CATALYTIC COMBUSTION OF ACRYLONITRILE OVER CuCeOx-HBETA CATALYSTS

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ABSTRACT

Purpose: Evaluate the acrylonitrile combustion using copper and cerium catalysts supported on BETA zeolite (CuCeOx-HBETA), aiming to reduce the emission of this pollutant in industrial exhaust gases.

Theoretical framework: Acrylonitrile (ACN) is one of the most used monomers in the chemical industry. However, it is a volatile organic compound (VOC) of high toxicity, being present in the exhaust gases of its own production process. In this context, selective catalytic combustion (SCC) stands as a highly promising technology for the removal of ACN in industrial gas effluents.

Method: CuCeOx-HBETA catalysts were prepared by wet impregnation. For characterize the catalysts, the techniques of X-ray diffractometry (XRD), Fourier transform infrared spectroscopy (FTIR) and reduction with hydrogen at programmed temperature (TPR-H₂) were used. Catalytic tests were carried out on ACN combustion by varying the reaction temperature.

Results and conclusion: The characterization results showed that copper and/or cerium oxides are present in the catalysts as nanoparticles. The addition of CeO₂ improved the dispersion and facilitated the reducibility of CuO. The CuCeOx-HBETA catalysts achieved high ACN conversions at temperatures (300-350°C) much lower than traditional thermal combustion (T > 900°C). The greater activity of the catalysts can be attributed to the presence of highly dispersed CuO species and isolated Cu²⁺ ions. The 10Cu10Ce-HBETA catalyst, with a copper/cerium ratio equal to 1, was the most active due to the best synergy between copper and cerium species.

Research implications: The research indicates great potential for the use of CuCeOx-HBETA catalysts in the combustion of ACN.

Originality/value: This study brings new contributions to the research of catalysts to be applied in the catalytic combustion of nitrile compounds.

Keywords: Acrylonitrile, Catalytic Combustion, Catalyst, Copper, Cerium.

COMBUSTÃO CATALÍTICA DE ACRILONITRILA SOBRE CATALISADORES CuCeOx-HBETA

RESUMO

Objetivo: Avaliar a combustão de acrilonitrila usando catalisadores de cobre e cério suportados na zeólita BETA (CuCeOx-HBETA), visando a redução da emissão desse poluente nos gases de exaustão industrial.

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Referencial teórico: A acrilonitrila (ACN) é um dos monômeros mais utilizados na indústria química. No entanto, é também um composto orgânico volátil (COV) de elevada toxicidade, estando presente nos gases de exaustão de seu próprio processo de produção. Nesse contexto, a combustão catalítica seletiva (CCS) destaca-se como uma tecnologia altamente promissora para a remoção de ACN em efluentes gasosos industriais.

Metodologia: Os catalisadores CuCeOx-HBETA foram preparados por impregnação úmida. Na caracterização dos catalisadores foram utilizadas as técnicas de difratometria de raios X (DRX), espectroscopia no infravermelho por transformada de Fourier (FTIR) e redução com hidrogênio à temperatura programada (RTP-H2). Os ensaios catalíticos foram realizados na combustão de ACN variando a temperatura de reação.

Resultados e conclusão: Os resultados de caracterização mostraram que os óxidos de cobre e/ou cério estão presentes nos catalisadores como nanopartículas. A adição de CeO2 melhorou a dispersão e facilitou a redutibilidade de CuO. Os catalisadores CuCeOx-HBETA atingiram altas conversões de ACN em temperaturas (300-350°C) muito mais baixas que a tradicional combustão térmica (T > 900°C). A maior atividade dos catalisadores pode ser atribuída à presença das espécies de CuO altamente dispersas e íons Cu2+ isolados. O catalisador 10Cu10Ce-HBETA, com razão cobre/cério igual a 1, foi o mais ativo devido à melhor sinergia entre as espécies de cobre e cério.

Implicações da pesquisa: A pesquisa indica grande potencial do uso de catalisadores CuCeOx-HBETA na combustão de ACN.

Originalidade/valor: Esse estudo traz novas contribuições para a pesquisa de catalisadores a serem aplicados na combustão catalítica de compostos nitrílicos.

Palavras-chave: Acrilonitrila, Combustão Catalítica, Catalisador, Cobre, Cério.

1 INTRODUCTION

The rapid social and economic development of the communities has led to the growing attention of the theme of environmental protection, especially to the reduction of the emission of toxic air pollutants. Currently, in many countries, several actions aimed at controlling air pollution have been implemented, including the creation and revision of environmental legislation regarding pollutant emission limits (Shaddick et al., 2020; Zhang et al., 2016). Among the pollutants, one can highlight the volatile organic compounds (VOCs), which include a wide range of chemical compounds. The vast majority of VOCs are toxic and impair air air quality when released into the atmosphere. The main sources of emissions of VOCs are anthropic (chemical industries, power plants and vehicle emissions, for example) and require appropriate treatment (Guo et al., 2021).

Acrylonitrile, as well as other nitrile compounds (acetonitrile and hydrocyanic acid), is part of the VOC family and is highly toxic to humans and animals. Acrylonitrile is released into the atmosphere during its own industrial production process and is carried away in the exhaust gases. The most widely used method by industry for the abatement of acrylonitrile emission is traditional thermal combustion (or incineration). However, thermal combustion has negative aspects, such as the need for high temperatures in the incinerator (T > 900°C), which means costly high fuel consumption. In addition, large amounts of nitrogen oxides (NOx) are generated by this method, resulting in secondary pollution (Liu et al., 2019; Zhang et al., 2015). The danger of acrylonitrile and of secondary pollutants generated in the traditional treatment of thermal combustion makes it necessary to search for more efficient treatments. As an alternative, selective catalytic combustion of acrylonitrile (CCS-ACN) is interesting due to the
lower reaction temperature associated with higher selectivity to harmless products (N₂, H₂O and CO₂). However, the challenge in CCS-ACN is to find the most active and highly selective catalyst for harmless products (Wei et al., 2021).

In this context, this study aimed to prepare and evaluate the performance of CuCeOx-HBETA catalysts in the catalytic combustion of acrylonitrile in order to identify the most active catalyst for the reaction. The chemical composition of the catalyst was modified by the proportion of copper and cerium. To contribute to the interpretation of the results, the techniques of X-ray diffractometry (DRX), Fourier transform infrared spectroscopy (FTIR) and reduction with hydrogen at the programmed temperature (RTP-H₂) were used.

2 THEORETICAL FRAME

The catalysts investigated in the catalytic combustion of acrylonitrile can be grouped into supported noble metals, transition metal oxides and transition metal-modified zeolites. In general, noble metal catalysts supported are those that exhibit the best activity in this reaction. However, the selectivity of N₂ has not been satisfactory when this type of catalyst is used, resulting in NOx formation (Zhao et al., 2006; Hung; Chu, 2006; Zhang et al., 2021). The high cost of noble metals is another factor limiting the practical application of these materials (Zhang et al., 2014).

Several transition metal oxides have been reported to be highly active in the catalytic combustion of acrylonitrile. Despite this, NOx formation at higher temperatures is a common problem, especially when these oxides are used in mass form, i.e. in the absence of a suitable support (Nanba et al., 2004; Hu et al., 2018). On the other hand, zeolytic catalysts modified with transition metals, especially copper, have received great attention for their good activity and selectivity at N₂ (Zhang et al., 2016; Liu et al., 2017).

Nanba and colleagues (2004) were the pioneers to observe that the Cu/HZSM-5 catalyst (copper-modified HZSM-5 zeolite) completely coverted acrylonitrile with 80% selectivity at N₂ at temperatures above 350°C. These results were attributed to the presence of species of Cu²⁺ isolated. Liu and collaborators (2019) prepared a series of catalysts based on copper-modified microporous zeolites (ZSM-5, BETA, MCM-22, MCM-49 and Y). The catalysts showed high conversions of acrylonitrile and selectivity to N₂. Recently, Cu-BETA has shown high activity and high yield to N₂ in the combustion of acetonitrile. The easy reducibility of highly dispersed copper species and the small crystalline size of CuO particles played key roles in the reaction (Ponciano & Batista, 2022). Zeolite BETA is a good candidate for catalyst support due to its wide pore opening, high specific area and three-dimensional channel system, and few studies are found using this zeolite

The addition of cerium to copper-containing zeolite catalysts may result in an improvement in the catalytic activity of these materials (Cao et al., 2015; DU et al., 2019; Wang et al., 2020). Du and collaborators (2019), for example, noted that doping Cu-ZSM-5 with cerium improved the catalyst performance in the selective catalytic combustion of acrylonitrile, due to the improvement in copper reducibility and also by the introduction of active oxygen species by CeO₂. Wang and collaborators (2020) prepared CuCeOx-HZSM-5 catalysts, which were used in the combustion of acetonitrile. Such catalysts exhibited excellent activity (95% CH₃CN conversion at 225°C). In the same direction, Zhang and colleagues (2022) observed that the addition of cerium in Cu-ZSM-5 catalysts effectively improved the mineralization rate of acetonitrile and selectivity of N₂. However, the number of researches with copper-cerium catalysts in the catalytic combustion of acrylonitrile, mainly supported in zeolite BETA, is still rare.

In this context, this work aims to contribute to the study of acrylonitrile combustion on copper-cerium catalysts supported in zeolite BETA (CuCeOx-HBETA). The CuO-CeO₂ ratio
will be varied in order to find the ideal composition of the catalyst that presents high conversion for the combustion of acrylonitrile.

3 METHODOLOGY

3.1 Preparation of catalysts

CuCeOx-HBETA catalysts have been prepared via wet impregnation using commercial NH₄-BETA zeolite (TRICAT, SiO₂/Al₂O₃), copper II nitrate and ammoniacal cerium IV nitrate. The salts were dissolved in distilled water and zeolite BETA was added under agitation for 10 h. The water was evaporated by heating, the solid dried in an oven at 120°C, and then calcined in a muffle furnace at 600°C for 2 hours. Zeolite NH₄-BETA has been calcined under the same conditions to obtain the HBETA sample.

Catalysts have been prepared with 20% m/m of total oxide on the zeolite BETA, namely: 20Cu-HBETA, 15Cu5Ce-HBETA, 10Cu10Ce-HBETA, 5Cu15Ce-HBETA and 20Ce-HBETA.

3.2 Characterization of catalysts

The catalysts were characterized by the techniques of X-ray diffractometry (DRX), Fourier transform infrared spectroscopy in total attenuated reflectance mode (ATR-FTIR) and hydrogen reduction at the programmed temperature (RTP-H₂).

The DRX analysis was performed on a Philips-PANalytical PW 1710 diffractometer operating with CuKa radiation (0.15406 nm) at a voltage of 35 kV and current of 50 mA. The speed used on the goniometer was 0.06º(2θ). min⁻¹ with angle range of 3.03 to 89.91° (2θ). The average size of crystallites was calculated by Scherrer's Equation (Equation 1), considering the highest intensity peaks of each crystalline phase.

\[
t = \frac{k\lambda}{\beta \cos \theta}
\]

Where:

- \( \beta \) = width measured at half the height of the highest peak intensity;
- \( k \) = proportionality constant. A spherical geometry with a value of 0.9 was allowed;
- \( \lambda \) = X-ray wavelength (\( \lambda = 0.15406 \) nm);
- \( \theta \) = angle of the largest peak in the diffractogram.

ATR-FTIR analyzes were done on a Bruker Alpha-P instrument equipped with a 4 mm² diamond ATR crystal window. The samples were analyzed as powder and previously dried in the air at 90 oC for 24 hours. The spectra were obtained in the spectral range of 4000 cm⁻¹ to 360 cm⁻¹ with a resolution of 4 cm-14 and 128 scans.

For the RTP-H₂ technique, a Micromeritics AutoChem II 2920 was used. Initially, a sample (50 mg) of the catalyst was inserted into a quartz reactor of type U. This was heated to 550 °C at a heating rate of 10 °C.min⁻¹, under synthetic air flow (30 mL.min⁻¹). Upon reaching the temperature, the material was kept in these conditions for 60 min and, after this period, cooled down to 50°C under a flow of He (30 mL.min⁻¹) as a drag gas. Finally, the material was heated to 950°C (10°C.min⁻¹) at a flow rate of 20 mL.min⁻¹ of a mixture of 10% H 24/N24 (v/v). A thermal conductivity detector was used to monitor the hydrogen concentration. The degree of reduction of metal species supported in zeolite was determined by Equation 2.
3.3 Catalytic Testing

The catalytic tests were conducted in a gas phase using a U-type reactor embedded with quartz wool and 50 mg catalyst. The reactor was fed a 50 mL min\(^{-1}\) continuous flow of a mixture containing 2.8\% v/v acrylonitrile in synthetic air. The reactor was operated at atmospheric pressure and the reaction temperature varied from 100\(^{\circ}\)C to 600\(^{\circ}\)C. The reactor was coupled in line with a mass spectrometer of the Pfeiffer Vacuum company's Thermo Star GSD 320 T model for analyzing the effluent from the reaction. The conversion (X) of acrylonitrile (ACN) was calculated using Equation 3.

\[
X (\%) = \left( \frac{\text{ACN(entera)} - \text{ACN(sai)}}{\text{ACN(entera)}} \right) \times 100
\]  

4 RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffractometry results of the CuCeOx-HBETA catalysts. The diffraction peaks at 20 = 7.6\(^{\circ}\) and 22.3\(^{\circ}\), characteristic of zeolite BETA (PDF#48-0074), are present in all diffraction charts. This indicates that the incorporation of copper and/or cerium oxides by the wet impregnation method did not alter the crystalline structure of zeolite BETA. However, comparing the diffractograms of the CuCeOx-HBETA catalysts with the HBETA diffraction shows a reduction in zeolite peak intensity probably caused by the reduction of zeolite mass in the catalyst (80\% m/m) and/or absorption of X-rays by oxides in the catalysts (WEI et al., 2021; CHOWDHURY & BHATTACHARYYA, 2019).

![Figure 1. X-ray diffratograms of CuCeOx-HBETA catalysts.](image-url)
The diffraction peaks located at 2θ = 35.6° and 38.9° are characteristic of CuO (PDF#48-1548) (Siddiqui al., 2018). These peaks can be clearly observed in the diffraction charts of the 20Cu-HBETA, 15Cu5Ce-HBETA and 10Cu10Ce-HBETA catalysts. A downward trend in intensity of these peaks can be observed with the reduction of the CuO content in the catalyst. On the other hand, no CuO peaks were observed in the 5Cu15Ce-HBETA diffraction. According to Lee et al. (2019), for copper contents of 5% or less by mass, there are generally no characteristic peaks of CuO when these species are present in the form of well-dispersed nanoparticles, which would be the case for the 5Cu15Ce-HBETA catalyst.

In Figure 1, the cubic phase of CeO₂ shows characteristic diffraction peaks at 2θ = 28.68°; 33.08°; 47.83° and 56.78° (PDF#34-0394) (LÓPEZ et al., 2015). The presence of CeO₂ peaks was observed in the diffractograms of all cerium-containing catalysts (20Ce-HBETA, 5Cu15Ce-HBETA, 10Cu10Ce-HBETA and 15Cu5Ce-HBETA). It is noted that the intensity of the CeO₂ peaks decreases with the reduction of the cerium content.

The catalyst performance may be influenced by the size of the crystalline. In general, catalysts with smaller crystallite sizes tend to have higher catalytic activity, due to the easier access of the reagents to the active sites (Vicente et al., 2016). Table 1 shows the average sizes of crystallites of copper and cerium oxides impregnated in the CuCeOx-HBETA catalysts and also in the zeolite HBETA. In this table it can be observed that the oxides of copper and cerium present in the catalysts, as well as the zeolitic phase HBETA, are nanocrystalline materials. CeO₂ showed nanocrystal sizes between 5.7 and 8.0 nm. It is noted that there was an increase in the size of CeO₂ crystalline with the increase in the cerium content, probably due to the agglomeration process (CALDAS, 2013). CuO had average crystal sizes close to 20 nm.

### Table 1. Average size of the crystallites of the CuCeOx-HBETA catalysts and the HBETA sample.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Crystalline phase</th>
<th>Crystalline size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20Ec-HBETA</td>
<td>EcO₂</td>
<td>8.0</td>
</tr>
<tr>
<td>5Cu15Ce-HBETA</td>
<td>EcO₂, CuO</td>
<td>6.5, *NA</td>
</tr>
<tr>
<td>10Cu10Ce-HBETA</td>
<td>EcO₂, CuO</td>
<td>6.4, 19.8</td>
</tr>
<tr>
<td>15Cu5Ce-HBETA</td>
<td>EcO₂, CuO</td>
<td>5.7, 19.8</td>
</tr>
<tr>
<td>20Cu-HBETA</td>
<td>CuO</td>
<td>19.5</td>
</tr>
<tr>
<td>HBETA</td>
<td>Zeolite BETA</td>
<td>21.3</td>
</tr>
</tbody>
</table>

*ND = Not detected by DRX.

**Source:** Author himself

Figure 2 shows the infrared spectra of the CuCeOx-HBETA catalysts. The band at 1230 cm⁻¹ is related to the vibrations of asymmetric stretching between tetrahedra T O₄ (T = Si, Al). Around 1072 cm⁻¹, one has the most intense band, referring to the vibrations of asymmetric stretching of the T-O bonds. The band at 792 cm⁻¹, in turn, corresponds to the symmetrical stretch vibration of the Si-O-Si bond. Bands at 520 and 570 cm⁻¹ are typical of the five-member rings of the zeolite BETA and are related to T-O-T vibration. Finally, the band at 420 cm⁻¹ corresponding to the angular deformation of the T-O-T bond (Boroń et al., 2014; Kim et al., 2013; Pereira et al., 2011; Do Nascimento et al., 2017; Tomlinson, et al., 2013; Kweon et al., 2022). These bands are characteristic of zeolite BETA and appear in the spectra of all samples. This indicates that the zeolitic structure was preserved after the impregnation of the copper and cerium oxides and the heat treatment (calcination), corroborating with the results of DRX.
The vibration in the range 1750-1550 cm\(^{-1}\) is attributed to the flexion of H-O-H bonds, due to the molecules of H\(_2\)O adsorbed on the surface of catalysts (Boroń et al., 2014; Do Nascimento et al., 2017; Hao et al., 2015). The bands between 3750-3000 cm\(^{-1}\) are related to the stretching of O-H bonds of hydroxyl groups. These may be associated with silanol groups, hydrated aluminum silicates, or also H\(_2\)O molecules adsorbed (Hadjivanov, 2014; Vimont, Thibault-starzyk, Lavalley, 2000). Within this region of the spectrum, bands between 3600 and 3650 cm\(^{-1}\) are characteristic of Bronsted acidity (Si-OH-Al) (Auerbach, Carrado, Dutta, 2003).

Bands of around 487 and 601 cm\(^{-1}\) can be attributed to the vibrations of the Cu(II)-O bonds (Radhakrishnan & Beena, 2014; Benhammada & Trache, 2022). The band referring to the Ce-O stretch vibration occurs around 555 cm\(^{-1}\) (Culica et al., 2020; Khan et al., 2013). However, in Figure 2 it was not possible to clearly identify the presence of these bands, characteristics of the oxides CuO and CeO\(_2\). This is possibly due to the fact that these bands coincide with the region of the bands referring to the T-O-T bonds of zeolite, which make up the major part of the catalysts (about 80% m/m). However, the formation of copper and cerium oxides was confirmed by DRX analysis.

Figure 3 shows the hydrogen reduction profiles of the CuCeOx-HBETA catalysts. The 20Cu-HBETA catalyst had three superimposed reduction peaks at 236°C (peak \(\alpha\)), 278°C (peak \(\beta\)) and 315°C (peak \(\gamma\)). The \(\alpha\) peak was attributed to the reduction of finely dispersed CuO in the support and also to the reduction of isolated cations of Cu\(^{2+}\) in Cu+, compensating for the load in the zeolite BETA (Nanba et al., 2005). The peaks \(\beta\) and \(\gamma\) can be associated with CuO in medium and large size particles, respectively. It is also possible that part of the H\(_2\) consumption at peak \(\beta\) is related to the reduction of Cu\(^{1+}\) cations in Cu00, considering that the reduction of Cu2+isolated cations occurs in two steps.
Figure 3. RTP-H$_2$ profiles of CuCeOx-HBETA catalysts.

Source: Author himself

The reduction profile of 20Ce-HBETA showed three low intensity peaks (427°C, 542°C and 725°C), revealing that the consumption of hydrogen on the supported cerium was substantially lower than that of the copper species. Reduction peaks below 560 °C are related to the reduction of oxygen anions present in the surface layers of the ceria. Above this temperature, there is the reduction of structural oxygen, belonging to the CeO$_2$ mass (Andreeva et al., 2002; Zhu et al., 2004; Gołąbek et al., 2019). Therefore, the first two peaks (427 °C and 542 °C) are probably related to the reduction of surface ceria, while the widest peak, centered at 725 °C, is associated with the reduction of bulk ceria. There is also a peak around 237 °C, which was also observed in the reduction profile of the HBETA support. In principle, zeolites should not show reduction peaks because they do not have reducible species. Thus, this peak may be related to some impurity in HBETA.

In the reduction profiles of 15Cu5Ce-HBETA, 10Cu10Ce-HBETA and 5Cu15Ce-HBETA, the disappearance of peak γ and a gradual reduction of peak β as the copper content is reduced, while peak α remains high. These results are consistent with the information obtained by DRX and indicate that the presence of CeO$_2$ contributed to the improvement of CuO dispersion (Fei et al., 2014; Zheng et al., 2020). Another observed fact was the displacement of the α peak to lower temperatures in the bimetallic catalysts. Although it was not a very expressive shift, such a result suggests that the introduction of CeO$_2$ improved the reducibility of CuO. Several studies have reported that the CeO$_2$-CuO interaction promotes the reducibility of CuO species, especially those highly dispersed (Caputo et al., 2008; He et al., 2014; Zhang et al., 2022).

Quantitative results of H$_2$ consumption in the decomposition of the α, β and γ peaks are shown in Table 2. The data obtained show that the total consumption of H$_2$ on materials is directly proportional to the content of impregnated copper. However, the distribution of copper species varies, and the formation of finely dispersed CuO and isolated Cu$^{2+}$ cations is favored by the reduction of copper content and presence of CeO$_2$. 
Table 2. Quantitative analysis of hydrogen consumption on CuCeOx-HBETA catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Peak α Temp (°C)</th>
<th>Consumption H₂ (μmol)</th>
<th>Peak β Temp (°C)</th>
<th>Consumption H₂ (μmol)</th>
<th>Peak γ Temp (°C)</th>
<th>Consumption H₂ (μmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20Cu-HBETA</td>
<td>248</td>
<td>59.60</td>
<td>274</td>
<td>18.46</td>
<td>309</td>
<td>44.79</td>
</tr>
<tr>
<td>15Cu5Ce-HBETA</td>
<td>240</td>
<td>58.57</td>
<td>281</td>
<td>28.35</td>
<td>___</td>
<td>___</td>
</tr>
<tr>
<td>10Cu10Ce-HBETA</td>
<td>228</td>
<td>52.77</td>
<td>277</td>
<td>7.33</td>
<td>___</td>
<td>___</td>
</tr>
<tr>
<td>5Cu15Ce-HBETA</td>
<td>218</td>
<td>25.29</td>
<td>233</td>
<td>2.79</td>
<td>___</td>
<td>___</td>
</tr>
</tbody>
</table>

Source: Author himself

Table 3 shows the degree of reduction of the copper species of the CuCeOx-HBETA catalysts. The results show that the Cu²⁺ cations (isolated or present in CuO) showed a high degree of reduction (close to 100%), suggesting that the copper atoms in the CuCeOx-HBETA catalysts are easily accessible to the H₂ reducing molecules. Accessibility to sites is an important parameter for the good performance of the catalyst.

Table 3. Degree of reduction of copper species in CuCeOx-HBETA catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Theoretical H₂ consumption (μmol)</th>
<th>Actual H₂ consumption (μmol)</th>
<th>Degree of reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20Cu-HBETA</td>
<td>125.79</td>
<td>122.85</td>
<td>97.67</td>
</tr>
<tr>
<td>15Cu5Ce-HBETA</td>
<td>94.34</td>
<td>86.92</td>
<td>92.14</td>
</tr>
<tr>
<td>10Cu10Ce-HBETA</td>
<td>62.89</td>
<td>60.09</td>
<td>95.55</td>
</tr>
<tr>
<td>5Cu15Ce-HBETA</td>
<td>31.45</td>
<td>28.09</td>
<td>89.32</td>
</tr>
</tbody>
</table>

Source: Author himself

Figure 4 shows the results of the combustion of acrylonitrile on the CuCeOx-HBETA catalysts. It can be observed that all catalysts showed activity in the combustion reaction of acrylonitrile and, with the exception of HBETA, achieved high conversions between 300-350 °C. It is worth noting that this temperature range is much lower in relation to the temperatures required for thermal combustion (T > 900°C). As can be seen in Figure 4, the conversion of acrylonitrile to HBETA starts around 500°C and does not exceed 45% at 600°C. This result is substantially lower than the other catalysts, showing that the presence of copper oxide and/or cerium supported in the zeolite HBETA was fundamental for the improvement of activity.

To establish the order of activity of the catalysts, the initial conversion temperatures (T₀) and the temperatures for 90% conversion of acrylonitrile (T₉₀) were analyzed. By this criterion, the lower the temperatures T₀ and T₉₀, the greater the catalyst activity. Table 4 shows temperatures T₀ and T₉₀ for CuCeOx-HBETA catalysts. Note the following descending order of activity: 10Cu10Ce-HBETA > 20Cu-HBETA > 15Cu5Ce-HBETA > 20Ce-HBETA ≈ 5Cu15Ce-HBETA > HBETA.
Comparing the temperatures $T_0$ and $T_{90}$ of the 20Cu-HBETA and 20Ce-HBETA catalysts, the activity of 20Cu-HBETA was found to be higher. Thus, it can be inferred that the copper species were the most relevant active sites for the combustion reaction of acrylonitrile, even though they were larger in size than crystallites. The highly dispersed CuO species and the isolated Cu$^{2+}$ ions are those that contribute most to the catalyst activity in the combustion of acrylonitrile. This hypothesis is in line with recent literature work (Zhang et al., 2021; Zhang et al., 2022). It is worth highlighting that the low activity of the 20Ce-HBETA catalyst may be related to the interaction of CeO$_2$ with the structure of the zeolite BETA. According to Couto (2022), CeO$_2$ interacts strongly with zeolite BETA, which leads to reduction of its redox capacity. The results of RTP-H$_2$ (Figure 3) revealed low reducibility of 20Ce-HBETA compared to copper-containing catalysts.

The 10Cu10Ce-HBETA catalyst was the most active. The results suggest that the ratio of 1:1 copper to cerium can potentiate the interaction between CuO and CeO$_2$, thus favoring reducibility and CuO activity in acrylonitrile combustion.

**5 CONCLUSION**

This work evaluated the performance of CuCeOx-HBETA catalysts in the combustion reaction of acrylonitrile. According to the DRX results, copper and/or cerium oxides are present in the catalysts as nanoparticles. CeO$_2$ had smaller nanocrystal sizes (5.7-8.0 nm) than CuO nanocrystals (~20 nm). In the FTIR analyzes, the CuCeOx-HBETA catalyst spectra and the HBETA spectra were found to be very similar. These results showed that the structure of...
the zeolite BETA was preserved after the wet impregnation and heat treatment process, corroborating with the results of DRX. Results of RTP-H$_2$ showed that CuO dispersion and reducibility were improved due to the presence of CeO$_2$.

The catalytic tests showed that the CuCeOx-HBETA catalysts achieved high conversions between 300-350°C, being much lower in relation to the temperatures required for thermal combustion (T > 900°C). The increased activity of catalysts can be attributed to the presence of highly dispersed CuO species and Cu$^{2+}$ ions isolated. The 10Cu10Ce-HBETA catalyst was the most active, suggesting that the interaction between copper and cerium species in this proportion can effectively contribute to the improvement of acrylonitrile conversion at low temperatures.

REFERENCES


Catalytic Combustion of Acrylonitrile over CuCeOx-HBETA Catalysts


He, C., Yu, Y., Yue, L., Qiao, N., Li, J., Shen, Q., ... & Hao, Z. (2014). Low-temperature removal of toluene and propanal over highly active mesoporous CuCeOx catalysts synthesized via a simple self-precipitation protocol. Applied Catalysis B: Environmental, 147, 156-166.


Shaddick, G., Thomas, M. L., Mudu, P., Ruggeri, G. & Gumy, S. (2020). Half the world’s population are exposed to increasing air pollution. NPJ Climate and Atmospheric Science, 3(1), 23.


