98%	
Cu/Sigma-1	DDR	8-ring	88%		85%

a long time periods (for example 64 h). As extremely high temperature excursions may also happen in real world applications, the Cu/zeolite catalyst also has to be durable after short time exposure to those extreme conditions, such as 900 °C/1 h hydrothermal exposure [14].

On the contrary, zeolites are metastable materials because of the nature of their porous framework structures. When a zeolite is exposed to high temperatures its framework structure tends to collapse forming denser crystalline phases [15]. Under hydrothermal conditions, water accelerates this phase transition by attacking the tetrahedral aluminum sites through a dealumination process [16,17]. The presence of Cu ions at the exchange sites of a zeolite can affect the dealumination process in two different ways depending on the temperature [18]. At a relatively low temperature, Cu ions at the exchange sites may shield water away from attacking the adjacent tetrahedral aluminum centers and hinder the dealumination process. At a relatively high temperature, Cu ions at the exchange sites can react with alumina forming stable copper aluminate (CuAl₂O₄) spinel, which accelerates the dealumination process and affects not only the zeolite function but also the Cu function of the Cu/zeolite catalysts, causing severe deactivation of the catalyst. In its early stage, even though the dealumination process may not cause an obvious structure change of the zeolite, it reduces the number of acidic and exchangeable sites, which can significantly deactivate a Cu/zeolite SCR catalyst. In fact, dealumination has been identified as one of the main deactivation mechanisms of Cu/zeolite SCR catalysts after high temperature hydrothermal exposure [19–22].

Recently it was reported that Cu SCR catalysts supported on zeolites with interconnected 8-ring small pores exhibited improve hydrothermal stability compared to the catalysts supported on the zeolites with 10-ring medium or 12-ring large pores [23,24]. As examples, Table 1 summarizes the NO_x conversions at 250 °C on a series of Cu/zeolite SCR catalysts reported by Andersen et al. [23]. In table, the “750 °C/24 h” and the “900 °C/1 h” each represents that the catalysts have been hydrothermally treated in a flow of 10% H₂O/air mixture at 750 °C for 24 h, or in a flow of 4.5% H₂O/air mixture at 900 °C for 1 h, respectively. The two hydrothermal treatment conditions were used to assess the long-term hydrothermal durability and the upper temperature limit of these catalysts. Both the large pore Cu/beta and the medium pore Cu/ZSM-5 catalysts showed very good SCR activity when they were fresh, but were severely deactivated after either “750 °C/24 h” or “900 °C/1 h” hydrothermal treatment. In contrast, all the small pore zeolite supported Cu SCR catalysts showed high NO_x conversion efficiency and maintained their activity after the hydrothermal treatments. The small pore zeolites in Table 1 cover a variety of framework structures, such as CHA, LEV, ERI, and DDR. The trend of improved hydrothermal durability was also reported on other small pore 8-ring zeolites with different framework structures, such as AFX, AEI, KEI, and SAV [25–30]. Therefore, it appears that the hydrothermal

stability of a Cu/zeolite catalyst is strongly influenced by the pore size of the zeolite support.

In this study, a detailed comparison of the hydrothermal stability of Cu SCR catalysts supported on a large pore 12-ring beta zeolite and on a small pore 8-ring high silica chabazite was carried out to understand how different pore sizes affect the hydrothermal stability of the two types of catalysts. In situ XRD measurements were applied to monitor the framework structure change of the catalysts under hydrothermal treatment conditions. The results clearly demonstrate that the pore size of the zeolite structure significantly affects the Cu/zeolite interaction with small pores preventing Cu from degrading the zeolite framework structure.

2. Experimental

2.1. Catalyst preparation

Powder samples of Cu/beta and Cu/chabazite, both with SiO₂ to Al₂O₃ ratios (SAR) of approximately 25, were prepared by ion exchange of Cu into the corresponding zeolites. The Cu loading was maintained at 3 wt.% for both samples. After ion exchange, the powder samples were calcined at 550 °C for 2 h. The powder samples together with the parent zeolites samples were used for the in situ XRD measurements.

For SCR activity evaluation, the powder samples were subsequently washcoated on monolithic substrates with a cell density of 62 cell/cm² and 0.11 mm wall thickness. Cores of 25.4 mm diameter and 50.8 mm length were taken from the monoliths for catalytic activity testing. Hydrothermal treatment and catalytic activity evaluation

To achieve reproducible results, a set of core samples were pre-treated at 650 °C for 2 h in air. This set of samples will be labeled as “degreened” catalysts. To assess the long-term hydrothermal stability of the catalysts, a separated set of core samples were hydrothermally treated at 670 °C for 64 h in a flow reactor with a gas containing 4.5% H₂O in air at a flow rate of 3 L/min. A third set of core samples were hydrothermally treated at 900 °C for 1 h with the same feed gas to determine the hydrothermal stability of the catalysts after an extremely high temperature exposure.

SCR activity of the hydrothermally treated samples was evaluated in a separate flow reactor following a 4-step protocol as reported by Kamasamudram et al. [31]. The feed gas composition is regulated by the mass flow controllers of each individual gas line. The typical gas feed composition was 350 ppm NO, 350 ppm NH₃, 14% O₂, 4.6% H₂O, 5% CO₂ and balance N₂. The flow rate was set at 12.9 L/min, corresponding to a gas hourly space velocity (GHSV) of 30,000 h⁻¹ over the catalysts. Steady state NO_x and NH₃ conversions, together with NH₃ storage capacity of the catalysts at 200, 250, 300, 350, 450, and 550 °C points were measured.

Separate HC inhibition tests were carried out at 300 °C. Once the steady state NO_x conversion was reached, 1000 ppm (as C₁) of propene (C₃H₆) or *n*-octane (n-C₈H₁₈) was added to the feed. NO_x conversion efficiency before and after HC addition was monitored to illustrate the HC inhibition effect on the catalysts.

2.2. In situ XRD measurements

In situ XRD measurements were conducted on a Bruker AXS D8 in parallel beam mode with an Anton Paar XRK 900 sample chamber adapted for hydrothermal conditions. Each powder sample was pressed into a 13-mm diameter pellet and loaded into the sample chamber under flowing atmosphere of 5% H₂O, 19% O₂, and 76% N₂. A dataset was collected at 50 °C when the system was stabilized. Then the cell temperature was increased stepwise from 50 to 900 °C at a ramping rate of 10 °C/min and 50 °C/step. The holding time at

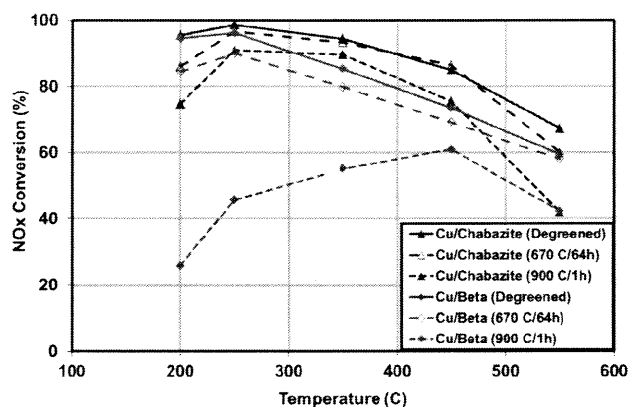


Fig. 1. NO_x conversion efficiency as a function of reaction temperature on Cu/beta and Cu/chabazite SCR catalysts before and after different hydrothermal treatment. (SCR reaction conditions: 350 ppm NO , 350 ppm NH_3 , 14% O_2 , 4.6% H_2O , 5% CO_2 , and balance N_2 , GHSV = $30,000 \text{ h}^{-1}$)

each step was about 20 min while an XRD scan was performed. The holding time was increased to 1 hour when the temperature reached 900°C . Three sets of XRD data were recorded during this period. The sample was subsequently cooled to 100°C stepwise and data were collected at 100°C increments. A final dataset was collected at 50°C at the end of the hydrothermal experiment. All datasets were collected as follows: $3\text{--}77^\circ 2\theta$ range with a step size of 0.029° and a collection time of 0.42 s/step . Each dataset took about 20 min to record. Cu $\text{K}\alpha$ radiation with a Ni filter was used as the X-ray source.

3. Results

3.1. Catalytic activity after hydrothermal treatments

The steady state NO_x conversion as a function of temperature over the Cu/beta and Cu/chabazite catalysts before and after different hydrothermal treatment is shown in Fig. 1. After a mild $650^\circ\text{C}/2 \text{ h}$ air treatment, both catalysts show high NO_x conversion in a wide temperature window. In the $200\text{--}350^\circ\text{C}$ region which is the typical temperature measured in the diesel exhaust, both catalysts achieve above 90% NO_x reduction efficiency. At temperatures above 300°C the NO_x conversion on the Cu/chabazite catalyst is $\sim 15\%$ higher, suggesting that the Cu/chabazite catalyst is more selective in utilizing NH_3 for NO_x reduction at those high temperatures. After hydrothermal treatment at 670°C for 64 h, $\sim 10\%$ decrease of NO_x conversion in the entire temperature window is observed on the Cu/beta catalyst, but only 10% decrease of NO_x conversion at the 200°C and 550°C points is seen on the Cu/chabazite catalyst. With the clear trend of deactivation, the Cu/beta zeolite barely meets 90% NO_x reduction efficiency. When the two catalysts are subject to hydrothermal treatment at 900°C for 1 h, the Cu/beta catalyst shows a significant drop of the NO_x conversion whereas the Cu/chabazite catalyst still maintains $>90\%$ NO_x conversion in the $250\text{--}350^\circ\text{C}$ temperature range even though a decline of NO_x conversion in the entire temperature region is noticeable. Clearly, the Cu/chabazite catalyst is more durable after the long-term hydrothermal treatment and can tolerate much higher temperature excursions.

The NH_3 storage capacity of the degreened and the $670^\circ\text{C}/64 \text{ h}$ hydrothermal treated catalysts is plotted in Fig. 2. Separate NH_3 TPD experiments on the parent zeolites indicate that they both have similar NH_3 storage prior to the addition of Cu. This is as expected for materials with similar SAR. Following Cu addition and degreening, the NH_3 storage between the two samples diverged

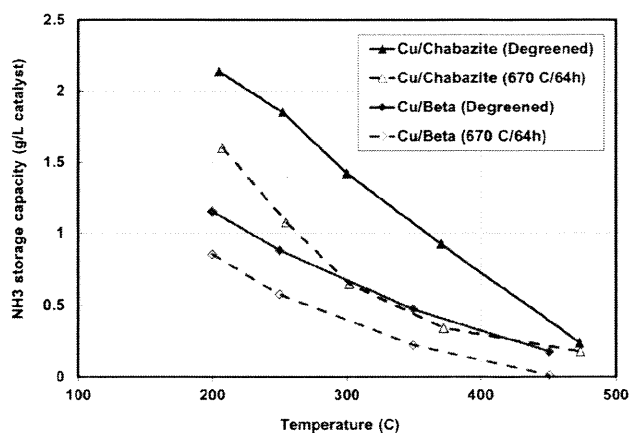


Fig. 2. NH_3 storage capacity of the Cu/beta and the Cu/chabazite SCR catalysts before and after $670^\circ\text{C}/64 \text{ h}$ hydrothermal treatment.

with the Cu/beta sample showing significantly lower degreened storage which is a clear indication of low acid site stability for the Cu/beta sample. Additional NH_3 storage capacity is lost on both the Cu/beta and the Cu/chabazite catalyst after hydrothermal treatment, and the Cu/chabazite catalyst still maintains higher NH_3 storage compared to the Cu/beta catalyst.

3.2. Pore size effect on HC inhibition

The beta zeolite support used in the Cu/beta catalyst is a 12-ring large pore zeolite with a BEA framework structure with the dimension of the openings being about $0.66\text{--}0.72 \text{ nm}$ in diameter. The chabazite zeolite support used in the Cu/chabazite catalyst is an 8-ring small pore zeolite with a CHA structure with the dimension of the openings being about 0.38 nm in diameter. Both types of pores are large enough for small gas molecules, such as O_2 , NO_x , and NH_3 , to freely enter the pores to participate in SCR reactions. They can respond differently if larger molecules or compounds are involved in reactions due to the spatial restriction.

To illustrate this molecular sieving effect, NO_x conversions at 300°C in response to the addition of propene or *n*-octane on the Cu/beta and Cu/chabazite catalysts are monitored as a function of time and shown in Fig. 3. In these experiments, when steady state NO_x conversion is achieved, 1000 ppm C_1 of C_3H_6 or *n*- C_8H_{18} is added into the feed (at time = 8 min in Fig. 3). When C_3H_6 , a short chain HC, is added into the gas mixture, a decline of the NO_x conversion is observed on both catalysts. This is due to HC entering the pores of the zeolite support and inhibiting the SCR reaction. The

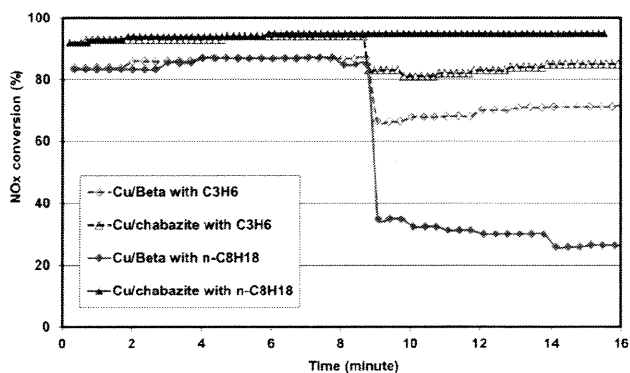


Fig. 3. NO_x conversion efficiency at 300°C before and after HC addition. (SCR reaction conditions: 350 ppm NO , 350 ppm NH_3 , 14% O_2 , 4.6% H_2O , 5% CO_2 , 1000 ppm C_1 (when added) and balance N_2 , GHSV = $30,000 \text{ h}^{-1}$)

decline of NO_x conversion on the Cu/beta zeolite is slightly more pronounced indicating a slightly more severe inhibition effect. When $n\text{-C}_8\text{H}_{18}$, a long chain HC, is added into the gas mixture, the NO_x conversion on the Cu/beta zeolite decreases to $\sim 30\%$, showing an even more severe HC inhibition effect. In contrast, no change of NO_x conversion is observed on the Cu/chabazite catalysts. At the temperature evaluated here, the HC inhibition effect is attributed to hydrocarbon masking of the active sites within the zeolite. Indeed the performance of catalyst recovers after a purge of the hydrocarbon species. Therefore, the results clearly demonstrate that large molecules, such as $n\text{-C}_8\text{H}_{18}$, which are able to enter the pores of a large pore zeolite can be excluded from entering the pores of a small pore zeolite.

3.3. In situ XRD measurement

To verify if the chabazite zeolite sample itself is hydrothermally more stable than the beta zeolite sample used in the study, in situ XRD measurements were carried out on the two parent zeolite samples. The XRD scans and the corresponding contour plot of the parent beta zeolite are compiled in Fig. 4. On heating from 50 to 200 °C, the intensity of the strong low angle peak at $2\theta = 7.9^\circ$ increases slightly. This is likely due to dehydration of the sample which leads to increased ordering. Above 200 °C, the intensity of this low angle reflection peak gradually decreases until it is not evident when the temperature reaches 900 °C. The sharper peak at $2\theta = 22.5^\circ$ shows a more subtle reduction in intensity, reaching a minimum during the 900 °C holding period. On cooling from 900 to 50 °C, both peaks at $2\theta = 7.9^\circ$ and 22.5° gradually return. This suggests that the decline of the intensities at high temperature is

caused by temperature induced disordering rather than complete zeolite framework structure collapse. Indeed, a comparison of the XRD patterns recorded at 50 °C before and after the in situ hydrothermal treatment reveals that the sample still maintains the BEA structure although a reduction of the peak intensity by about 1/3 is observable at $2\theta = 7.9^\circ$.

Fig. 5 shows the XRD scans and the corresponding contour plot of the parent chabazite zeolite. Similar to what observed on the beta zeolite sample, the intensity of the XRD peaks increases upon heating from 50 to 250 °C, then gradually decreases and reaches a minimum during the 900 °C holding period. The intensity of the XRD peaks returns when the sample is cooled from 900 to 50 °C. A comparison of the XRD patterns recorded at 50 °C before and after the 900 °C hydrothermal treatment indicates about 2/3 decrease in intensity for the peak at $2\theta = 9.4^\circ$ but no other obvious change of the reflection pattern. Therefore, both the beta zeolite and the chabazite support used in this study have reasonably good hydrothermal stability. Although they both become less ordered, their framework structures remain intact after 900 ° hydrothermal exposure.

Similar in situ XRD hydrothermal experiments were carried out on the corresponding Cu/zeolite SCR catalysts. Fig. 6 shows the XRD scans and the corresponding contour plot of the Cu/beta SCR catalyst. The XRD pattern of the sample before the hydrothermal treatment shows only BEA structure with no Cu related bulk compounds identified, suggesting a very high Cu dispersion on the sample. Upon heating from 50 up to 800 °C, the diffraction patterns and the change of peak intensity of the sample follow the same trend as observed on the parent beta sample. At temperatures above 800 °C, however, a drastic reduction of the peak intensity

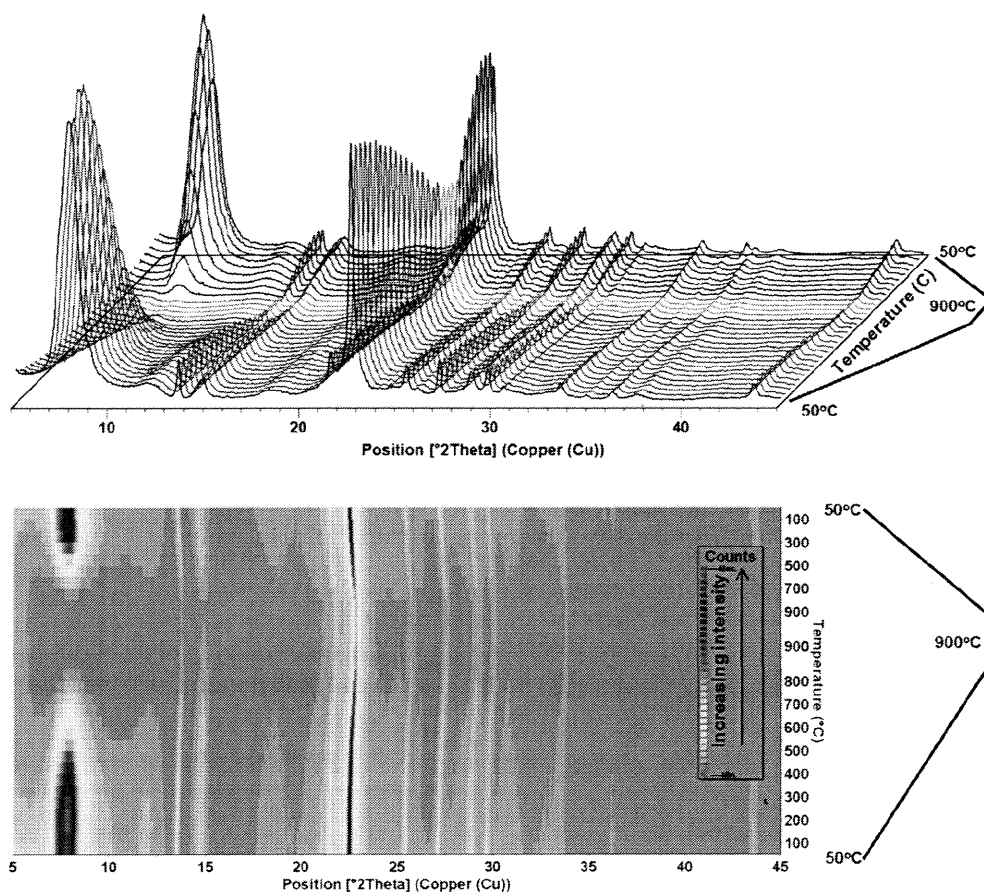


Fig. 4. In situ XRD scans and the contour plot of a beta zeolite during hydrothermal treatment

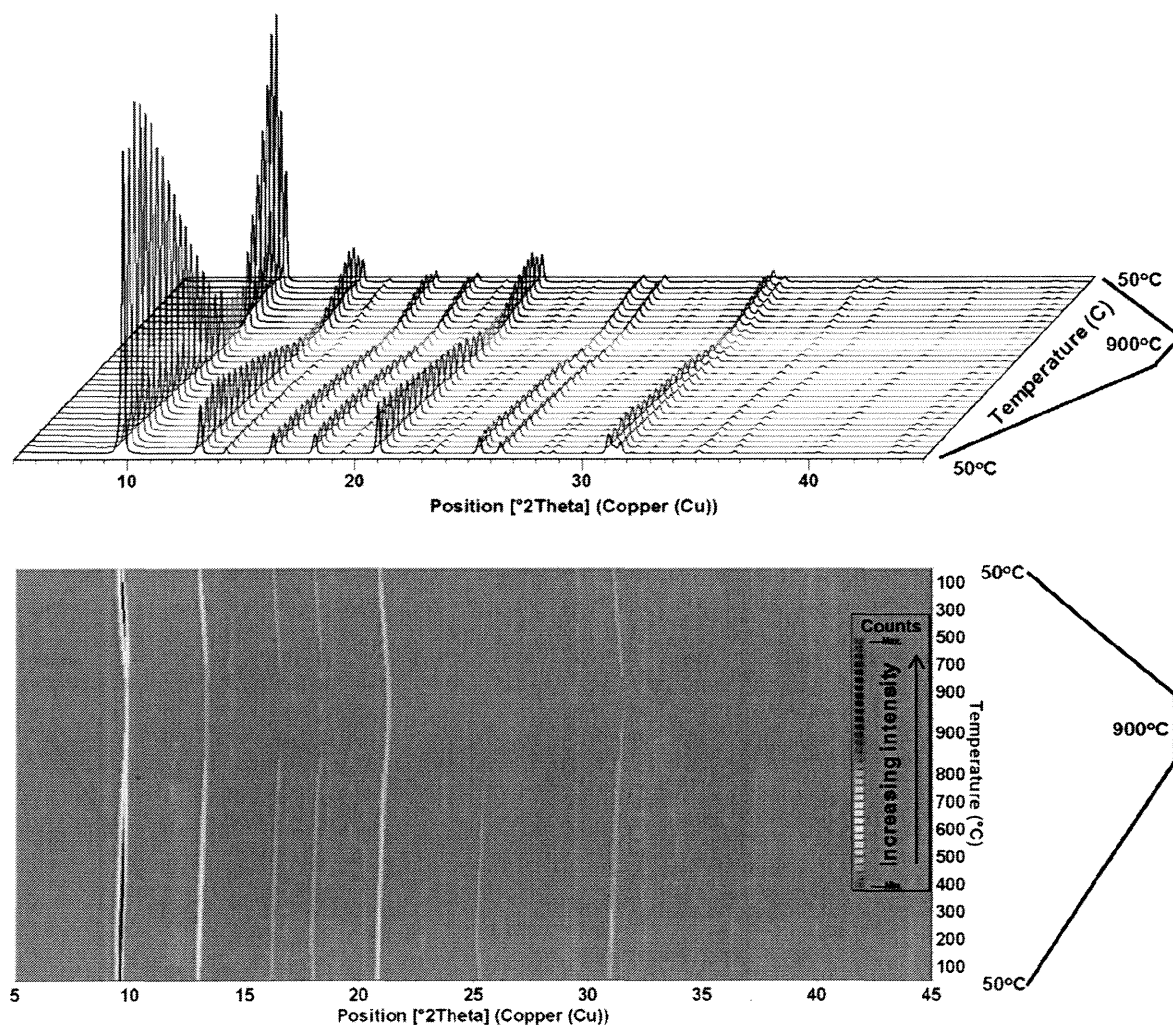


Fig. 5. In situ XRD scans and the contour plot of a chabazite during hydrothermal treatment.

(more obvious at $2\theta = 22.5^\circ$) becomes apparent. The diffraction peaks that can be attributed to a BEA structure are no longer evident when the temperature reaches 900°C and for the remainder of the hydrothermal experiment. This clearly indicates a complete collapse of the beta zeolite structure of the sample once it is exposed to above 800°C . A few minor XRD peaks are visible on the sample after the 900°C hydrothermal treatment, which can be assigned to aluminum silicate and silica. Even though no crystalline copper oxides or copper aluminates are evident on the 900°C treated sample, formation of these compounds in clusters cannot be ruled out because of the low concentration of Cu in the sample.

The XRD scans and the corresponding contour plot of the Cu/chabazite SCR catalyst are shown in Fig. 7. The XRD patterns and the change of the peak intensity during the hydrothermal treatment of the Cu/chabazite sample are nearly identical to that of the chabazite parent zeolite. The CHA structure remains during the entire hydrothermal experiment. After the 900°C hydrothermal treatment, the Cu/chabazite sample still shows only CHA structure although the intensity reduction of the peak at $2\theta = 9.4^\circ$ is more pronounced ($\sim 3/4$ decrease) than that observed on the parent chabazite ($\sim 2/3$ decrease in intensity).

The difference of the hydrothermal stability between the Cu/beta and the Cu/chabazite SCR catalysts is apparent by comparing Figs. 6 and 7. To further illustrate the difference, Fig. 8 plots the relative intensity of the second most intensive XRD peak of the two

samples and their parent zeolites as a function of temperature during the temperature ramp-up portion of the in situ hydrothermal experiments. The most intense peak at the low angle is not used because the temperature broadening effect on the low angle peak is too severe. The second most intensive XRD peak is at $2\theta = 22.5^\circ$ for the beta zeolite samples and at $2\theta = 21.0^\circ$ for the chabazite samples. In Fig. 8, both the beta and the chabazite parent zeolites show about 50% decrease of the relative intensity with temperature increased from 50 to 900°C . A similar trend is observed for the Cu/chabazite sample. The Cu/beta zeolite also shows a similar trend as the other three samples at temperatures below 800°C . Above this temperature, however, a precipitous decline of the peak intensity is observed and the sample completely loses its BEA structure when temperature reaches 900°C . The results clearly demonstrate that at high temperatures Cu accelerates the collapse of beta zeolite framework whereas such a Cu/zeolite negative interaction does not happen on the Cu/chabazite sample.

4. Discussion

The comparison of the SCR activity of Cu/chabazite and Cu/beta catalysts before and after different hydrothermal treatment shown in Fig. 1 clearly demonstrates that the Cu/chabazite catalyst is more stable either after a long-term hydrothermal treatment or after a short time hydrothermal exposure to an extremely high

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