

Removal of BTX Compounds in Air by Total Catalytic Oxidation Promoted by Catalysts Based on $\text{SiO}_{2(1-x)}\text{Cu}_x$

Rosana Balzer,^{*,a} Valdez Drago,^b Wido H. Schreiner^c and Luiz F. D. Probst^a

^aDepartment of Chemistry and ^bDepartment of Physics, Federal University of Santa Catarina (UFSC), 88040-900 Florianópolis-SC, Brazil

^cDepartment of Physics, Federal University of Paraná (UFPR), 81531-970 Curitiba-PR, Brazil

O objetivo deste estudo foi reduzir a emissão de compostos orgânicos como BTX (benzeno, tolueno e xilenos), devido à sua toxicidade e efeitos adversos ao meio ambiente. Neste sentido, os catalisadores ($\text{SiO}_{2(1-x)}\text{Cu}_x$) foram desenvolvidos para apresentar elevada atividade catalítica na conversão de BTX em CO_2 e H_2O sem a necessidade do uso de solventes e materiais prejudiciais ao meio ambiente, com baixo custo de produção e excelente reprodutibilidade. O Cu foi impregnado (2,99; 5,01; 10,01 e 19,97%) em suportes (SiO_2) por impregnação úmida a partir de nitrato de cobre(II). O estudo foi realizado na faixa de temperatura de 50-350 °C. Os catalisadores descritos nesse artigo apresentam elevada atividade catalítica na oxidação total de BTX. A conversão de benzeno neste estudo excedeu 85% a 150 °C.

The aim of this study was to reduce the emissions of organic compounds, such as BTX (benzene, toluene and xylenes), due to their toxicity and adverse effects on the environment. In this regard, catalysts ($\text{SiO}_{2(1-x)}\text{Cu}_x$) were developed which exhibit high catalytic activity for converting BTX compounds to CO_2 and H_2O , and which do not require the use of solvents and materials detrimental to the environment, with low production cost and good reproducibility. Cu (from copper(II) nitrate) was loaded (2.99; 5.01; 10.01 and 19.97 wt.%) onto supports (SiO_2) by wet impregnation. The study was carried out within the temperature range of 50-350 °C. The catalysts described in this paper have high catalytic activity in the total oxidation of BTX. The conversion of benzene in this study exceeded 85% at 150 °C.

Keywords: copper, SiO_2 , BTX, catalytic oxidation

Introduction

The contamination of atmospheric air, soil and groundwater by volatile organic compounds has been of concern in recent years mainly due to the high levels of petroleum hydrocarbon compounds emitted into the atmosphere with harmful consequences.¹⁻⁴ The potential pollutant gasoline is directly related to aromatic hydrocarbons, namely benzene, toluene and xylenes (known as BTX compounds or simply BTXs).^{5,6}

Due to the high toxicity of BTX compounds and the resulting adverse effects in contaminated systems, the search for control and remediation procedures is of great importance. Catalytic oxidation has been recognized as an efficient method to reduce air pollution, particularly atmospheric concentrations of volatile organic compounds.

The advantages of catalytic oxidation include the fact that it can operate at relatively low temperatures and no byproducts are formed.^{7,8}

Andreeva *et al.* reported studies on the effect of Au and V_2O_5 on the oxidation of benzene in systems with $\text{Au}/\text{V}_2\text{O}_5/\text{TiO}_2$ and $\text{Au}/\text{V}_2\text{O}_5/\text{ZrO}_2$. The conversion of benzene obtained at 250 °C was 70% for $\text{Au}/\text{V}_2\text{O}_5/\text{ZrO}_2$ and 90% for $\text{Au}/\text{V}_2\text{O}_5/\text{TiO}_2$.^{4,6,7}

Wu *et al.* reported a study on the effect of the catalysts Au/ZnO , $\text{Au}/\text{Al}_2\text{O}_3$ and Au/MgO on the oxidation of benzene, toluene and *p*-xylene and the most efficient was Au/ZnO . At 300 °C the conversion of benzene slightly exceeded that of toluene (which was around 60%) while the conversion of *p*-xylene did not reach 35%.⁹

The development of a catalyst with high specific activity at low temperatures, that is, high selectivity and low preparation cost, remains a challenging goal in the total oxidation of BTXs.

*e-mail: rosanabalzer@gmail.com

In this context, the objective of this study was to investigate the capability of the base catalysts $\text{SiO}_{2(1-x)}\text{Cu}_x$ in relation to the total conversion of benzene, toluene and xylenes to CO_2 and H_2O .

Experimental

Preparation of catalysts

Four supported metal catalysts were prepared using silicon dioxide (SiO_2 , 70-230 mesh) (Vetec[®]) as the support. The precursor salt was copper(II) nitrate (Vetec[®]), which was dissolved in distilled water and added to the support. Subsequently, the materials were dried in an oven for 24 hours at 100 °C and then calcined in a muffle furnace with circulating air at a heating rate of 5 °C min⁻¹, starting at ambient temperature and increasing to 550 °C, this temperature being held for 4 hours. Samples were then crushed and sieved (to provide particles between 177 and 210 μm). The catalysts were identified as $\text{SiO}_{2(1-x)}\text{Cu}_x$ where x (mol%) is: $\text{SiO}_{2(0.97)}\text{Cu}_{0.03}$; $\text{SiO}_{2(0.95)}\text{Cu}_{0.05}$; $\text{SiO}_{2(0.9)}\text{Cu}_{0.1}$ and $\text{SiO}_{2(0.8)}\text{Cu}_{0.2}$.

Characterization of the catalysts

The specific surface areas of the catalysts (S_{BET}) were determined using a Nova 2200e analyzer (Quantachrome Instruments[®]). The surface areas were calculated applying the Brunauer Emmett Teller (BET) method by isothermal gas adsorption/desorption of N_2 at 77 K using 40 points. The crystalline structures of the catalysts were analyzed by X-ray powder diffraction (Bruker-AXS Siemens[®]) with CuK_α radiation ($V = 40$ kV; $I = 30$ mA). The morphology and microstructure of the catalysts were observed by scanning electron microscopy (SEM, JEOL JSM-6390LV) and field emission transmission electron microscopy (FETEM, JEOL JEM-1011). The chemical composition

and metal content of the catalysts were analyzed by energy-dispersive X-ray spectroscopy (EDX). The binding energies of the elements were determined by X-ray photoemission spectroscopy (XPS) (VG Microtech 3000).

Catalytic activity tests

The activity of the catalysts was measured in a fixed tubular quartz reactor under atmospheric pressure. The following conditions were chosen: catalyst volume 0.090 cm³, inlet benzene (Vetec[®]) concentration 2.5 g m⁻³, toluene (Vetec[®]) concentration 0.65 g m⁻³ and *o*-xylene (Vetec[®]) concentration 0.45 g m⁻³ in air and temperature range 50-350 °C. The kinetic data were collected after at least 1 h on-stream at room temperature. The only products were CO_2 and H_2O as determined by GC-MS and FTIR. The reactant and product mixtures were analyzed with an on-line gas chromatograph equipped with a FID detector and an HP-5 column.

The catalytic activity was expressed as the degree of conversion of the BTX compounds. The conversion of BTXs was calculated as follows in equation 1:

$$BTXs(\%) = \frac{[BTXs]_{in} - [BTXs]_{out}}{[BTXs]_{in}} \times 100\% \quad (1)$$

where BTXs (%) = percentage of BTXs converted; $[BTXs]_{in}$ = input BTX concentration; $[BTXs]_{out}$ = output BTX concentration.

Results and Discussion

Structural and textural properties of the catalysts

The values for the surface area, pore volume and pore diameter of the catalysts are presented in Table 1.

As expected, there was a reduction in all of these parameters as the metal content increased. This reduction

Table 1. Textural data for the supported copper catalysts

Sample	BET / (m ² g ⁻¹) Before / after calcination	Vp / (cm ³ g ⁻¹) Before / after calcination	Dp / nm Before / after calcination	Average CuO size / nm ^a	Average CuO size / nm ^b	Cu loading wt% ^c	Cu dispersion % ^d
SiO_2	376 / 365	0.76 / 0.74	4.08 / 4.06	-	-	-	-
$\text{SiO}_{2(0.97)}\text{Cu}_{0.03}$	311 / 299	0.62 / 0.60	4.06 / 4.05	46	15.1	2.99	7.98
$\text{SiO}_{2(0.95)}\text{Cu}_{0.05}$	309 / 298	0.60 / 0.57	4.06 / 4.04	53	18.5	5.01	6.52
$\text{SiO}_{2(0.9)}\text{Cu}_{0.1}$	292 / 281	0.58 / 0.55	4.05 / 4.01	59	21.6	10.01	5.58
$\text{SiO}_{2(0.8)}\text{Cu}_{0.2}$	248 / 234	0.51 / 0.48	4.04 / 4.00	65	23.3	19.97	5.17

Vp = pore volume; Dp = pore diameter; ^adetermined by XRD; ^bobtained by HRTEM; ^ccalculated from semi-quantitative EDX data; ^dcalculated using formula (Wu *et al.* 2011): $D_{Cu} = 6n_s M_{Cu} / r_{Cu} N_A d_{Cu}$, where n_s is the number of Cu atoms at the surface per unit area (1.7×10^{19} m⁻²), M_{Cu} is the molar mass of copper (63.546 g mol⁻¹), r_{Cu} is the density of copper (8.92 g cm⁻³), N_A is Avogadro's number (6.023×10^{23} mol⁻¹) and d_{Cu} is the average Cu particle size (obtained by HRTEM).

may be related to the high calcination temperature of 550 °C (Table 1).

The isotherms obtained were analyzed by comparison with the classification of the IUPAC (International Union of Pure and Applied Chemistry) and it was found that the catalysts have pores of regular cylindrical and/or polyhedral shape with open ends with type IV isotherms and type H1 hysteresis (Figure 1).²

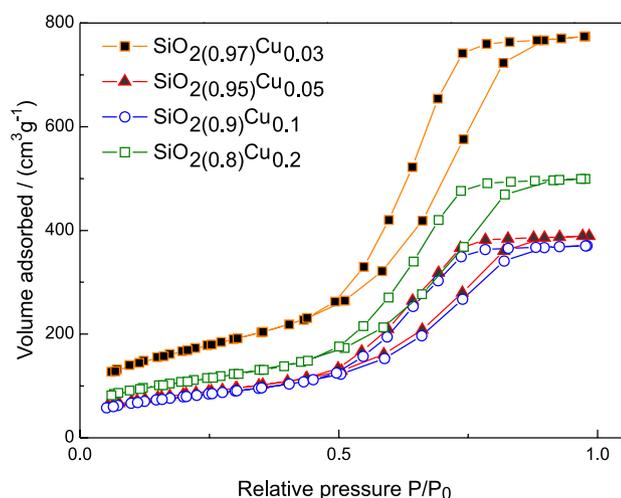


Figure 1. Nitrogen isotherms of the catalysts $\text{SiO}_{2(1-x)}\text{Cu}_x$.

The X-ray diffractograms are shown in Figure 2, in which the diffraction peaks ($2\theta = 33, 35, 38, 48, 54, 58, 62, 65, 66$ e 68°) are assigned to the reflections for the tenorite (CuO) phase, a monoclinic crystal system (JCPDS data file 045-0937). The peak at $2\theta = 22^\circ$ is characteristic of silicon oxide. The peaks are more intense for CuO (11-1) ($2\theta = 35^\circ$) and CuO (111) ($2\theta = 38^\circ$). Therefore, it can be concluded that the large crystal size, good stability and

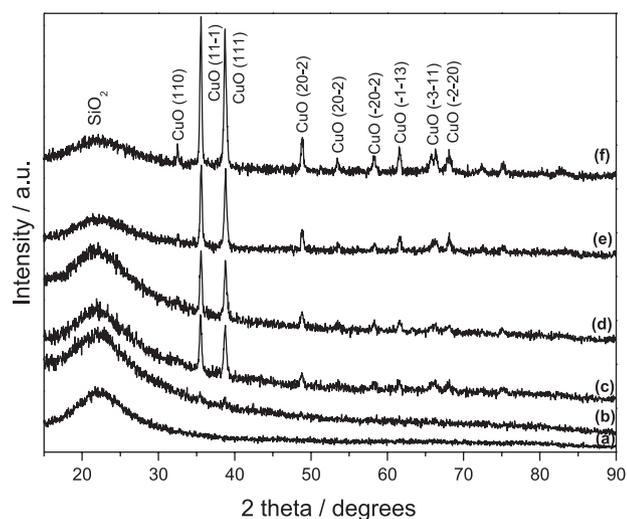


Figure 2. XRD patterns for the samples (a) SiO_2 ; (b) $\text{SiO}_{2(0.97)}\text{Cu}_{0.03}$; (c) $\text{SiO}_{2(0.95)}\text{Cu}_{0.05}$; (d) $\text{SiO}_{2(0.9)}\text{Cu}_{0.1}$ and (e) $\text{SiO}_{2(0.8)}\text{Cu}_{0.2}$.

close contact between the Cu and SiO_2 particles favors the catalytic performance of the Cu/SiO_2 catalyst.^{10,11}

Morphology and chemical composition of catalysts

Figure 3A-D shows the morphology of the $\text{Cu}-\text{SiO}_2$ catalyst particles in the shape of a hemisphere. The EDX analysis confirmed the presence of the element Cu, as shown in Table 1. The higher the copper content the lower the degree of metal dispersion in the catalyst due to the more pronounced formation of agglomerates in catalysts with higher metal content, as observed by SEM.

In Figure 4A-C copper oxide particles with a hemispherical shape and contact between the copper and silicon oxides at the perimeter can be observed. The size of copper-containing particles had a Gaussian distribution as represented in Figure 4D and the particle size distribution for each of the catalysts is shown in Table 1. The result shows a strong interaction between the metal and silicon oxides in the catalyst, where the particles appear to be faceted when adsorbed on the support, which could induce defects or the formation of active sites at which the reaction occurs easily, which favors the catalytic activity of the catalysts Cu/SiO_2 .⁹

Oxidation state and binding energy of the catalysts

The XPS analysis (Figure 5) yielded the values for the bond energy of the electrons O_{1s} (532.4 eV), $\text{Si } 2p_{1/2}2p$ (103.3 eV) and $\text{Cu } 2p_{3/2}$ (933.4 eV) before and after the catalytic reaction. These were used to determine the oxidation state of the elements present and to observe whether changes occurred during the catalytic reaction.¹²⁻¹⁵

It was observed that the value obtained for the binding energy of the electron $\text{Si } 2p_{1/2}$ is consistent with that reported in the literature, suggesting that in these catalysts all of the silicon is present in the form of Si(IV) .^{13,16,17} The value for the binding energy of $\text{Cu } 2p_{3/2}$ in the catalysts studied was 933 eV which, on-comparing with results reported in the literature, is attributed to the presence of copper(II) oxide. This value is reported as 933.4 eV in the literature.^{12, 16 18, 19}

Catalyst performance for BTX (benzene, toluene and o-xylene) oxidation

Figure 6 shows the conversion of BTXs as a function of the reaction temperature for the catalysts studied.

The catalyst $\text{SiO}_{2(0.9)}\text{Cu}_{0.1}$ showed higher catalytic activity toward the BTX compounds. The catalytic activity of the catalyst $\text{SiO}_{2(0.8)}\text{Cu}_{0.2}$ may be related to the excessive

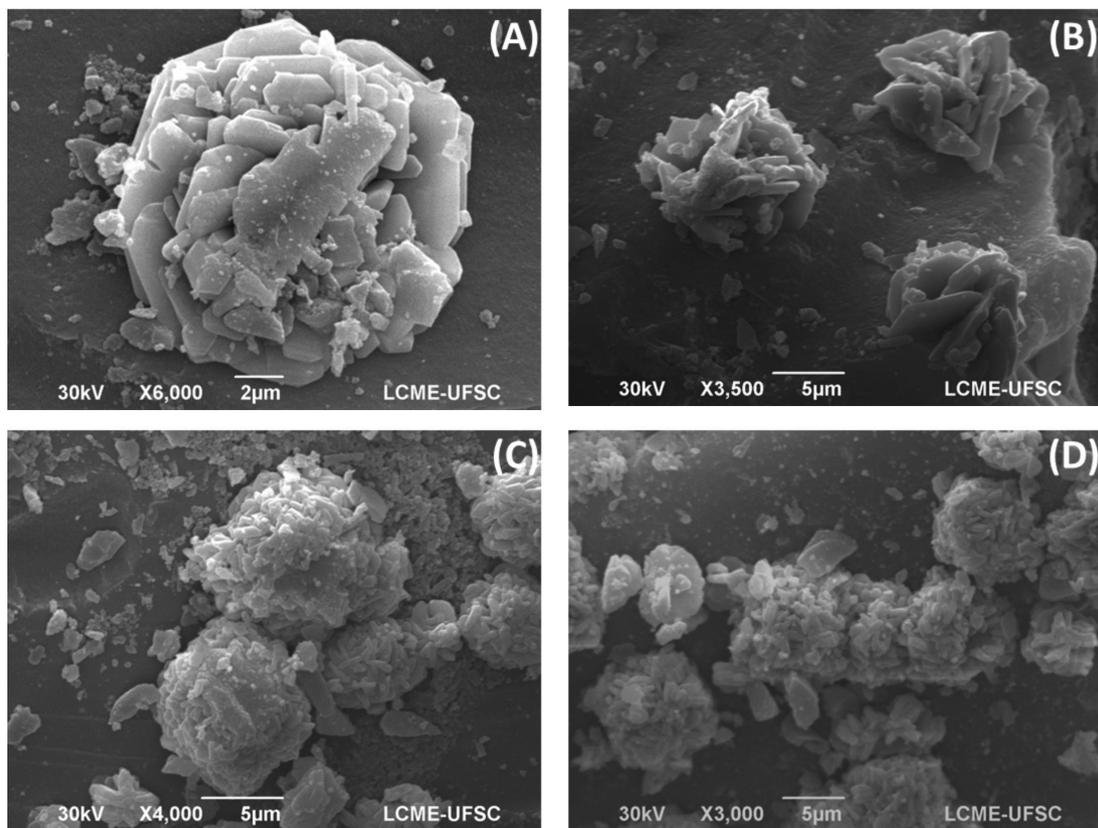


Figure 3. SEM images of (A) $\text{SiO}_{2(0.97)}\text{Cu}_{0.03}$; (B) $\text{SiO}_{2(0.95)}\text{Cu}_{0.05}$; (C) $\text{SiO}_{2(0.9)}\text{Cu}_{0.1}$ and (D) $\text{SiO}_{2(0.8)}\text{Cu}_{0.2}$.

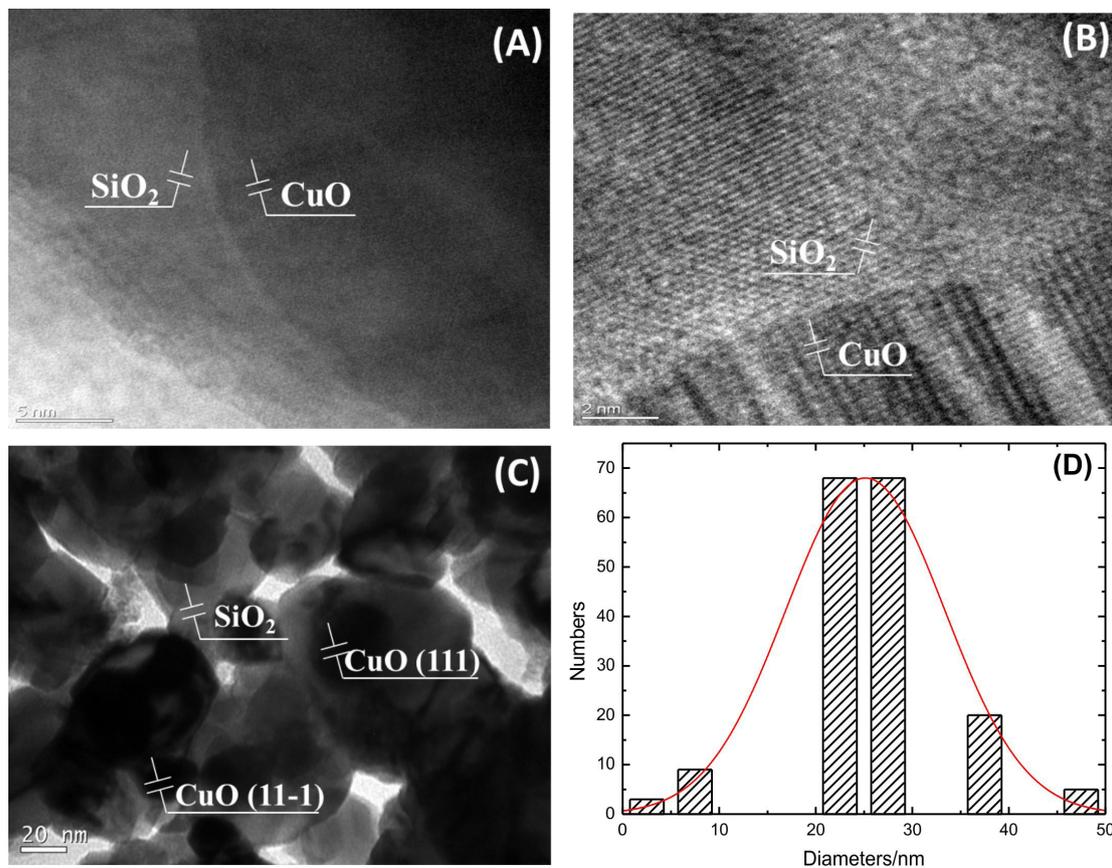


Figure 4. TEM images of (A) $\text{SiO}_{2(0.95)}\text{Cu}_{0.05}$; (B) $\text{SiO}_{2(0.8)}\text{Cu}_{0.2}$; (C) $\text{SiO}_{2(0.9)}\text{Cu}_{0.1}$ and (D) particle size distribution for copper of $\text{SiO}_{2(0.9)}\text{Cu}_{0.1}$.

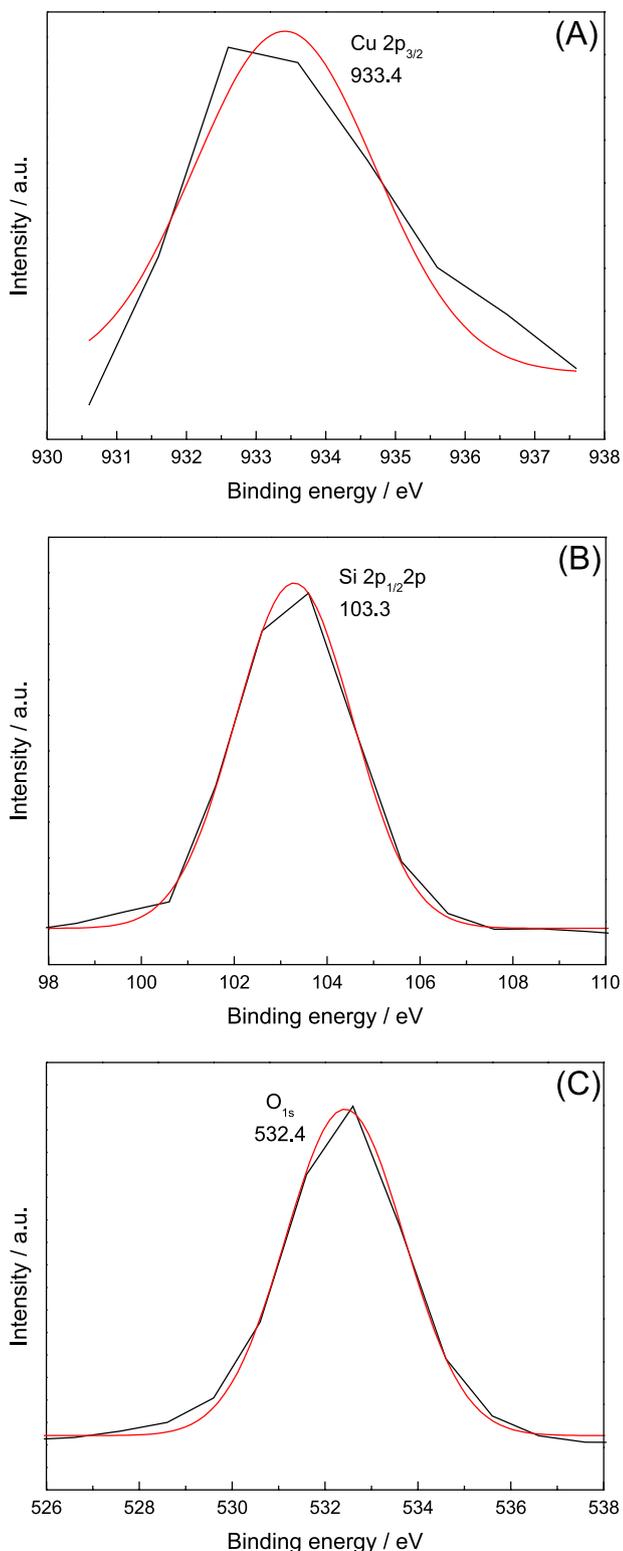


Figure 5. XPS spectra of the catalysts $\text{SiO}_{2(1-x)}\text{Cu}_x$: (A) region Cu 2p_{3/2}; (B) region Si 2p_{1/2,2p} and (C) region O 1s.

formation of agglomerated particles on the surface, reducing the metal dispersion, according to Table 1. As expected the catalyst $\text{SiO}_{2(0.97)}\text{Cu}_{0.03}$ had a lower catalytic activity than the other catalysts tested, due to its lower metal content.

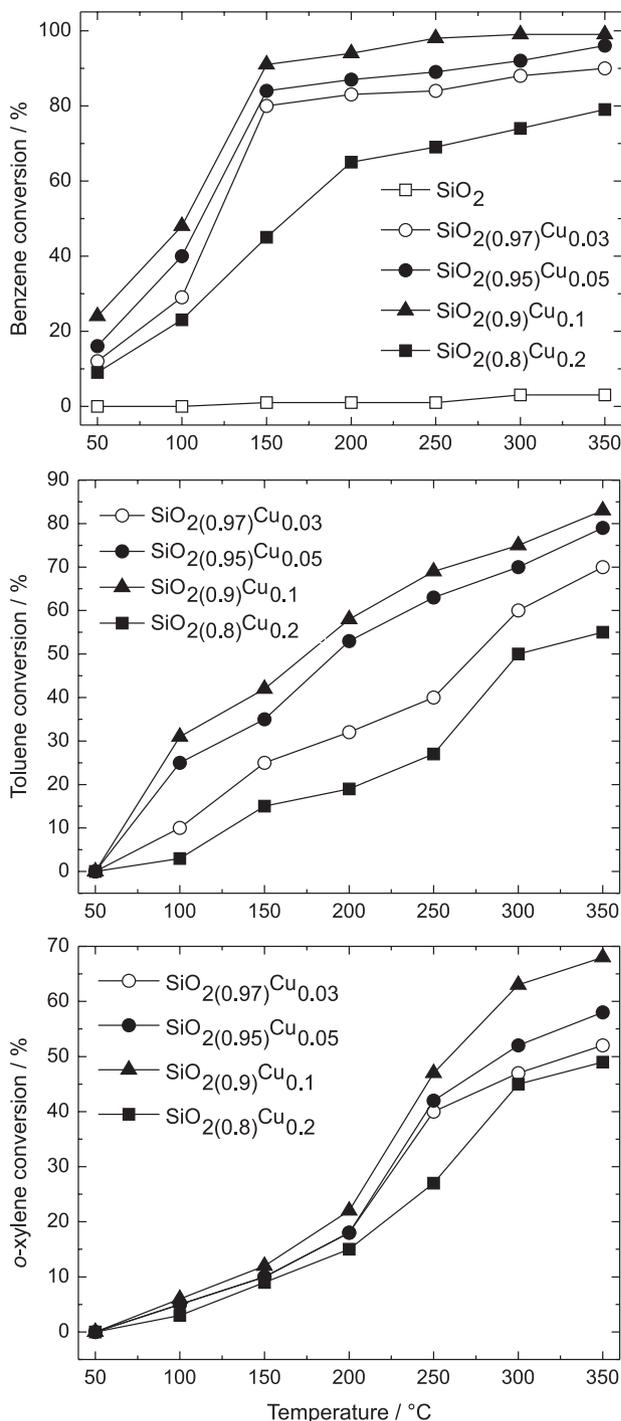


Figure 6. BTX conversion as a function of reaction temperature for different catalysts under varying reaction conditions: benzene 2.0 g m⁻³, toluene 0.5 g m⁻³, o-xylene 0.4 g m⁻³. Total flow rate: 20 ml min⁻¹.

On comparing the catalytic activity of the Cu/SiO₂ products with other catalysts described in the literature that are highly active in BTX oxidation (Table 2), it can be seen that the $T_{\text{benzene50}}$ temperature (benzene conversion up to 50%) is 106 °C for $\text{SiO}_{2(0.9)}\text{Cu}_{0.1}$, 124 °C for $\text{SiO}_{2(0.95)}\text{Cu}_{0.05}$ and 162 °C for $\text{SiO}_{2(0.97)}\text{Cu}_{0.03}$. These values are comparable with those reported in literature for the catalyst Cu/ $\gamma\text{-Al}_2\text{O}_3$,

Table 2. Comparison of data published in the literature with those obtained in this study

Sample	BTX			BTX in air (benzene /toluene or <i>o</i> -xylene)	Ref.
	T _{benzene50} / °C	T _{toluene50} / °C	T _{<i>o</i>-xylene30} / °C		
SiO _{2(0.9)} Cu _{0.1}	106	175	212	782 ppmv BTX in air	This study
SiO _{2(0.95)} Cu _{0.05}	124	191	225	782 ppmv BTX in air	This study
SiO _{2(0.97)} Cu _{0.03}	162	150	230	782 ppmv BTX in air	This study
5% Cu/ γ -Al ₂ O ₃	ca. 310	ca. 280	ca. 275	800 ppmv BTX in air	20
15% Cu/ γ -Al ₂ O ₃	-	> 280	-	1000 ppmv BTX in air	20
5%Cu/TiO ₂ (rutile)	-	> 280	-	900 ppmv BTX in air	20
1.5% Au/ZnO	130	ca. 235	ca. 250	603 ppmv BTX, 10% O ₂ , 90% N ₂	9
0.30%Pt/AC	131	-	-	640 ppmv BTX in air	21
3%Au/V ₂ O ₅ /TiO ₂	ca. 150	-	-	1206 ppmv BTX in air	3

1.5% Au/ZnO, 0.30% Pt/AC and 3% Au/V₂O₅/TiO₂ (Table 2). In fact, the benzene conversion exceeds 80% for the catalyst Cu/SiO₂ at 150 °C, and is higher than the values for the catalysts Cu/ γ -Al₂O₃, 1.5% Au/ZnO and 3% Au/V₂O₅/TiO₂ (0%, 80% and 63% respectively). Table 2 also shows the values for T_{toluene50} (toluene conversion up to 50%) and T_{*o*-xylene30} (*o*-xylene conversion up to 30%).^{3,9,20,21} The results of these experiments revealed that the SiO₂ support has no activity and reports in the literature for other catalysts indicate that interaction between Cu and SiO₂ could improve the catalytic activity of Cu/SiO₂ in relation to BTX oxidation.^{9,21}

According to the results shown in Figure 6, the activity of the Cu/SiO₂ catalyst decreases in the order benzene > toluene > *o*-xylene. The conversion of benzene is higher than those of toluene and *o*-xylene in the same concentrations and reaction conditions. This indicates that the catalytic activity in relation to aromatic compounds is highly dependent on the relative adsorption strength of the model compounds, the strength of the weakest carbon-hydrogen bond in the structure and the ionization potential of the methyl derivatives.^{9,11,12}

It is well known that the oxidation of BTX compounds promoted by solid oxide catalysts can proceed by the Mars-van Krevelen mechanism, in which the key steps are the supply of oxygen by the reducible oxide, the introduction of the oxygen (originating from the oxide lattice) into the substrate molecule and the re-oxidation of the reduced solid by the oxygen-containing gaseous phase, which is the rate-determining step of the reaction.^{9,22,23} According to the Mars-van Krevelen mechanism, the BTX oxidation rate is determined by the concentration of BTX chemisorbed onto the Cu-containing particles close to the periphery of the Cu-SiO₂ interface. The active oxygen species formed on the metal-support interface or on the support close to the metal directly participate in the catalytic

oxidation, and the metal coated on the support serves as the adsorption site for BTXs. The catalytic cycle involves the chemisorption of BTX onto Cu-containing particles, migration of the chemisorbed BTX to the Cu-SiO₂ interface, O₂ activation on the defect sites in the SiO₂ or at the Cu-SiO₂ interface, the formation of active oxygen species and the reaction between the chemisorbed BTX and active oxygen species at the interface.^{9,20,24,25}

Conclusions

The SiO_{2(0.9)}Cu_{0.1} product exhibits higher activity compared with other catalysts reported in the literature (5% and 15% Cu/ γ -Al₂O₃, 5% Cu/TiO₂(rutile), 1.5% Au/ZnO and 3% Au/V₂O₅/TiO₂) with regard to BTX oxidation. The benzene conversion for the SiO_{2(0.9)}Cu_{0.1} catalyst exceeded 85% at 150 °C, which is comparable to the values for 1.5% Au/ZnO and 3% Au/V₂O₅/TiO₂. The high catalytic activity could be attributed to the high stability observed due to a greater energy of interaction between the Cu-SiO₂ catalysts in this study. Thus, the catalysts of the base Cu/SiO₂ proved to be highly efficient in the conversion of BTX compounds.

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