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High activity of mononuclear copper present in the framework of CuSiBEA zeolites in the selective catalytic reduction of NO with NH₃

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Table : 1

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Abstract

Cu_xSiBEA zeolites (with $x = 1 - 7.5$ Cu wt %) prepared by a two-step postsynthesis method which consists in the first step of dealumination of parent BEA zeolite to obtain aluminum-free SiBEA support and then in the second step, of contacting the obtained material with an aqueous solution of copper nitrate, were used in this work as catalysts of SCR of NO with ammonia. XRD, TPR and FTIR investigations showed that up to 2 wt % of Cu was successfully incorporated into zeolite beta structure as framework mononuclear Cu(II). The FTIR of pyridine sorption revealed that the incorporation of copper into zeolite framework led to the creation of new Lewis acidic sites which were responsible for high activity of Cu_xSiBEA zeolite catalysts in SCR of NO with ammonia. The catalytic activity of Cu_xSiBEA in SCR of NO with ammonia used as a reducing agent strongly depends on the nature and environmental of copper in BEA structure. The $\text{Cu}_{1.0}\text{SiBEA}$ catalyst with predominantly framework Cu(II) was the most active and selective among the tested samples in wide temperature range. In contrast, the application of Cu_xSiBEA zeolite catalysts with higher Cu content (> than 2 wt % of Cu) containing a mixture of framework and extra-framework Cu(II) resulted in low NO conversion in SCR at high temperature range, as well as, the high concentration of undesired N_2O in outgas stream. It indicates that octahedral Cu(II) and/or copper oxides present in extra-framework position of SiBEA zeolite promote at high temperature ammonia oxidation.

1. Introduction

Selective catalytic reduction of NO_x with ammonia is a widely applied method of nitric oxides removal from exhaust of power plants [1, 2]. It is also of interest for the treatment of NO_x emissions from heavy duty diesel engines [3, 4]. In case of stationary sources, the standard SCR catalyst is $\text{V}_2\text{O}_5/\text{TiO}_2/\text{MnO}_3$. However due to its narrow temperature window it cannot be applied for mobile sources. Moreover, conventional three way catalysts are not able to remove NO_x from diesel engine because of oxygen over abundance. Thus, other types of catalysts are intensively studied, in order to find the most efficient one. Among the many tested candidates [5-7], the most promising are zeolite-based materials promoted with transition metal ions such as Cu and/or Fe [8-11].

Many researches indicated isolated metal ions in exchanged positions as active species responsible for high NO conversion and excellent N_2 selectivity. Xue et al. [12] concluded that Cu^{2+} ions displaced into cavity of SAPO-34 are responsible for high activity at low temperature. However, Pereda-Ayo et al. [13] observed that isolated Cu(II) ions located in pores of BETA and ZSM-5 zeolite maintained NO_x conversion at high temperature range. Additionally, there are still a lot of questions to answer about reaction mechanisms and the formation of by-products from competitive reactions of ammonia oxidation.

Others very important factors for potential catalysts application on industry scale are their stability and durability. It is well known that zeolite materials may be damaged by hydrothermal treatment resulting in dealumination [14], crystalline structure disordering [15] or metal ions migration [16, 17]. In order to avoid such effects and retain catalytic properties for a long time, improvements in catalyst synthesis or post-synthesis modification are proposed. One of the such proposal way was the application of materials with CHA zeolite structure which seemed to be more resistant to steam than large pores zeolites [18, 19]. On the

other hand, Dzwigaj et al. [20, 21] have proposed two-step postsynthesis method as an attractive alternative to obtain almost completely dealuminated beta zeolite with excellent dispersion of metal ions in the form of isolated mononuclear framework species. They used two-step postsynthesis method which consists of the creation of vacant T-atom sites by nitric acid treatment of parent beta zeolite and the subsequent incorporation of metal ions into framework of SiBEA zeolite by reaction with silanol groups associated with vacant T-atom sites.

In this work the two-step postsynthesis method was applied to obtain zeolite beta catalysts with isolated mononuclear Cu(II) incorporated into zeolite framework highly active in selective catalytic reduction of NO with NH₃.

2. Experimental

2.1. Catalyst preparation

A TEABEA zeolite with atomic Si/Al ratio of 17 was treated i) in air at 823 K for 15 h to remove organic template and obtain an organic-free HAIBEA zeolite (Si/Al = 19) or ii) with nitric acid solution ($c = 13 \text{ mol dm}^{-3}$, 353 K) over 4 h in order to remove aluminum species and obtain SiBEA zeolite. As obtained SiBEA with atomic Si/Al ratio of 1300 was washed several times with distilled water and dried at 368 K overnight. SiBEA zeolite was contacted with an aqueous copper nitrate solution which concentration varied from 1.96×10^{-3} to $1.47 \times 10^{-2} \text{ mol dm}^{-3}$ and stirred for 24 h at 298 K. Then, the suspension was stirred in the evaporator under vacuum of a water pump for 2 h at 333 K, until water was evaporated. Cu-containing SiBEA samples after calcination at 773 K (2 K h^{-1}) for 3 h were labeled as C-Cu_xSiBEA (with $x = 1 - 7.5 \text{ wt } \%$), where C state for calcined.

2.2. Catalysts characterization

XRD profiles were recorded at room temperature on a PANalytical Empyrean diffractometer using the CuK α radiation ($\lambda = 154.05$ pm).

Acidic properties of zeolite samples were determined by adsorption of pyridine (Py) followed by infrared spectroscopy. First, the samples were prepared in form of self-supported wafers of ca. 10 mg cm^{-2} and transferred into the IR cell. The activation procedure before pyridine sorption was as follows: (i) the wafers were calcined in a static atmosphere of O₂ ($<3.0 \times 10^4$ Pa) at 723 K for 3 h and then outgassed under secondary vacuum at 573 K (10^{-3} Pa) for 1 h, (ii) the wafers were contacted at room temperature with gaseous Py (133 Pa) via a separate cell containing liquid pyridine. The spectra were recorded with a Bruker Vector 22 spectrometer (resolution 2 cm^{-1} , 128 scans) after desorption at 423 and 573 K for 1 h. The final spectra were obtained after subtraction of the spectrum recorded before pyridine adsorption from the one obtained after pyridine adsorption. The concentration of Brønsted and Lewis acidic sites was estimated using parameters calculated by Emeis [22].

The TPR-H₂ measurements were carried out on an AutoChem 2910 apparatus (Micromeretics) equipped with a thermal conductivity detector (TCD) in the temperature range of 298–1250 K with a linear heating rate of 7 K min^{-1} , hydrogen stream flow (5% H₂/Ar) of $40 \text{ cm}^3 \text{ min}^{-1}$ and samples weight of 0.1 g.

2.3. Catalytic measurements

The activity of CuSiBEA catalysts in selective catalytic reduction (SCR) of NO with ammonia was measured in a conventional fixed-bed reactor. Temperature was measured inside the reactor with a thermocouple and controlled with an electronic controller (LUMEL RE19). The composition of reaction mixture was: 1000 ppm NO, 1000 ppm NH₃, 3.5 vol.% O₂ and He as balance. The gas mixture was fed using calibrated electronic mass flow

controllers (BETA-ERG). The total gas flow was $0.1 \text{ dm}^3 \text{ min}^{-1}$ and catalyst mass was 0.2 g. Additional set of tests for several catalyst with addition of 500 ppm SO_2 to substrate stream was carried out in order to study influence of SO_2 presence on catalyst performance. The concentration of NO and N_2O were analyzed by FTIR detectors (ABB 2000 AO series). The NO_2 forming over SCR process was catalytically converted into NO with ABB Advance SCC-K converter before the exhaust gas was analyzed on the FTIR detectors. Thus, total amount of NO_x was registered as to NO concentration.

Before the catalytic tests the samples were pretreated in oxygen/helium mixture ($0.1 \text{ dm}^3 \text{ min}^{-1}$) in the temperature range 298–798 K with a linear heating rate of 2 K min^{-1} and then for 1 h at 798 K. The standard test conditions were 1 h at 423–773 K with increasing the reaction temperature every 50 K interval. The NO conversions were calculated from the measured concentration of nitric oxide. N_2 selectivity was calculated based on following formula:

$$N_2 \text{ selectivity (\%)} = \frac{([\text{NO}]_{in} - [\text{NO}]_{out}) - [\text{N}_2\text{O}]_{out}}{[\text{NO}]_{in} - [\text{NO}]_{out}} \times 100 \quad (1)$$

applied earlier by Moreno-Tost et al. [23] and Bin et al. [24].

The SCR reaction rates per gram of Cu were calculated from NO conversion with the equation [12]:

$$R_r [\text{mol}_{NO} \cdot \text{g}_{Cu}^{-1} \cdot \text{s}^{-1}] = \frac{X_{NO} \times V [\text{dm}^3 \cdot \text{s}^{-1}]}{m [\text{g}] \times 22.4 [\text{dm}^3 \cdot \text{mol}^{-1}]} \quad (2)$$

where R_r is reaction rate, X_{NO} NO conversion, V flow rate and m mass of Cu.

3. Results and discussions

3.1. XRD and FTIR studies

Changes in the structure of zeolite BEA may be monitored by XRD measurements within a given series of zeolite samples taking into account the position of the diffraction reflex (302) at $2\theta = 22.5^\circ\text{--}22.6^\circ$ which shifts are the evidences of contraction and/or expansion of zeolites structure.

For HAlBEA zeolite the d_{302} spacing decreased from 3.943 Å (with 2θ of 22.53°) to 3.911 Å (SiBEA) (with 2θ of 22.72°) suggesting the zeolite structure contraction consistent with the dealumination of zeolite BEA. The impregnation of SiBEA with Cu precursor led to the increase of the d_{302} spacing, from 3.911 Å (SiBEA) (with 2θ of 22.72°) to 3.926 Å ($\text{Cu}_{1.0}\text{SiBEA}$) (with 2θ of 22.63°) and to 3.933 Å ($\text{Cu}_{2.0}\text{SiBEA}$) (with 2θ of 22.59°) (**Fig. 1**). The shifts of the main diffraction reflex positions may be interpreted as the expansion of the BEA structure and the incorporation of Cu ions into the framework of SiBEA zeolite, in agreement with the earlier study on MoSiBEA and CoSiBEA zeolites [25, 26].

Moreover, none of the studied diffractograms contained reflexes related to other phases, indicating no amorphization of zeolite structure and no formation of copper oxides crystallites.

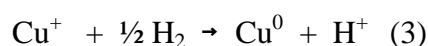
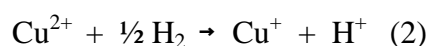
Infrared spectroscopy is a powerful tool to examine the structure and the environment of active species in microporous materials, especially in case of surface hydroxyl groups. **Figure 2** shows the FTIR spectra of SiBEA, $\text{Cu}_{2.0}\text{SiBEA}$ and $\text{Cu}_{4.0}\text{SiBEA}$ zeolites. For SiBEA three characteristic bands at 3736, 3705 and 3520 cm^{-1} may be attributed to isolated internal, terminal internal and hydrogen-bonded silanol groups, respectively, situated at vacant T-atom sites forming hydroxyl nests [14, 27]. The impregnation of SiBEA with copper nitrate solution led to a significant decrease of intensity of hydroxyl group bands at 3705 and 3520 cm^{-1} , probably due to the reaction between SiO-H and Cu^{2+} ions leading to the incorporation of copper into the framework of CuSiBEA zeolites, in line with earlier reports [25, 26].

3.2. Reducibility of the copper species determined by TPR

Hydrogen consumption experiments were carried out to study copper species present in C-Cu_xSiBEA zeolites. According to previous investigations on copper-containing zeolites, two types of reduction reaction pathways may be related to copper species. Generally, copper occurred as polynuclear extra-framework species is reduced to metallic copper in a direct reaction (1) with hydrogen [13, 28]



On the other hand Cu(II) species present as framework species or isolated ions in zeolites cavities are reduced in a two-steps process:



The presence of different copper species is strongly related to copper loading [13, 29]. The higher the Cu content, the more cluster forms of copper and/or copper oxides are expected.

The H₂-TPR patterns of C-Cu_{1.0}SiBEA and C-Cu_{2.0}SiBEA (**Fig. 3**) exhibit one main peak at 480 K with a shoulder at 465 K as well as broad and low intense signal at 585 K. The peaks at 465 and 480 K may be referred to the reduction of two types of mononuclear framework Cu(II) to Cu(I). The creation of two types of copper framework species is related to two different kinds of aluminum present in the parent BEA zeolite that have been removed upon the first step of postsynthesis procedure [14].

The second broad peak with a maximum at 585 K may arise from the partial reduction of Cu(I) species to Cu(0). The lower integral area of this signal than that seen at 465-480 K

may suggest that reduction of copper(I) species to metallic form was not complete, as a result of strong interaction between SiBEA support and copper.

For C-Cu_{4.0}SiBEA sample containing a mixture of framework and extra-framework copper(II) species, much more intense signals were detected. Compared to C-Cu_{1.0}SiBEA and C-Cu_{2.0}SiBEA, the additional signals appeared at 490 and 525 K. The main reduction peak at 490 K may be related to the direct reduction of extra-framework octahedral (Cu(II)) whereas the reduction peak at 525 K may be related to the reduction of copper oxides occurring in zeolite pores in line with earlier work on Cu containing BEA and ZSM-5 zeolites [13, 30].

Thus according to TPR results, the catalysts loaded with Cu up to 2 wt % contain predominantly mononuclear copper species. On the other hand, C-Cu_{4.0}SiBEA catalyst contains a mixture of framework and extra-framework Cu(II) species, while C-Cu_{7.5}SiBEA contains mainly copper oxides in extra-framework position.

3.3. The nature and strength of acidic centers determined by FTIR

Acidic properties of CuSiBEA zeolites were determined with FTIR experiments following pyridine sorption.

Figure 4 exhibits FTIR spectra of SiBEA, Cu_{2.0}SiBEA and Cu_{4.0}SiBEA after adsorption of pyridine at room temperature and desorption at 423 K. For SiBEA five bands of very low intensity are seen at 1638, 1600, 1546, 1491 and 1448 cm⁻¹, confirming the presence of a low number of strong Brønsted and Lewis acidic sites, in agreement with the studies of BEA and ZSM-5 zeolites [29, 31]. Presence of small amount of strong acidic centers is related to the remaining aluminum (ca. 0.1 wt % of initial Al content) that were not completely removed upon acid nitric treatment [14]. The introduction of copper into SiBEA framework led to the formation of a new type of Lewis acidic centers, confirmed by the appearance of the bands at 1610 and 1450 cm⁻¹, consistent with other reports on copper containing zeolites [32,

33]. Moreover, the introduction of copper decreased the concentration of Brønsted acidic sites, probably due to the exchange of Cu(II) ions with bridging acidic protons (**Table 1**). However, the lower frequencies of the band of pyridine for Cu_{2,0}SiBEA and Cu_{4,0}SiBEA zeolites at 1450 and 1611 cm⁻¹ in comparison to parent BEA zeolite (bands at 1455 and 1622 cm⁻¹) [14], indicate the lower strength of Cu(II) related to Lewis acidic sites that those arising from Al(III) species.

Furthermore, almost the same number of Lewis acidic centers was registered for both Cu_{2,0}SiBEA and Cu_{4,0}SiBEA catalysts, suggesting that only mononuclear copper species possess acidic character in contrast to extra-framework copper species. This conclusion is in line with reports of Cu ion-exchanged zeolites [34, 35].

3.4. Catalytic activity of Cu_xSiBEA zeolites

The performance of the Cu_xSiBEA zeolites differs with reaction temperature, copper loading and the form of copper species present in these catalysts. As was reported earlier in our work [36], SiBEA support exhibited very low activity in NH₃-SCR, with NO conversion lower than 15% in the whole temperature range. The introduction of copper into zeolite structure resulted in a significant increase of NO conversion for all catalysts, indicating that copper species are active sites in NH₃-SCR reaction.

In low temperature range (423 – 573 K) all catalysts showed excellent activity with NO conversion of 90 % (**Fig. 5**). The highest NO conversion – 100 % – was registered for Cu_{7,5}SiBEA zeolite at 523 K. Such remarkable activity at low temperature is not very often reported. Generally, the highest activity of Cu-containing zeolites was observed at moderate temperatures (573 – 673 K) [13, 34]. For Cu_{4,0}SiBEA and Cu_{7,5}SiBEA zeolites after increasing the reaction temperature up to 573 K, NO conversion started to decrease, especially at high temperature range (673 – 773 K) (from ~ 80 % to ~ 10 %). On the other hand,

Cu_{1,0}SiBEA and Cu_{2,0}SiBEA, containing predominantly mononuclear Cu(II) species, stayed much more active, with NO conversion around 50 % at 773 K.

Similar behavior of copper promoted zeolites was observed earlier. Wang et al. [37] and Pereda-Ayo et al. [13] explained the decrease in NO conversion in NH₃-SCR at moderate and high temperatures by oxidation of ammonia with O₂ or the appearance of secondary reaction



They mentioned also that ammonia oxidation was strongly favored by polynuclear copper species, such as copper oxides. These conclusions are consistent with our experimental results.

Figure 6 reveals N₂O formation as a side-product in SCR process. The application of Cu_{4,0}SiBEA catalyst, containing the mixture of framework and extra-framework copper species, and Cu_{7,5}SiBEA catalyst, containing mainly copper oxides, resulted in the formation of large amounts of N₂O in outgases stream, indicating the oxidation of ammonia with gaseous oxygen. However, when Cu_{1,0}SiBEA catalyst was used, a very low formation of N₂O was observed in whole studied temperature range. This unique performance may be related to the presence of predominantly mononuclear Cu(II) species, occurring in the framework of SiBEA zeolite. Our results are in line with the studies on copper exchanged ZSM-5, Beta, SAPO-34 and chabazite zeolites where mononuclear Cu²⁺ ions situated in the exchanged positions were responsible for high NO conversion and N₂ selectivity [12, 13, 33, 37, 38].

In **Figure 7** the N₂ selectivity is given, calculated from NO conversion and N₂O formation according to equation (1). It may be seen that for Cu_{1,0}SiBEA catalyst, N₂ selectivity was the highest of all studied samples and always above 91 %. With the increasing copper content and increasing the reaction temperature, selectivity to N₂ dropped. As may be

expected, the poorest N₂ selectivity (~65 %) was registered for Cu_{7.5}SiBEA catalyst at high temperature range.

In order to discuss catalysts activity as a function of active material loading reaction rates for all studied catalysts per gram Cu were calculated. The results are displayed in **Figure 8**. They clearly show that the most active species in NH₃-SCR are isolated framework Cu(II) species, predominantly present in Cu_{1.0}SiBEA catalyst.

3.5. The influence of SO₂ addition on catalytic activity of Cu_xSiBEA zeolites

Combustion of coal as well as liquid fuels containing sulfur even at low concentration, results in the presence of SO₂ and SO₃ in the exhaust gases. Sulfur oxides may strongly influence catalyst performance in selective catalytic reduction with ammonia [39, 40]. In order to check the resistance of our catalysts towards sulfur poisoning, a new set of catalytic tests with the addition of 500 ppm of SO₂ was carried out (**Fig. 9**).

The presence of sulfur dioxide led to severe decrease in NO conversion at low temperature for both Cu_{1.0}SiBEA and Cu_{4.0}SiBEA catalyst. The NO conversion is low probably due to reaction of sulfur dioxide and copper species and/or the formation of ammonia sulphates. However, when reaction temperature was raised to 623 K a significant increase in NO conversion was observed. Moreover, for Cu_{1.0}SiBEA catalyst activity at 673 – 723 K was very similar to that observed for the test without SO₂. This remarkable activity may be ascribed to the presence of framework mononuclear copper(II) which seen to be more resistant to sulfur contamination than extra-framework polynuclear copper.

4. Conclusions

XRD, TPR and FTIR studies revealed the successful copper incorporation into SiBEA zeolite framework with two-step postsynthesis method for low Cu content (up to 2 wt %). For

the catalysts containing 4 and 7.5 wt % of Cu, a mixture of framework and extra-framework copper species was detected.

Pyridine sorption allowed to establish that the incorporation of copper(II) into zeolite framework led to the formation of new Lewis acidic sites with moderate strength.

The application of Cu_{1.0}SiBEA zeolites with predominantly framework mononuclear copper(II) for selective catalytic reduction with ammonia resulted in high activity in the wide temperature range, with simultaneous N₂ selectivity above 90%.

The formation of N₂O increased with Cu content due to the presence in Cu_xSiBEA zeolites of copper oxides which promote rather ammonia oxidation in moderate and high temperature than NO reduction, leading to poor selectivity to N₂ and low NO conversion.

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Figure captions

Figure 1. XRD patterns of HAIBEA, SiBEA, Cu_{1.0}SiBEA, Cu_{2.0}SiBEA, Cu_{4.0}SiBEA and Cu_{7.5}SiBEA zeolites.

Figure 2. FTIR spectra of SiBEA, Cu_{2.0}SiBEA, Cu_{4.0}SiBEA zeolites.

Figure 3. TPR patterns of C-Cu_{1.0}SiBEA, C-Cu_{2.0}SiBEA, C-Cu_{4.0}SiBEA and C-Cu_{7.5}SiBEA zeolites.

Figure 4. FTIR spectra recorded at room temperature of SiBEA, Cu_{2.0}SiBEA and Cu_{4.0}SiBEA zeolites after adsorption of pyridine (133 Pa) for 1 h at room temperature and desorption at 423 K for 1 h.

Figure 5. NO conversion in SCR of NO with NH₃ on Cu_{1.0}SiBEA, Cu_{2.0}SiBEA, Cu_{4.0}SiBEA and Cu_{7.5}SiBEA zeolite catalysts.

Figure 6. N₂O formation in SCR of NO with NH₃ on Cu_{1.0}SiBEA, Cu_{2.0}SiBEA, Cu_{4.0}SiBEA and Cu_{7.5}SiBEA zeolite catalysts.

Figure 7. N₂ selectivity in SCR of NO with NH₃ on Cu_{1.0}SiBEA, Cu_{2.0}SiBEA, Cu_{4.0}SiBEA and Cu_{7.5}SiBEA zeolites catalysts.

Figure 8. Catalytic activity of Cu_{1.0}SiBEA, Cu_{2.0}SiBEA, Cu_{4.0}SiBEA and Cu_{7.5}SiBEA zeolite catalysts in SCR of NO with NH₃ – Reaction rate per gram of Cu.

Figure 9. NO conversion in SCR of NO with NH₃ on Cu_{1.0}SiBEA and Cu_{4.0}SiBEA zeolite catalysts without and with addition of 500 ppm of SO₂.

Table 1. Amounts of Brønsted and Lewis Acidic Centers on SiBEA, Cu_{2.0}SiBEA and Cu_{4.0}SiBEA.

Sample	Brønsted acidic centers ($\mu\text{mol g}^{-1}$)	Lewis acidic centers ($\mu\text{mol g}^{-1}$)
SiBEA	6	2
Cu _{2.0} SiBEA	3	52
Cu _{4.0} SiBEA	1	50

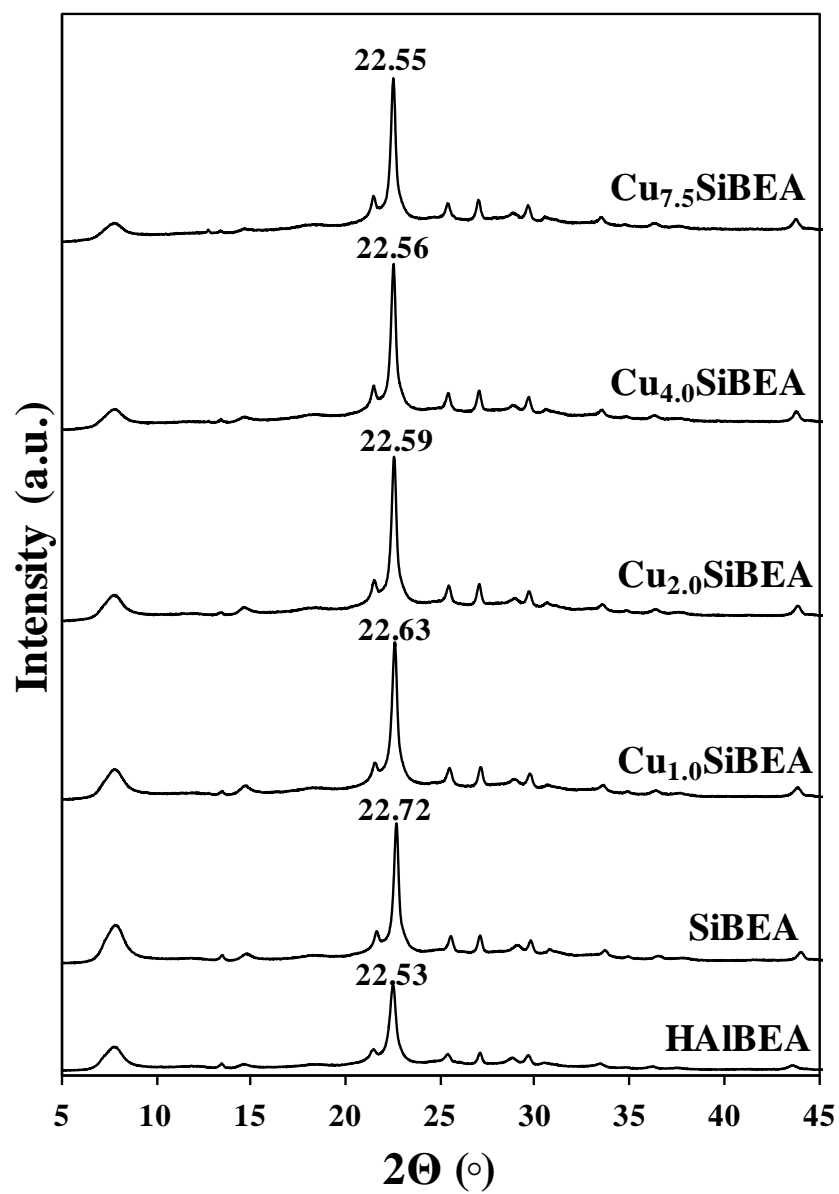


Figure 1

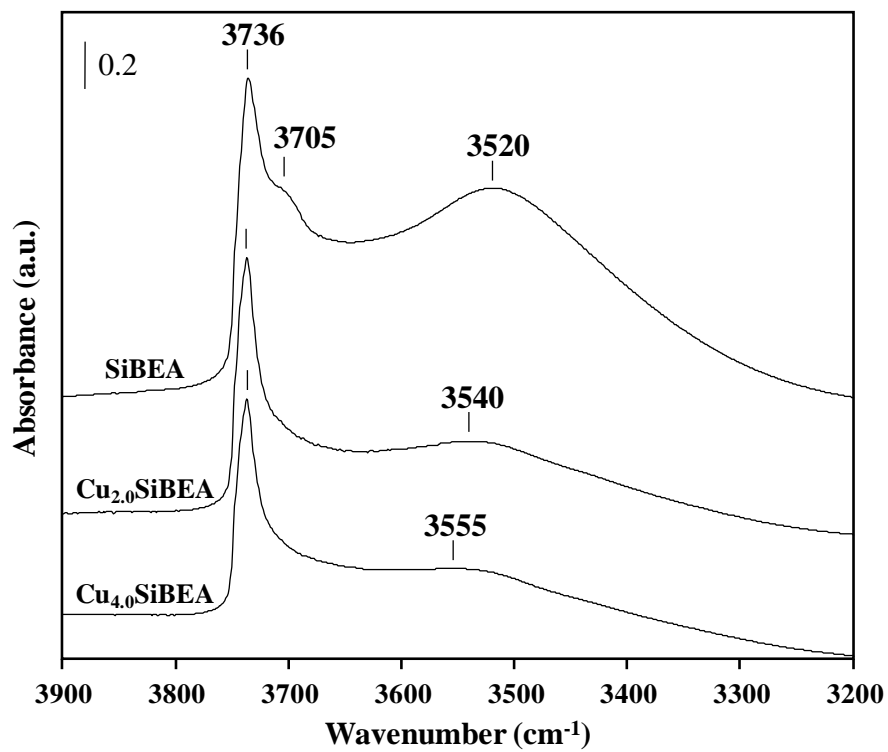


Figure 2

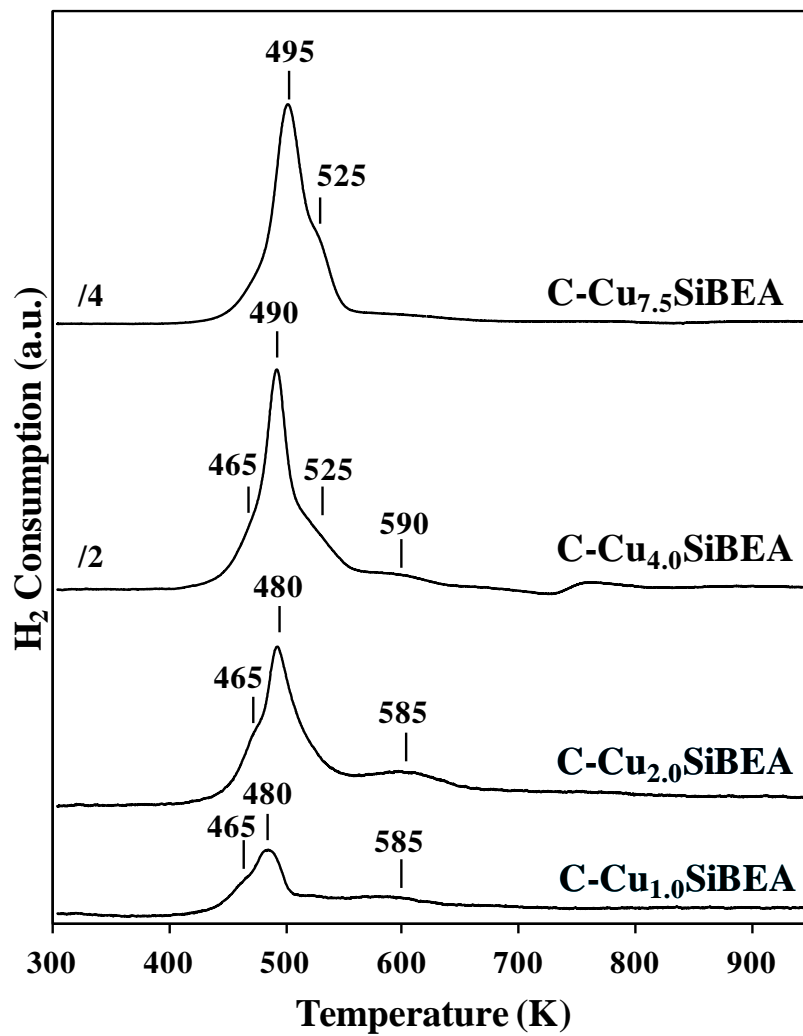


Figure 3

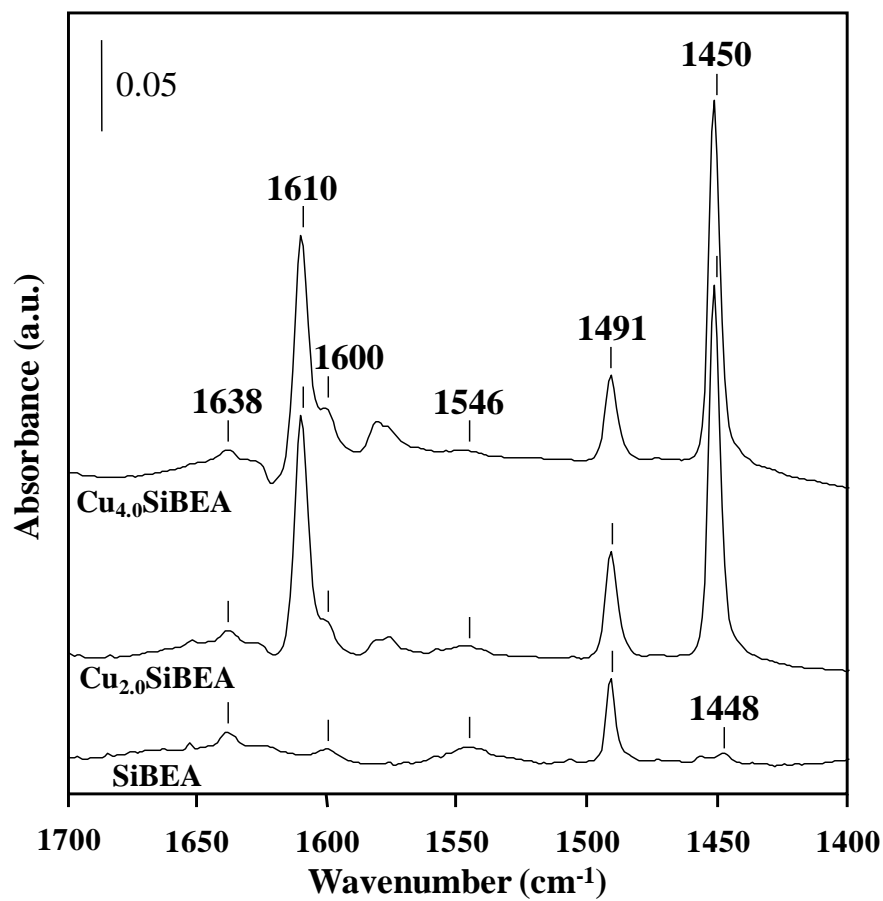


Figure 4

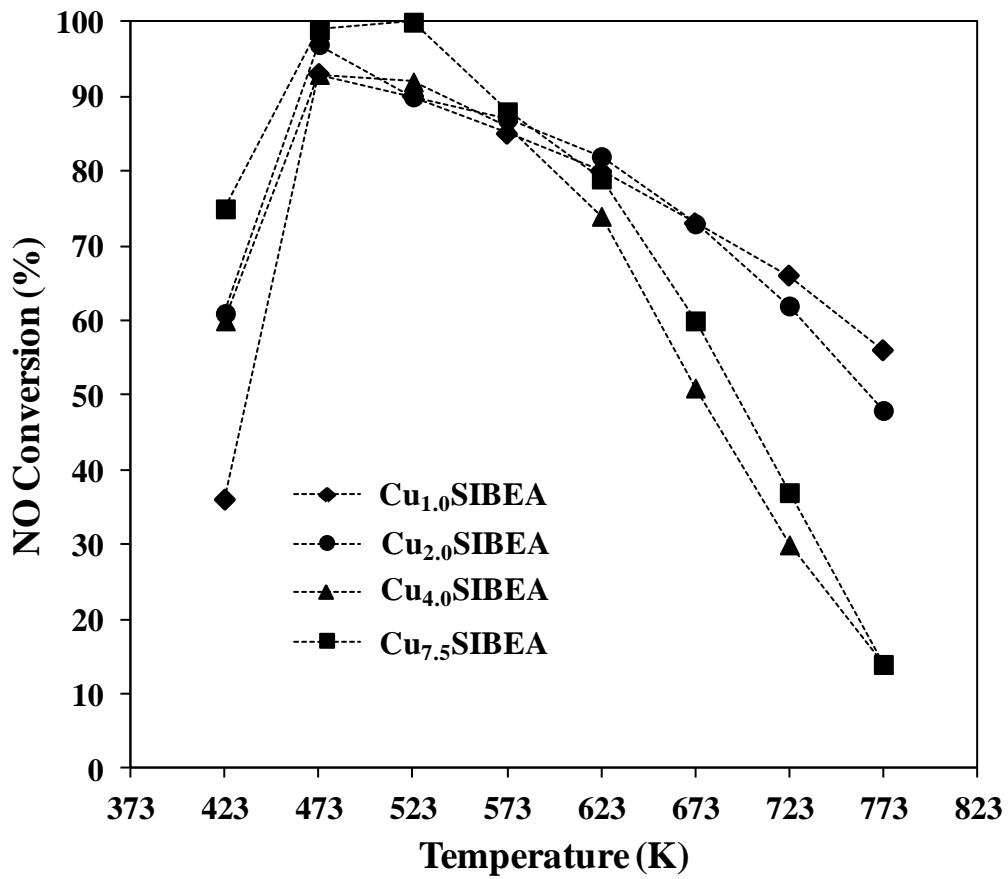


Figure 5

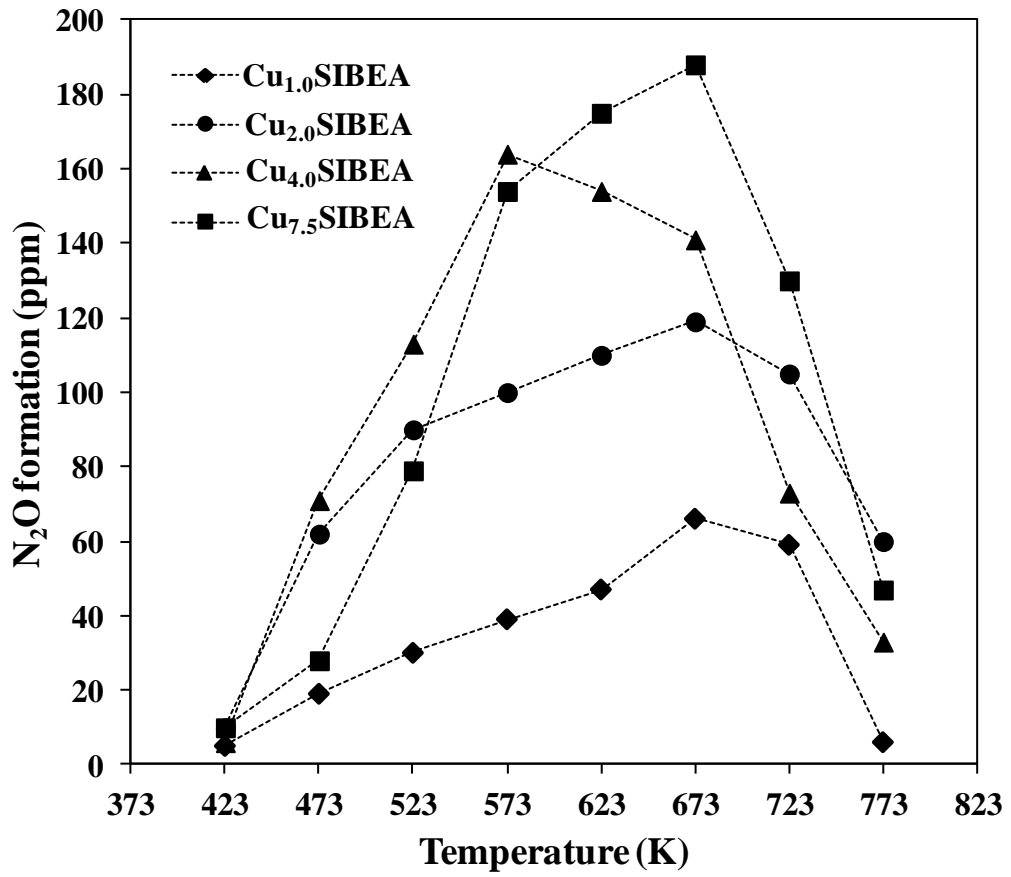


Figure 6

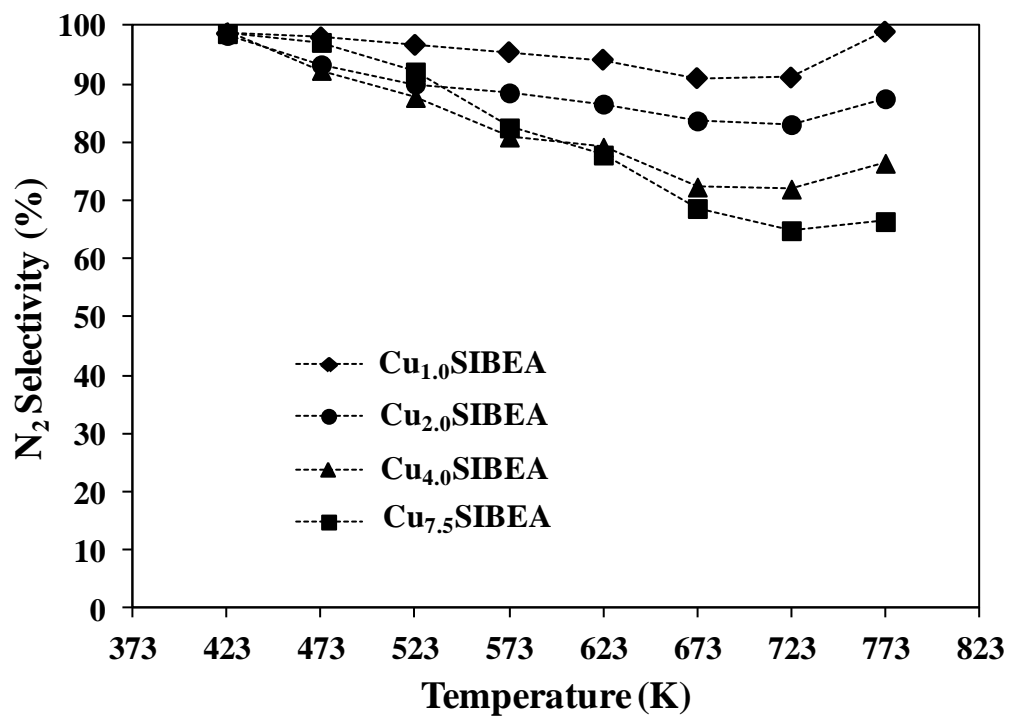


Figure 7

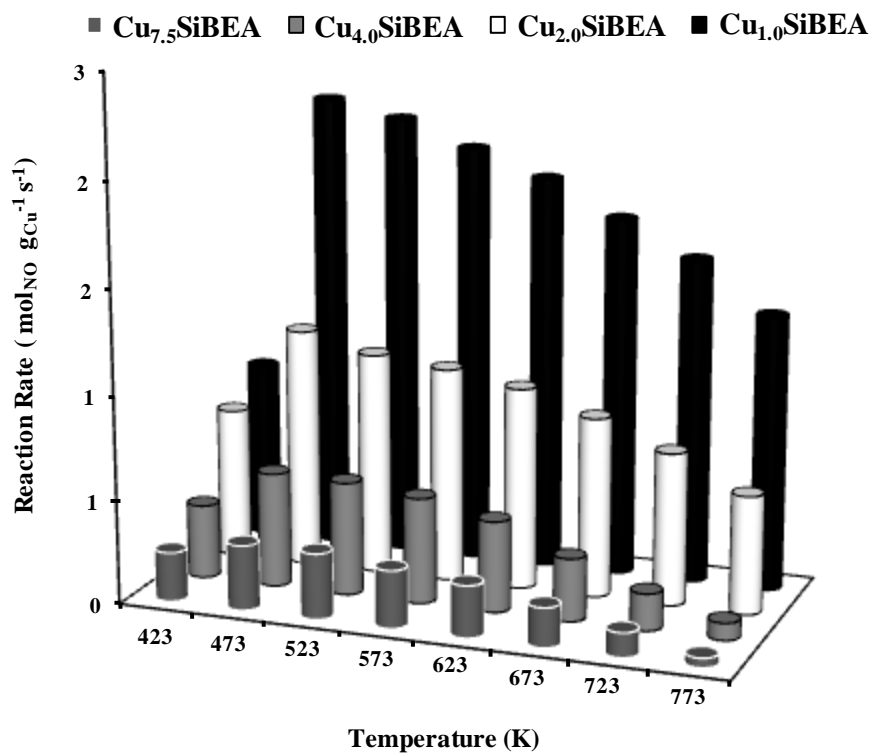


Figure 8

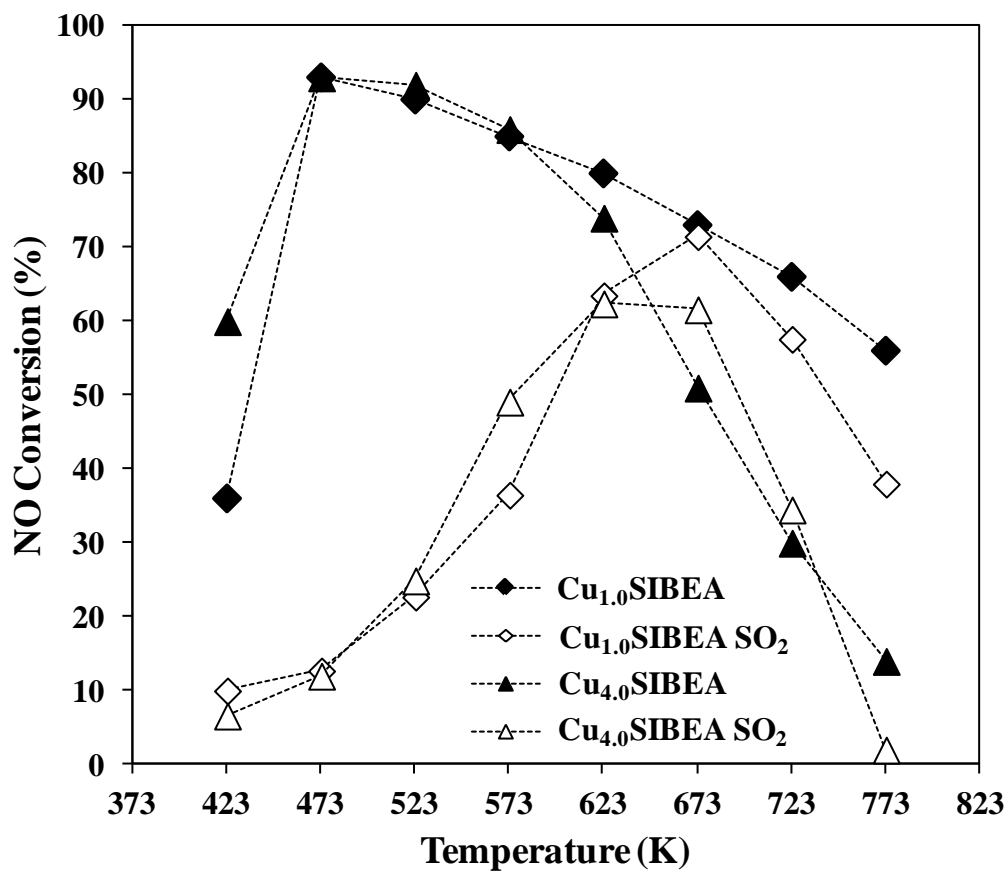


Figure 9