One-pot hydrothermal synthesis of CuBi co-doped mesoporous zeolite Beta for the removal of NOx by selective catalytic reduction with ammonia

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A series of CuBi co-doped mesoporous zeolite Beta (CuxBi1-yBeta) were prepared by a facile one-pot hydrothermal treatment approach and were characterized by XRD, N2 adsorption-desorption, TEM/SEM, XPS, H2-TPR, NH3-TPD and in situ DRIFTS. The catalysts CuxBi1-yBeta were applied to the removal of NOx by selective catalytic reduction with ammonia (NH3-SCR), especially the optimized CuxBi1-yBeta achieved the high efficiency for the removal of NOx and N2 selectivity, superior water and sulfur resistance as well as good durability. The excellent catalytic performance could be attributed to the acid sites of the support and the synergistic effect between copper and bismuth species. Moreover, in situ DRIFTS results showed that amides NH2 and NH4+ generated from NH3 adsorption could be responsible for the high selective catalytic reduction of NOx to N2. In addition, a possible catalytic reaction mechanism on CuxBi1-yBeta for the removal of NOx by NH3-SCR was proposed for explaining this catalytic process.

Nowadays, it is still of great challenges for the effectively catalytic purification of diesel exhausts, especially for the NOx from diesel engine, since the conventional three-way catalysts are no longer effective in selective reducing NOx1. The commercial selective catalytic reduction with ammonia (NH3-SCR) catalyst for the removal of NOx, i.e. V2O5-WO3/TiO2, only shows high catalytic efficiency in a narrow temperature window of 300–400 °C2, besides, the poor water and sulfur resistance as well as the toxicity of V2O5 also greatly prohibit the popularity of vanadium-based composite oxides. Therefore, researchers have devoted to develop a new kind of non-vanadia catalysts to overcome the disadvantages of vanadium-based composite oxides1. It was reported that compared to the traditional V2O5-WO3/TiO2, non-vanadia catalyst not only presents the wider NH3-SCR temperature windows with high N2 selectivity, but also owns good durability and strong resistance against H2O and SO2.

Very recently, zeolite-based catalysts with high surface areas and pore volume, abundant acidity sites, outstanding thermal and hydrothermal stability, as good catalyst supports, have attracted much research attention in selective catalytic reduction NOx by ammonia3–5. However, small microporous channels of zeolite greatly prevented the diffusion and transport of some large molecules, resulting in the low catalytic performance in a great majority of traditional catalytic reactions6. Therefore, a novel zeolite with mesoporous structure has been developed, which combines the advantages of conventional crystalline zeolite and mesoporous material, to enable the quick access for the diffusion and transport attributed to the hierarchically porous structure. It is generally believed that mesoporous zeolites possess remarkably higher catalytic activity and longer catalytic lifetime than

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conventional zeolites owing to the crystalline framework and the hierarchically porous structure. Thereinto, the mesoporous Beta zeolite (mBeta) with unique three-dimensional network of large pores (12MR) exhibits much high surface area and excellent hydrothermal stability, which is widely applied in fine chemistry. In the past decades, a number of synthetic approaches of mBeta have been explored and some encouraging results have been obtained. Such as, Xiao et al., synthesized highly mesoporous single-crystalline zeolite beta by using a commercial polymer, polydiallyldimethylammonium chloride (PDADMA) as both structure-directing agent and porogen, which showed better hydrothermal stability and higher catalytic activity than conventional zeolite Beta in large molecules involved acid-catalyzed reactions. In addition, many metal oxides were reported to have good performance in the removal of NOx by NH3-SCR, e.g., Cu-loaded zeolite beta exhibited a good activity and hydrothermal stability in the NH3-SCR of NOx. It is also reported that the introduction of Bi2O3 can improve the SO2 resistance.

On the basis of our previous work, a novel CuBi co-doped mesoporous zeolite Beta (CuBi-mBeta) has been synthesized by one-pot hydrothermal treatment approach, by which the copper and bismuth species can be well dispersed into the framework of mesoporous zeolite Beta. Therein, the optimized prepared catalyst CuBi-mBeta exhibits very high catalytic activity for the selective catalytic reduction of NOx with NH3. In addition, the N2 selectivity, water vapor and sulfur resistance and durability of the CuBi-mBeta catalyst have been detailedly investigated. Finally, a possible catalytic mechanism of SCR of NOx with ammonia on this prepared catalyst CuBi-mBeta is proposed to clarify the catalytic process.

Results
Structure Characteristics. The powder XRD patterns of mBeta, Cu-mBeta, Bi-mBeta and CuBi-mBeta are shown in Fig. 1. It is found that all prepared samples keep the diffraction peak of typical zeolite beta structure, and no diffraction peaks corresponding to copper and bismuth species can be detected. Therefore, it is believed that the copper and bismuth species could be well-incorporated into the framework of zeolite as ions or highly dispersed into the mesoporous channels as metal oxides. It is noted that compared with the mBeta, the doping of Bi species can cause the inevitable destruction of zeolite framework to a certain extent, and the intensity of XRD peak of CuxBi-y-mBeta decreases with the increase of Bi-loading content, as shown in Fig. 1.

The N2 adsorption isotherms and pore size distribution curves for samples mBeta, Cu-mBeta, Bi-mBeta and CuBi-mBeta are shown in Fig. 2 and the corresponding pore structure parameters of all the samples are summarized in Table 1. All the samples exhibit typical type IV isotherms, confirming the presence of mesoporous structure. The reference sample mBeta shows well-defined mesopore of 3.8 nm, and the BET surface area and total pore volume are calculated to be 556 m2/g and 0.34 cm3/g, respectively, including the mesoporous surface area (166 m2/g) and mesoporous volume (0.16 cm3/g), respectively. Compared with the mBeta, the surface areas of Cu-mBeta, Bi-mBeta and CuBi-mBeta show obvious decrease after loading amount of copper and bismuth species, which is resulted from the generation of non-framework Cu or/and Bi ions (i.e., CuO and Bi2O3) with the increase of Cu or Bi content, and inducing the collapse of pore structure of zeolite to some extent. Even so, the prepared CuBi-mBeta still keep high BET surface area and pore volume after doping with Cu and Bi species (Table 1), indicative of the unblocked mesoporous channels due to the high dispersity of Cu and Bi species. It is noted that the optimized CuBi-mBeta with the mesopore size of 3.6 nm shows high BET surface area (539 m2/g) and total pore volume (0.46 cm3/g).

The SEM image of as-prepared CuBi-mBeta, as shown in Fig. 3a, presents a rough surface morphology, demonstrating that the mesoporous structure has penetrated into the zeolite crystals by one-pot hydrothermal synthesis process. Additionally, no oxide aggregations can be found, as shown in Fig. 3a,b, indicating that the doped metal oxides are highly dispersed into the carrier mBeta. The clearly crystal lattices can be found in the high-magnification TEM image (Fig. 3c), confirming the zeolite crystallized structure. The element mapping in Fig. 3d–h further confirms that Cu and Bi species are highly dispersed into mesoporous zeolite Beta, which is consistent with the above results of XRD patterns.
Spectroscopy Characteristics. The X-ray transmission spectroscopy (XPS) result of the Cu$_1$Bi$_1$-mBeta is shown in Fig. 4a. The binding energy levels of Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ at around 934.5 eV and 954.2 eV, respectively (denoted with ★), accompanied by a shoulder peak of about 10 eV higher binding energy, are attributable to Cu(II). Additionally, the distinctive peaks at 936.6 eV and 956.4 eV, (denoted with ▼) can be ascribed...
to Cu(I), indicating that Cu species have variable valencies in the obtained sample Cu$_{1}$Bi$_{1}$-mBeta. In addition, the prepared Cu$_{1}$Bi$_{1}$-mBeta presents higher binding energy peak intensities of Cu(II) (934.5 eV) than that of Cu(I) (936.6 eV), as shown in Fig. 4a, suggesting that Cu$_{1}$Bi$_{1}$-mBeta contains much more amounts of Cu(II) than Cu(I)$.^{15,16}$ Figure 4b shows the Bi 4f XPS spectrum of Cu$_{1}$Bi$_{1}$-mBeta catalyst. Compared to pure Bi$_{2}$O$_{3}$ at 164.2 eV and 158.9 eV, the Cu$_{1}$Bi$_{1}$-mBeta shows the Bi 4f$_{5/2}$ and Bi 4f$_{7/2}$ a little higher binding energies at 164.6 eV and 159.5 eV, respectively, which is attributed to the interaction between Bi and Cu or the support mBeta$.^{17–19}$

The H$_2$-TPR profiles of Cu-mBeta, Bi-mBeta and a series of Cu$_x$Bi$_y$-mBeta samples are shown in Fig. 5. It is found that the reference single loaded sample Cu-mBeta shows two weak reduction peaks at around 220°C and 290°C, indicating a two-step reduction of Cu$^{2+}$ ions, i.e., firstly to Cu$^+$ and then to Cu$^{0,21}$. In addition, the reduction peak at 310°C of reference Bi-mBeta can be ascribed to the reduction of Bi$_2$O$_3$. The H$_2$-TPR profiles of co-loaded samples Cu$_x$Bi$_y$-mBeta show a distinctively different redox behavior from either Cu-mBeta or Bi-mBeta, and present enhanced reduction peak at 250–350°C, attributed to the strong interaction between the active species CuO and Bi$_2$O$_3$. In addition, the reduction peak gradually shifts toward lower temperature range (from 350 to 310°C) with the increase of Bi content (Fig. 5 and Table 1), confirming that the addition of Bi$_2$O$_3$ is beneficial to promote the catalytic redox reaction$^{22}$. NH$_3$-TPD experiments were carried out to obtain the acidity information of the prepared catalysts, as shown in Fig. 6. It is clear that a low-temperature peak at 150°C and a high-temperature peak at 300°C can be observed for the sample mBeta, which is assigned to weakly Lewis acid sites and strong Brønsted acid sites, respectively$^{23,24}$. It is noted that all the samples Cu-mBeta, Bi-mBeta and Cu$_x$Bi$_y$-mBeta show weaker low-temperature peaks than that of the reference mBeta, owing to the part destruction of zeolite framework structure after introducing Cu and Bi species. However, it is interesting that only the Cu$_1$Bi$_1$-mBeta shows a similar desorption peak at high-temperature range (300–400 °C) to the mBeta, indicating that the Cu$_1$Bi$_1$-mBeta sample still keeps the strong acidity site of mBeta. The presence of rich acidic sites (Brønsted acid and Lewis acid) produced from the framework Al atoms and copper/bismuth species are helpful to the adsorption and activation of NH$_3$, and thus producing many ammonia species, including NH$_2$, coordinated NH$_3$ and ionic NH$_4^+$, which can greatly promote the selective catalytic reduction of NO$_x$, as shown in Fig. 7.

The reaction of adsorbed NH$_3$ species towards NO$^+$O$_2$ was evaluated by the in situ IR spectra at 250°C and the results are shown in Fig. 7. When the catalyst are exposed to NH$_3$ for the 60 min and purged with N$_2$, the peaks related to coordinated NH$_3$ on Lewis acid sites (3125, 3002, 1611, 1245 and 1115 cm$^{-1}$) and ionic NH$_4^+$ bound to Bronsted acid sites (3601 and 1440 cm$^{-1}$) are clearly observed$^{15,25–27}$. Afterwards, the coordinated NH$_3$
on acidic sites could undergo the oxidative dehydrogenation to form NH₂ species (1560 cm⁻¹), then produce intermediate specie NH₂NO when NO and O₂ were added into reaction gas. It is noted that all the ammonia species, including NH₂, coordinated NH₃ and ionic NH₄⁺ bound, disappeared after NO⁺O₂ purge, indicating that those ammonia species could participate in the reduction of NOₓ. Meanwhile, when NO and O₂ were added into reaction gas, the bands at 1235, 1367, 1542 and 1601 cm⁻¹ could be detected in IR spectra. Thereinto, the bands at 1235 and 1367 cm⁻¹ were assigned to monodentate nitrate, while the bands at 1542 and 1601 cm⁻¹ are associated with bidentate nitrate and adsorbed NO₂, respectively. More interestingly, two peculiar peaks at 3335 and 3265 cm⁻¹ related to the adsorbed NH₃ on acid sites became stronger with the increase of exposing time in the NO⁺O₂, indicating that some acidic sites on the surface of the catalyst were released and then preferably adsorbed the NH₃ after NO and O₂ pass over the catalyst.

**Catalytic performance.** Figure 8 shows the NH₃-SCR results of mBeta, Cu-mBeta, Bi-mBeta and a series of CuₓBiᵧ-mBeta catalysts. The NOₓ conversions over the prepared catalysts under high hourly space velocity of 64000 h⁻¹ are shown in Fig. 8a. Compared with the references mBeta, Bi-mBeta and Cu-mBeta, the sample CuₓBiᵧ-mBeta show higher catalytic activity for the SCR of NOₓ. Especially, the optimized sample Cu₁Bi₁-mBeta with the 4.38 wt% Cu and 4.83 wt% Bi exhibits the highest catalytic performance, i.e., the NOₓ conversion efficient is above 90% within the wide operation temperature window of 170 °C to 400 °C. While, the excess doping of Cu and Bi species could induce the formation of oxides aggregates and thus decrease the active surface area (Table 1), e.g., the excess Bi would cover part of active center and results a lower catalytic activity. Therefore, the optimized sample CuₓBiᵧ-mBeta with the 1:1 ratio of Cu and Bi shows the highest catalytic performance. The results of N₂ selectivity of these catalysts were shown in Fig. 8b. For comparison, the reference Bi-mBeta shows a low N₂ selectivity, particular in 200 °C, owing to the part destruction of zeolite framwork with the addition of Bi species, as demonstrated by XRD results, which can affect the strong acidic sites (Fig. 6), thus decrease the adsorption ability of NH₃ on the reference Bi-mBeta. Furthermore, the CuₓBiᵧ-mBeta catalyst also presents as high as up to 100% N₂ selectivity in the whole temperature range investigated. It is believed that the high dispersity of active species
Cu and Bi on the support mesoporous zeolite, the richer acidic sites and the strong interaction between the active copper and bismuth species on the Cu1Bi1-mBeta could be main contributions to the catalytic activity.

It is well known that the real diesel exhaust presents large number of water vapor and trace S compounds, therefore, the effects of H2O and SO2 on the SCR catalytic activity are also investigated on the samples Cu1Bi1-mBeta. It is evident that compared with the reference mBeta, Cu1Bi1-mBeta catalyst shows an excellent SO2 resistance in the NH3-SCR above 200 °C (Fig. 8c). Even in the co-presence of H2O and SO2, the Cu1Bi1-mBeta catalyst still exhibits high activity of over 85% NOx conversion from 200 °C to 430 °C. The results of durability tested at 250 °C, as shown in Fig. 8d, indicate that the Cu1Bi1-mBeta is very stable in the presence of SO2 (or H2O and SO2). It is believed that the highly crystalline zeolite framework enables the catalyst to keep good stability against H2O, and the highly dispersity active species Bi can improve the SO2 resistance to some extent13, which is very important for the NH3-SCR of NOx in the co-existence of H2O and SO2.

Discussion

Based on the above results and discussions, a possible catalytic reaction mechanism for the SCR of NOx was proposed, as illustrated in Fig. 9. Firstly, there are a large amount of oxygen vacancies (V0) presented in the sample support mBeta due to the doping of hetero atoms Cu+ and Al3+ in the [SiO4], leading to the generation of numerous surface activated oxygen (O*) by adsorbing the O2, as shown in Step 1 (Fig. 9). Meanwhile, the existence of Bi2O3 was reported22,28 to be beneficial for the reduction of Cu2+ to Cu+, and NO could be easily adsorbed and activated by the Cu2+ and generated the NO+ and NO+ at higher temperatures or lower temperatures, respectively29,30. Afterwards, these activated NO+ and NO+ could react with the surface activated oxygen (O*) and thus produce large numbers of NO2, as shown in Step 1 (Fig. 9). When the concentration ratio of NO and NO2 in reaction gas reaches to 1:1, the quick SCR reaction (NO + NO2 + 2NH3 = 2N2 + 3H2O) occurs, during which the NOx conversion efficiency at low temperature can be greatly improved. Secondly, the presence of rich acidic sites (Brønsted acid and Lewis acid) produced from the framework Al atoms and copper/bismuth species is helpful to the adsorption and activation of NH3, i.e., the NH3 adsorbed on strong Brønsted acid sites could be activated and generate NH4+, which was discovered from the in situ DRIFTs (Fig. 7), as shown in Step 2 (Fig. 9). Meanwhile, the NH3 molecules could also be adsorbed on the weak Lewis acid sites to generate NH3(ads) and react with the activated oxygen (O*) to produce the amines NH/NH2, as confirmed by the in situ DRIFTs (Fig. 7). Finally, the produced amide NH/NH2 and NH4+ could directly react with NOx on the highly dispersed
active sites and generate N₂, as shown in Step 3 (Fig. 9). It is believed that the existence of highly dispersed varied valence Cu species and acidic sites can accelerate the adsorption and activation of NO and NH₃ in this reaction system, which greatly increases the NH₃-SCR in the removal of NOₓ.

In conclusion, a series of CuxBiₙ-mBeta catalysts have been prepared by a facile one-pot hydrothermal treatment approach. The optimized Cu₁Bi₁-mBeta shows an excellent NH₃-SCR activity and high N₂ selectivity (closely to 100%) toward NOₓ in a broad operation temperature window (170–400 °C). On the one hand, the mesopores structure is helpful for the homogeneous dispersion of active species, which can improve the diffusion and transport of reactants and products. Also, the highly crystalline zeolite framework enables the catalyst to keep good resistance toward water vapor. On the other hand, the highly dispersity of copper and bismuth active species, as well as the synergistic catalytic effect between copper and bismuth species and the richer acidic sites of the zeolite promote the reduction of CuO and generation of intermediate NO₂. Meanwhile, the large number of amide NH/NH₂ and NH₄⁺ generated from NH₃ adsorption, as the key intermediates, greatly accelerate the selective catalytic reduction of NOₓ. More interesting, the prepared catalyst shows good durability and high resistance against H₂O and SO₂, which could also be ascribed to the crystalline zeolite framework and the highly dispersity active sites. The CuBi-mBeta catalyst with distinctive micro-mesoporous structure demonstrates excellent NH₃-SCR activity and high stability, which, as we believe, will present promising prospect in the practical application of catalytic purification of diesel exhausts.

Methods

Preparation of the mesoporous zeolite Beta (mBeta). Typically, 0.05 g NaCl and 0.15 g KCl were added into 2 mL distilled water and 14.4 g TEAOH solution. Afterwards, 3.9 g H₂SiO₃ was dissolved into the above mentioned solution and stirred at 313 K for 6 h. Next, the solution containing 0.033 g NaOH, 0.17 g NaAlO₂ and 2 mL distilled water was slowly added into the resultant solution and further stirred at 313 K for 6 h. Finally, 0.5 g CTAB solution was added into the obtained solution and further stirred at 353 K for 8 h. The obtained mixed solution was hydrothermally treated for 48 h at 423 K. Subsequently, the products were washed with distilled water and dried at 383 K for 12 h. The final product mBeta was obtained after calcinations at 823 K for 6 h to remove any organics.

Preparation of CuₓBiₙ-mBeta. Typically, 0.05 g NaCl and 0.15 g KCl were added into 2 mL distilled water and 14.4 g TEAOH solution. Afterwards, 3.9 g H₂SiO₃ was dissolved into the above mentioned solution and stirred at 313 K for 6 h. Then, the solution containing 0.033 g NaOH, 0.17 g NaAlO₂ and 2 mL distilled water was slowly added into the resultant solution and further stirred at 313 K for 6 h. Next, 1 mmol Cu(NO₃)₂•3H₂O, 1 mmol Bi(NO₃)₃•5H₂O and 2 mL distilled water was slowly added into the above precursor solution and further stirred at 313 K for 6 h. Then, 0.5 g CTAB solution was added into the obtained solution and further stirred at 353 K for 8 h. Next, the obtained mixed solution was hydrothermally treated for 48 h at 423 K. Subsequently, the products were washed with distilled water and dried at 383 K for 12 h. The final product CuₓBiₙ-mBeta, was obtained after calcinations at 823 K for 6 h to remove any organics.

For comparison, the Cuₙ-mBeta, Biₙ-mBeta and CuₓBiₙ-mBeta were synthesized by a facile one-pot hydrothermal treatment approach, similarly to the above process of Cu₁Bi₁-mBeta. Herein, the x and y represent the millimole amount of Cu and Bi in the initial precursor solution, respectively. In addition, the final pH value of the synthetic gel including copper and bismuth species is about 11.
Sample characterization. The XRD patterns were recorded on a Rigaku D/Max-2200PC X-ray diffractometer using Cu target at 40 kV and 40 mA. The N₂ adsorption and desorption measurements were performed using Micromeritics Tristar 3000 at 77 K. The total surface area and pore volume were calculated using the BET and BJH method. Field emission scanning electron microscopy (SEM) analysis was performed on a JEOL JSM6700F electron microscope. Field emission transmission electron microscopy (TEM) analysis was conducted with a JEOLE 2000CX electron microscope operated at 200 keV. X-ray photoelectron spectroscopy (XPS) signals were collected on a Thermo Scientific ESCALAB 250 instrument using monochromated Al X-ray resource at 1486.6 eV operated at 15 kW. The temperature-programmed reduction with hydrogen (H₂-TPR) and temperature programmed desorption of ammonia (NH₃-TPD) were performed on Micromeritics Chemisorb 2750 instrument attached with ChemiSoft Tpx software. TPR was carried out from room temperature to 900 °C under 5% H₂ in Ar at a flow rate of 25 mL/min. The H₂ signal was detected by a thermal conductivity detector (TCD). The NH₃-TPD of the samples was carried out from room temperature to 800 °C at a flow rate of 25 mL/min. The amount of NH₃ desorbed was measured using a thermal conductivity detector (TCD). In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was performed on a Bruker spectrometer equipped with an MCT detector. Prior to each experiment, the sample was pretreated at 400 °C for 1 h in a flow of N₂ and then cooled down to 200 °C. The background spectrum was collected in flowing N₂ and automatically subtracted from the sample spectrum. The activity for each experiment, the sample was pretreated at 400 °C for 1 h in a flow of N₂ and then cooled down to 200 °C. The total flow rate of the feed gas was 300 mL/min, corresponding to a GHSV of 64,000 h⁻¹. The product gas was analyzed by a chemiluminescence NO/NO₂ analyzer (Thermal Scientific, model 42i-HL) and gas chromatograph (Shimadzu GC 2014 equipped with Porapak Q and Molecular sieve 5A columns). The activity data were collected when the catalytic reaction practically reached steady-state condition at each temperature.

Catalytic activity test. The catalysis measurements were carried out in a fixed-bed quartz reactor using 0.2 g catalyst of 40–60 meshes. Before catalytic test, the catalysts were dried at 423 K for 16 h. The feed gas mixture contained 500 ppm NO, 500 ppm NH₃, 0 or 3% H₂O, 0 or 50 ppm SO₂, 5% O₂ and Ar as the balance gas. The total flow rate of the feed gas was 300 mL/min, corresponding to a GHSV of 64,000 h⁻¹. The composition of the product gas was analyzed by a chemiluminescence NO/NO₂ analyzer (Thermal Scientific, model 42i-HL) and gas chromatograph (Shimadzu GC 2014 equipped with Porapak Q and Molecular sieve 5A columns). The activity data were collected when the catalytic reaction practically reached steady-state condition at each temperature.

The NOₓ (XNOₓ) and NH₃ (XNH₃) conversions and N₂ selectivity (SNO₂) were calculated as

\[
X_{\text{NOx}} = \frac{C_{\text{in}}^{\text{NOx}} - C_{\text{out}}^{\text{NOx}}}{C_{\text{in}}^{\text{NOx}}} \times 100
\]

\[
X_{\text{NH3}} = \frac{C_{\text{in}}^{\text{NH3}} - C_{\text{out}}^{\text{NH3}}}{C_{\text{in}}^{\text{NH3}}} \times 100
\]

\[
S_{\text{N2}} = \frac{2C_{\text{out}}^{\text{N2}}}{C_{\text{in}}^{\text{NH3}}X_{\text{NH3}} + C_{\text{in}}^{\text{NOx}}X_{\text{NOx}}} \times 100
\]

where NOₓ includes NO and NO₂, C presents the concentration of the “i” species, and the “in” and “out” present the gas concentration of inlet and the outlet of the reactor, respectively.

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Author Contributions
Z.X. conceived the preparation method, synthesized and characterization of the CuBi co-doped mesoporous zeolite Beta. Z.X., X.Z., H.W. and H.C. analyzed the experimental results and preparation of the manuscript draft. L.C., H.Z., Y.L. and L.P. supervised and finalized the project. All authors discussed the results and contributed to the final manuscript.

Additional Information
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