Short communication

New use for succinylated sugarcane bagasse containing adsorbed Cu$^{2+}$ and Ni$^{2+}$: Efficient catalysts for gas-phase $n$-hexane and $n$-heptane oxidation reactions

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A B S T R A C T

This study describes the use of succinylated twice-mercerized sugarcane bagasse containing adsorbed Cu$^{2+}$ or Ni$^{2+}$ ions from spiked aqueous solutions (2MSBA-Cu and 2MSBA-Ni) as heterogeneous catalysts for the catalytic oxidation of $n$-hexane and $n$-heptane in gas phase. To the best of our knowledge, this is the first study in which a spent adsorbent material based on lignocellulose biomass is used in the catalytic oxidation of volatile organic compounds. The adsorbent and spent adsorbent materials were characterized by FTIR, TGA and XRD. The amount of Cu$^{2+}$ and Ni$^{2+}$ adsorbed on 2MSBA was 0.49 and 2.49 mmol g$^{-1}$, respectively. The catalysts were active for total oxidation of $n$-hexane and $n$-heptane, even at low temperatures. 2MSBA-Cu exhibited higher catalytic activity than 2MSBA-Ni and surprisingly their performances were comparable or superior to those of some catalysts reported in the literature, including noble metal-based catalysts.

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1. Introduction

In recent years, agricultural by-products such as sugarcane bagasse have received much attention because they are available in large amounts at a low cost in various countries around the world (Ramos et al., 2015). Various studies have reported the use of raw lignocellulose materials or chemically modified lignocellulose materials for treatment of wastewaters produced by various industries (Ahmaruzzaman, 2011; Salman et al., 2015). However, when the adsorbents loaded with metal ions do not exhibit a good desorption capacity to be reused in the treatment process, they have to be disposed as hazardous solid wastes. In this sense, adsorption only involves the problem of transferring pollutants from an aqueous phase to a solid phase through immobilization (Ramos et al., 2015; Teodoro et al., 2016). Thus, adsorption as a wastewater treatment technique only partially solves the problem of pollution of water bodies with toxic metal ions, representing a loss of potential of the adsorbent materials.

For example, spent adsorbent materials used in the treatment of aqueous solutions containing transition metals such as chromium(III) and cobalt(II) were used as heterogeneous catalysts in catalytic oxidation of terpenes by da Silva et al. (2013), and presented higher conversions in comparison to classic catalysts composed of inorganic materials. Therefore, this is a simple example of how spent adsorbent materials can be reused in other applications instead of being discarded, which adds value to these solid residues and improves the economic feasibility of the process (da Silva et al., 2013; Ramos et al., 2015 Ramos et al., 2015).

In this context, the present study aimed to evaluate the use of an important agricultural by-product, i.e. sugarcane bagasse, modified with succinic anhydride and loaded with copper(II) and nickel(II), as heterogenous catalysts for the removal of model volatile organic compounds ($n$-hexane and $n$-heptane) through oxidation in gas phase. Volatile organic compounds are highly toxic contaminants which can be harmful to human health and the environment. Among the various removal techniques, catalytic oxidation is one...
of the most promising due to advantages such as high degradation efficiency, low operating temperature and no secondary pollution (Huang et al., 2015; Kamal et al., 2016; Rusu and Dumitriu, 2003).

2. Material and methods

2.1. Chemicals

Succinic anhydride, pyridine, n-hexane, n-heptane and CuSO₄·5H₂O were purchased from Vetec (Brazil), NiCl₂·6H₂O, NaOH, CH₃Cl₂, CH₃COOH (99.5%), CaCl₂, NaHCO₃ were purchased from Synth (Brazil). Quantitative filter paper (black ribbon, JP-41) was purchased from JProtab (Brazil). Sugarcane bagasse stalks were collected at Ouro Preto, Minas Gerais, Brazil.

2.2. Catalyst preparation

Raw sugarcane bagasse (SB) was milled using a tungsten ring mill and the fraction retained on a 200-mesh screen (0.075 mm) was extracted in a Soxhlet apparatus with hexane-ethanol (1:1, v/v) for 24 h. Extracted SB was twice-mercerized with aqueous NaOH solution (20 wt.%) at 25 °C for 16 h under magnetic stirring (300 rpm). Solid and liquid fractions were separated by vacuum filtration (glass Büchner funnel, porosity 2) and the solid was rinsed with distilled water until the pH of the washing water was neutral. Then, twice-mercerized SB (2MSB) was washed with ethanol and acetone and dried in an oven at 90 °C for 1 h. 2MSB (5.5 g), succinic anhydride (27.7 g) and anhydrous pyridine (165 mL) were added to a round-bottomed flask. Then, the flask was equipped with a reflux condenser attached to a drying tube packed with anhydrous calcium chloride (powder). The flask was put in a heating mantle and heated at 120 °C for 15 h. The product (2MSBA) was was in a glass Büchner funnel (porosity 3) with acetic acid in methylene chloride (1.0 molL⁻¹), ethanol, distilled water, saturated aqueous biconcave solution, distilled water, ethanol and acetone and then dried in an oven at 90 °C for 1 h (Gurgel et al., 2008).

Samples of 2MSBA (100 mg) were separately treated with aqueous spiked solution of Cu²⁺ (3.0 mmolL⁻¹) and Ni²⁺ (3.0 mmolL⁻¹) at pH 5 and 25 °C in an orbital shaker (130 rpm) for 2 h. Solid and liquid fractions were separated by a single filtration and the solids were rinsed with distilled water and acetone and dried in an oven at 90 °C for 1 h to obtain the catalysts 2MSBA-Cu and 2MSBA-Ni, respectively (da Silva et al., 2013).

2.3. Catalyst characterization

The weight gain and number of carboxylic acid groups released after chemical modification of 2MSB with succinic anhydride were determined according Gurgel et al. (2008). 2MSBA-Cu and 2MSBA-Ni were characterized by Fourier transform infrared (FTIR) spectroscopy by mixing 1.0 mg of the catalysts with 100.0 mg of spectroscopy grade KBr. The solid solutions were pressed in a hydraulic press at 8 tons for 30 s to obtain 13 mm KBr pellets (Pike CrushIR, model 181-1110, Pike Technologies). The spectra were recorded on an ABB Bomen MB 3000 FTIR spectrometer (Quebec, Canada) equipped with ZnSe optics and a deuterated triglycine sulfate (DTGS) detector set at a resolution of 4 cm⁻¹ from 500 to 4000 cm⁻¹ and 32 scans per sample. 2MSBA-Cu and 2MSBA-Ni were analyzed on a thermogravimetric analyzer (Mettler Toledo, model TGA/DSC STARE system version 11.00). Samples of 2MSBA-Cu and 2MSBA-Ni (5–6 mg) were weighed into alumina crucibles and analyzed from 25 to 800 °C at a heating rate of 10 °C min⁻¹ under synthetic air atmosphere flowing at 50 ml min⁻¹. During the heating, a 90 °C isotherm for 40 min was performed for stabilization of the catalysts. 2MSBA-Cu and 2MSBA-Ni were also analyzed on a LabX XRD 6100 X-ray diffractometer (Shimadzu) equipped with CuKα radiation (λ = 1.5406 Å), operating at a voltage of 40 kV and a current of 30 mA. The diffractograms of catalysts were recorded within the 20 (Bragg angle) range from 7 to 70° at a scan rate of 2° min⁻¹.

The amount of metal ions adsorbed on 2MSBA-Cu and 2MSBA-Ni was measured by desorbing metal ions from 2MSBA-Cu and 2MSBA-Ni. Samples of 20.0 mg of 2MSBA-Cu and 2MSBA-Ni were weighed into 125 mL Erlenmeyers flasks and 20.0 mL of aqueous 1.0 mol L⁻¹ HNO₃ solution was added to each flask. The flasks were stirred (Tecnal, model TE-424) at 25 °C for 2 min at 100 rpm. Then, the suspensions were filtered off using a single filtration (JP-41 filter paper) and the concentration of each metal ion was determined by a flame atomic absorption spectrophotometer (FAAS) (Varian, model SpectraAA 50B) at wavelengths of 324.8 nm for Cu²⁺ and 232 nm for Ni²⁺, respectively. The desorption experiments were performed in triplicate for each adsorbent loaded with Cu²⁺ or Ni²⁺. The amount of metal ions adsorbed on 2MSBA-Cu and 2MSBA-Ni was calculated according to Teodor et al. (2016).

2.4. Catalytic activity measurements

The catalytic activity of the 2MSBA-Cu and 2MSBA-Ni was measured in a fixed-bed tubular quartz reactor (39.5 cm length and 9 mm inner diameter) under atmospheric pressure. The following conditions were chosen: 0.1000 g catalyst, inlet n-hexane concentration of 2.0 g m⁻³ and inlet n-heptane concentration of 0.85 g m⁻³ in air, gas flow rate of 20 cm³ min⁻¹ and 0.3 s of residence time, gas hourly space velocity 12000 h⁻¹ and temperature range 25–175 °C. The reactants and the composition of the reactor effluent were analyzed in a gas chromatograph (Shimadzu GC 8A), equipped with a thermal conductivity detector (TCD), a Porapak-Q and a 5 Å molecular sieve column with Ar as the carrier gas. The gas chromatograph was calibrated against known concentrations of n-hexane and n-heptane and the decrease in the respective peak areas was used to measure the catalytic conversion, which was calculated as the ratio of the converted to the inlet quantity of alkanes.

3. Results and discussion

3.1. Catalysts characterization

2MSBA presented a weight gain of 140% and a number of carboxylic acid groups (nCOOH) of 5.2 mmol g⁻¹. The amount of metal ions adsorbed on 2MSBA-Cu and 2MSBA-Ni determined by desorption with an aqueous 1.0 mol L⁻¹ HNO₃ solution was 0.49 ± 0.01 mmol g⁻¹ and 2.49 ± 0.01 mmol g⁻¹, respectively. These results show that 2MSBA-Ni contains a higher amount of metallic cations than 2MSBA-Cu.

The FTIR spectra of 2MSBA (basic form), 2MSBA-Cu and 2MSBA-Ni (Fig. 1a) exhibit a band at 2941 cm⁻¹ related to asymmetric stretching of CH₃ due to the introduction of succinyl group and a band at 1744 cm⁻¹ related to asymmetric and symmetric stretching of ester group, by which succinyl group is linked to 2MSB. The bands at 1622 and 1421 cm⁻¹ and 1580 and 1421 cm⁻¹ for 2MSBA-Cu and 2MSBA-Ni, respectively, are related to asymmetric and symmetric stretching of carboxylate group complexed with Cu²⁺ and Ni²⁺. The spectrum of 2MSBA exhibits bands also related to asymmetric and symmetric stretching of carboxylate group at 1558 and 1390 cm⁻¹. The different positions of these bands for 2MSBA-Cu and 2MSBA-Ni in comparison to 2MSBA are related to asymmetric stretching of carboxylated groups complexed with Cu²⁺ and Ni²⁺, which indicates a difference in the complexion mode of metal ions.

The profiles of thermal decompositions (TGA) (Figures not shown) of 2MSBA-Cu and 2MSBA-Ni exhibited the first weight
losses close to 60–70 °C due to vaporization of bound water. The onset temperatures ($T_{\text{onset}}$) of 2MSBA-Cu and 2MSBA-Ni were 182.5 °C and 285 °C, which indicate a better thermal stability for 2MSBA-Ni than for 2MSBA-Cu. This result suggests that the metal content of the catalysts directly influenced in their thermal stabilities. Although the $T_{\text{onset}}$ of the catalysts were higher than the maximum temperature used in the catalytic tests (175 °C), the $T_{\text{onset}}$ of 2MSBA-Cu was in the border of the maximum temperature used in the catalytic tests. Therefore, to avoid the thermal decomposition of the catalysts, $T_{\text{onset}}$ must be taken into account for applications in the oxidation reaction of VOCs in gas phase. In addition, 2MSBA-Cu exhibited one main decomposition event ($T_{D1} = 244$ °C) while 2MSBA-Ni exhibited three main decomposition events ($T_{D1} = 336$ °C, $T_{D2} = 365$ °C and $T_{D3} = 382$ °C).

The XRD analysis of 2MSBA-Cu and 2MSBA-Ni revealed that the mercerization treatments of SB partially converted cellulose I to cellulose II. The diffractograms of 2MSBA-Cu and 2MSBA-Ni (Figures not shown) exhibited typical patterns of cellulose I and cellulose II with the main diffraction signals at 2θ at 22.7° and 20.2°.

3.2. Catalytic tests

2MSBA-Cu and 2MSBA-Ni samples were investigated as solid catalysts towards the gas-phase $n$-hexane and $n$-heptane oxidation reactions. Fig. 1b shows the reagent conversion as a function of the reaction temperature. The only products detected in the experiments were $\text{H}_2\text{O}$ and $\text{CO}_2$. Without the catalyst, thermal oxidation of the alkanes started at approximately 350 °C and achieved 3% conversion at 500 °C. In the presence of the catalyst, no significant conversion was detected at 25 °C but the catalysts exhibited activities starting from 50 °C, especially 2MSBA-Cu, reaching almost 10% of $n$-hexane conversion. Besides, this catalyst could oxidize 55% of $n$-hexane and 51% of $n$-heptane at temperatures as low as 175 °C. The catalysts showed a similar tendency, that is, the reagent conversion increased with the increase in the reaction temperature. Although 2MSBA-Cu has a lower metallic cation content, this catalyst presented the highest alkane conversion levels in all reaction temperatures than 2MSBA-Ni, indicating that Cu is most suitable than Ni for these reactions. Table 1 shows the light-off temperature ($T_{50}$, temperature for the 50% $n$-hexane and 50% $n$-heptane conversion) for $n$-hexane and $n$-heptane oxidation over the most active catalyst in the present study and some catalysts reported by previous investigations (Anić et al., 2011; Araújo et al., 2013; Cellier et al., 2007; Garrido Pedrosa et al., 2003; Ihm et al., 2004; Todorova et al., 2009; Zhong and Zeng, 2007). It is interesting to note that the performances of the catalysts synthesized in the present study are comparable or superior to those reported in the literature, as depicted in Table 1. In these reactions, the catalytic activities are dependent on the operational conditions employed (Huang et al., 2015; Li et al., 2009; Liotta, 2010; Rusu and Dumitriu, 2003). Although the data presented in Table 1 has been reported using different reaction conditions, and therefore, the comparison between the catalyst behaviors must be done with caution, this table is useful to give the reader an idea of the catalytic potential of the samples prepared in the present study. Through the comparison of the catalysts prepared in the present study with the noble metal-based catalysts, it can be observed that the $T_{50}$ of 2MSBA-Cu for $n$-hexane oxidation is much lower than those of the most catalysts and close to the value of the 2.9 wt.%Au/MnO$_2$–DP. Besides, by comparing the $T_{50}$ of 2MSBA-Cu and non-noble metal-based catalysts, it is clear that the former has an improved performance for $n$-hexane oxidation. The $T_{50}$ was 160 °C over 2MSBA-Cu, which was slightly higher than that of the $\gamma$-MnO$_2$ (151 °C) and lower than those of the Ce$_{0.90}$Sn$_{0.10}$O$_2$ (300 °C) and (8.2 wt.%Ce15.12 wt.%Co)/SiO$_2$ (233 °C), respectively. For $n$-heptane oxidation, 2MSBA-Cu presented a $T_{50}$ much lower than Co$_3$O$_4$–CeO$_2$. Although high conversion levels could not be achieved due to physicochemical limitations of the catalysts, such as low thermal resistance, this modest comparison of the activity of 2MSBACu with other reported catalysts indicates that this disadvantage can be compensated by the simplicity of obtaining the catalytic materials at a low cost; and the catalytic system reported in the present study can be considered as a good

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$T_{50}$ (°C)</th>
<th>Volatile organic compound</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2MSBA-Cu</td>
<td>160</td>
<td>$n$-hexane</td>
<td>This study</td>
</tr>
<tr>
<td>Ce$<em>{0.90}$Sn$</em>{0.10}$O$_2$</td>
<td>300</td>
<td>$n$-hexane</td>
<td>Araújo et al. (2013)</td>
</tr>
<tr>
<td>Co$_3$O$_4$–CeO$_2$</td>
<td>233</td>
<td>$n$-hexane</td>
<td>Todorova et al. (2009)</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>151</td>
<td>$n$-hexane</td>
<td>Cellier et al. (2007)</td>
</tr>
<tr>
<td>2.9 wt.%Au/MnO$_2$–DP</td>
<td>158</td>
<td>$n$-hexane</td>
<td>Cellier et al. (2007)</td>
</tr>
<tr>
<td>2.5 wt.%Au/TiO$_2$–IP–DP</td>
<td>260</td>
<td>$n$-hexane</td>
<td>Cellier et al. (2007)</td>
</tr>
<tr>
<td>0.3%Pt/$\gamma$Al$_2$O$_3$</td>
<td>236</td>
<td>$n$-hexane</td>
<td>Zhong and Zeng (2007)</td>
</tr>
<tr>
<td>0.3%Pt/LaSrCoO$_4$</td>
<td>227</td>
<td>$n$-hexane</td>
<td>Zhong and Zeng (2007)</td>
</tr>
<tr>
<td>0.4Mo/Fe–1 nm (D)</td>
<td>198</td>
<td>$n$-hexane</td>
<td>Anić et al. (2011)</td>
</tr>
<tr>
<td>5 wt.%Pt/$\gamma$Al$_2$O$_3$</td>
<td>190</td>
<td>$n$-heptane</td>
<td>Ihm et al. (2004)</td>
</tr>
<tr>
<td>Co$_3$O$_4$–CeO$_2$</td>
<td>450</td>
<td>$n$-heptane</td>
<td>Garrido Pedrosa et al. (2003)</td>
</tr>
<tr>
<td>2MSBA-Cu</td>
<td>170</td>
<td>$n$-heptane</td>
<td>This study</td>
</tr>
</tbody>
</table>
candidate for the \(n\)-hexane and \(n\)-heptane oxidation reactions at low temperatures.

4. Conclusions

A new use for the spent adsorbent material, succinylated twice-mercerized sugarcane (2MSBA) bagasse containing adsorbed Cu\(^{2+}\) and Ni\(^{2+}\) ions, in the catalytic oxidation of \(n\)-hexane and \(n\)-heptane in gas phase was proposed. 2MSBA was successful characterized by weight gain, amount of carboxylic acid groups, FTIR, TGA and XRD. 2MSBA was an efficient adsorbent for the removal of Cu\(^{2+}\) and Ni\(^{2+}\) from spiked aqueous solutions. The results revealed that the synthesized materials showed good activity for the proposed reactions. The catalysts prepared have improved performances compared to some important catalysts reported in the literature. These results demonstrated that it is possible to propose a catalytic process in a green chemistry context by combining the preparation of a biomass-based catalyst and its application in a process for elimination of harmful pollutants such as \(n\)-hexane and \(n\)-heptane.

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