



SYNTHESIS AND CHARACTERIZATION OF $\text{CuCl}_2/\text{SiO}_2$ CATALYST FOR THE OXYCHLORINATION OF METHANE

^a Nascimento, J. C. ¹; ^b Sousa, J. F.; ^a Rojas, L. O. A.; ^c Fontes, F. A. O.

^a Centro de Tecnologia do Gás Natural e Energias Renováveis

^b Departamento de Engenharia Química - Universidade Federal do Rio Grande do Norte

^c Departamento de Engenharia Mecânica - Universidade Federal do Rio Grande do Norte

ABSTRACT

CuCl_2 catalysts supported on silica were used in the oxychlorination of methane. The materials were synthesized by the ion-exchange technique in a basic solution, using a copper-ammonia complex with 3 and 6 % of nominal copper load. The materials were characterized by Thermogravimetry (TG), X-ray Fluorescence Spectroscopy (XRF), Temperature Programmed Reduction (TPR), Scanning Electron Microscopy with X-ray microanalysis (SEM/EDS), BET specific area, and Pore Distribution. The characterization confirmed the presence of copper on the support surface, concluding that the ion-exchange technique was adequate for the catalyst synthesis. During reaction assays, an oxychlorination bench-scale unit was employed. The tests were carried out at 673 and 773 K. The results demonstrated the influence of temperature and catalyst copper content on methane conversion.

KEYWORDS

synthesis and characterization; copper; methane; oxychlorination; fixed-bed reactor

¹ To whom all correspondence should be addressed.

Address: Centro de Tecnologia do Gás Natural e Energias Renováveis, Av. Capitão-Mor Gouveia 1480, Natal(RN), Brazil
CEP: 59063-400 | Telephone: (55) 84 3204-8192 | e-mail: carlos@ctgas.com.br
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1. INTRODUCTION

The massive and growing supply of natural gas in recent years has been motivating research on the use of this energy source. The increasing demand for petrochemical products, primarily ethylene and propylene, has stimulated the development of alternative methods of production using natural gas. One of these conversion methods is the catalytic oxychlorination of methane, which produces halogens that ultimately act as precursors in the production of olefins.

Methane chlorination is an exothermic reaction that releases about 23 kcal/mol of heat. This can be achieved industrially through the direct action of chlorine or through oxychlorination, using hydrochloric acid, oxygen, and a catalyst. One advantage of this process is the possibility of using hydrogen chloride instead of chlorine gas (Garcia and Resasco, 1987). With respect to research on hydrocarbons, oxychlorination is an important operation in the petroleum and gas sectors due to the possibility of adding value to the final product. In spite of this, there are few publications on this subject in both national and international literatures. This fact is related to difficulties in carrying out the procedure, since the equipment used may be prone to corrosion caused by exposure to hydrochloric acid, besides causing catalyst poisoning by the chlorinated phase.

This study aimed to synthesize, characterize, and evaluate $\text{CuCl}_2/\text{SiO}_2$ catalysts, with a copper content of 3 and 6 %, designated 3 CuCl_2 and 6 CuCl_2 respectively. The experiment performed the conversion of methane through catalytic oxychlorination in a differential fixed-bed reactor. The samples were then subjected to the following characterization techniques: Thermogravimetry (TG); X-Ray Fluorescence (XRF); Temperature-Programmed Reduction (TPR); Scanning Electron Microscopy equipped with Electron Dispersive Spectroscopy (SEM-EDS); and BET, for determination of the specific area and specific pore volume. These techniques were used to assess the influence of copper content and reaction temperature on methane conversion.

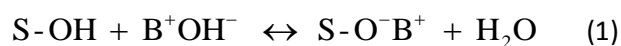
2. MATERIALS AND METHODS

2.1 Synthesis of the $\text{CuCl}_2/\text{SiO}_2$ catalyst

The catalyst was prepared using the ion-exchange method in a basic medium, in accordance with the methodology employed by Shimokawabe et al. (1983). Synthesis of the $\text{CuCl}_2/\text{SiO}_2$ catalyst consisted of the following steps: silica activation, preparation of the copper complex solution, copper incorporation onto silica, calcinations and chlorination. The precursor materials used in the synthesis of the $\text{CuCl}_2/\text{SiO}_2$ catalyst were copper(II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) and microspherical silica (SiO_2). In this work, silica was used as a support because it does not interact significantly with the copper(II) chloride produced (Garcia and Resasco, 1989), thus enabling an appropriate interpretation of the catalytic effects. The first three steps of the synthesis procedure were performed at room temperature and ammonia hydroxide was added to adjust the pH between 10 and 12.

2.1.1 Silica activation

The preliminary stage of catalyst synthesis was silica activation. Initially, two individual 5.0 g silica samples were weighed and added to different 250 mL beakers containing 100 mL of deionized water. Then, 100 mL of a 2 M ammonium hydroxide solution (NH_4OH) were added. The solution was stirred for 2 h. Finally, the suspension was allowed to settle for 12 h. Silica in contact with a high-pH alkaline solution (Brunelle, 1978) has a negatively charged surface, enabling the electrostatic adsorption of a cation according to the following reaction model:



where S-OH represents a surface adsorption site and B^+OH^- is a base.

2.1.2 Preparation of copper complex solution

After silica activation, the next step was the preparation of the tetraamminecopper(II) sulfate complex. Initially, two solutions of the precursor salt [copper(II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$)] were prepared with different metallic copper

contents (3 and 6 %), corresponding to a 5.0 g load on the support (silica). Then, these solutions were added to individual 250 mL beakers containing 100 mL of deionized water, to which 100 mL of a 2 M ammonium hydroxide solution were then added. The resulting suspension was stirred for 2 h, thus forming the tetraamminecopper(II) sulfate complex $\{[\text{Cu}(\text{NH}_3)_4]\text{SO}_4\}$ with an intense blue color. Finally, the solution was allowed to rest for 12 h.

2.1.3 Incorporation of copper into silica

In this third stage, two support suspensions were mixed with two complex solutions in separate 500 mL beakers and stirred for 1 h. The solutions were then vacuum-filtered and washed with deionized water for 20 minutes, in triplicate. Finally, the filtered cake was oven-dried at a temperature between 383 and 393 K for 12 h. This washing step is required to eliminate possible impurities in the catalyst (Perego and Villa, 1997), such as sulfate ions present in the precursor.

2.1.4 Calcination

After the incorporation of copper onto silica, the catalyst samples were calcined at a temperature of 773 K for 3 h under a dynamic atmosphere of oxygen and nitrogen in a fixed-bed reactor. Initially, the samples were heated from room temperature to 773 K at a heating rate of 10 K/min under a synthetic air flow of 50 mL/min. The purpose of calcination was to obtain copper(II) oxide (CuO) supported on silica.

2.1.5 Chlorination

Soon after calcination, the samples were chlorinated at a temperature of 323 K for 10 minutes under a dynamic atmosphere of nitrogen and hydrogen chloride in a fixed-bed reactor. The samples were heated from room temperature to 323 K at a heating rate of 5 K/min under a nitrogen flow of 25 mL/min. Next, the gas was replaced with hydrogen chloride. Flow rate and temperature conditions were maintained during this stage of the experiment.

2.2 Characterization of the $\text{CuCl}_2/\text{SiO}_2$ catalyst

2.2.1 Thermogravimetry (TG)

Thermogravimetric analyses were performed with the purpose of determining the best conditions for the decomposition of the tetraamminecopper(II) sulfate complex to obtain the copper oxide (CuO) and assess how the catalyst behavior is affected by temperature. Two samples of approximately 12 mg, calcined and non-calcined, with metal loads of 3 and 6 % copper, respectively, were subjected to dynamic analyses, with temperature programming from room temperature to 1,273 K, under a synthetic air flow of 30 mL/min, at a heating rate of 10 K/min.

2.2.2 X-Ray Fluorescence (XRF)

To analyze the chemical compositions of the catalyst prepared, the samples were subjected to X-Ray Fluorescence (XRF). The preparation of the catalyst samples for analysis consisted in pressing them unto obtaining tablets. After this procedure, the tablets were subjected to X-rays from an excitation source under a vacuum atmosphere and the XRF spectra were recorded.

2.2.3 Temperature-Programmed Reduction (TPR)

The Temperature-Programmed Reduction (TPR) analyses were obtained in a conventional apparatus to verify the formation of copper oxide during calcination, as well as the reduction temperature. In the temperature-programmed reduction (TPR) analyses, approximately 20 mg of the samples were injected in a "U"-form quartz reactor, powered by a reductive gas mixture (10 % H_2 – 90 % Ar) at a flow rate of 30 mL/min. A heating rate of 10 K/min was programmed, from room temperature to 1,273 K.

2.2.4 Scanning Electron Microscopy equipped with Electron Dispersive Spectroscopy (SEM-EDS)

The Scanning Electron Microscopy (SEM) analyses aimed to characterize the morphology of the catalysts. Chemical composition analyses were also performed to quantify the amount of copper in the samples through Electron Dispersive Spectroscopy (EDS) coupled to the SEM. Initially, the samples were placed on a carbon tape. Then, gold was deposited in order to metalize the sample. This technique allows for image detection of the sample surface. Finally, vacuum was applied

in the SEM chamber and the electron beam emission was focused on the samples.

2.2.5 BET Technique

The analyses to determine the specific area and specific pore volume were obtained by the BET technique. Samples of catalysts with different copper loads (3 and 6 %) and silica were analyzed. The samples were previously treated at 473 K under vacuum for 2 h to eliminate the water adsorbed during handling and possible condensates existing in the pores of the solids.

2.3 Catalytic tests

The catalytic tests of the $\text{CuCl}_2/\text{SiO}_2$ samples were performed in a differential fixed-bed system, operating at a pressure of 1.1 bar. To minimize the corrosive effects of hydrogen chloride on the experimental apparatus, a reactive gas mixture comprising methane, hydrogen chloride, and oxygen diluted in nitrogen, supplied by White Martins, was used in the gravimetric method, instead of individual reagent gases. The proportion relative to the composition of the gaseous reagents ($\text{CH}_4:\text{HCl}:\text{O}_2$) in the reactive gas mixture used (see Table 1) was in accordance with [Garcia and Resasco \(1987\)](#). The catalytic test conditions are presented in Table 2.

The catalytic experiments' temperature was measured by a thermocouple placed next to the catalyst bed and connected to an electronic temperature controller. The catalyst mass used was about 210 mg. The reactor was fed with a fixed flow of the reactive gas mixture, set at 20 mL/min by a mass flow controller. At the exit of the apparatus, the gas flow was measured using a volumetric flow meter. Each experiment lasted approximately 270 minutes (45 minutes of heating, 180 minutes at a constant temperature, and 45 minutes of cooling). With respect to the gaseous constituents (CH_4 , chloromethane, CO , CO_2) present in the reactor effluent, it was possible to determine the methane conversion using the Thermo Electron Corporation's Trace GC Ultra model gas chromatograph belonging to the CTGAS-ER (Gas Technology Center and Renewable Energies, Natal/RN-Brazil). A total of four experiments were conducted, varying only the copper load on the catalyst and the reaction temperature. The other conditions (pressure and reactive gas mixture flow rate) were kept constant.

Figure 1 shows the schematic diagram of the catalytic reaction apparatus.

Table 1. Composition of the gas mixture used in catalytic tests.

Component	Composition	Measurement uncertainty
Nitrogen	91.930 % mol/mol	+/- 0.21%
Methane	5.039 % mol/mol	+/- 0.35%
Hydrogen chloride	2.030 % mol/mol	+/- 0.35%
Oxygen	1.005 % mol/mol	+/- 0.60%

Table 2. Catalytic test conditions.

Assay	Copper content in the catalyst / %	Temperature / K
I	3	673
II	3	773
III	6	673
IV	6	773

2.3.1 Preparation of the reaction system

The first step in the preparation of the reaction system was the cleaning of the reactor with distilled water, followed by washing it with cyclohexane. Then, the reactor was oven-dried at 393 K for 30 minutes to remove any traces of liquid. After drying, glass wool was placed at the edges of the bed to avoid dragging of the catalyst promoted by the reactive gas mixture flow. The feeding of the gas phase to the reactor was carried out using commercial cylinders.

At the reactor inlet, a gauge and three-way manual ball valves were connected to create a bypass in the reaction system. At the outlet, a double acrylic filter, filled with barium hydroxide and polyethylene spheres, was connected to retain any non-reacted chloride ions. This trap was similar to that used in the experiments of [Reddy et al \(2008\)](#). Downstream of the filter, a three-way ball valve was inserted to provide a path for the vent and another valve was positioned with the purpose of performing a chromatographic analysis. A retention valve was placed upstream of the filter to prevent gas counterflow.

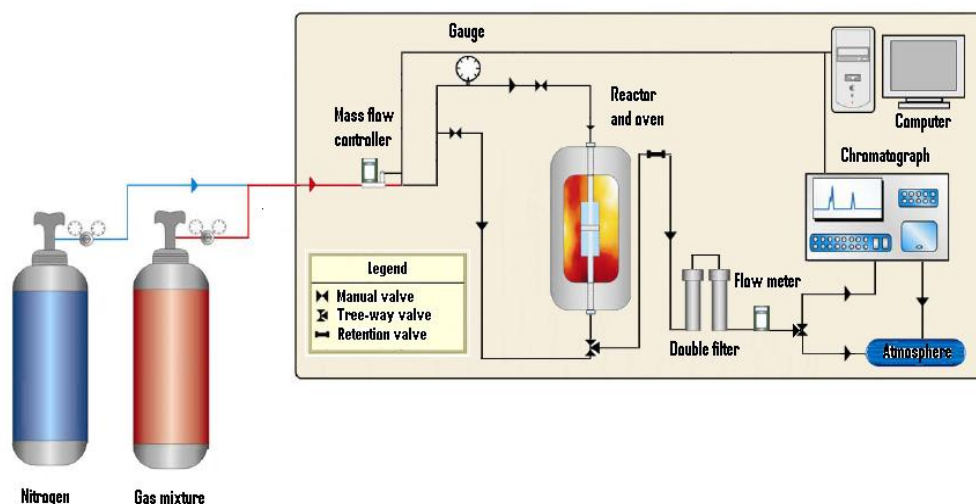


Figure 1. Schematic diagram of the catalytic reaction apparatus.

2.3.2 Methane reaction operation via catalytic oxychlorination

After preparing the reaction system, the methane oxychlorination reaction was started. Initially, air tightness tests were performed by pressurizing the reaction system to 5 bar with nitrogen to check for possible leaks. First, the gases were passed directly, without entering the reactor, to adjust the flows and stabilize the unit. Next, the reactor purge was initiated using nitrogen at 20 mL/min for 30 minutes. After purging and stabilizing the reactor, nitrogen was replaced with the reactive gas mixture by means of the valve in the by-pass position, that is, without crossing the catalytic bed. Subsequently, the reactor heating was then programmed by the electronic temperature controller to a heating rate of 10 K/min. Then, the reactive gas mixture was fed to the reactor. Finally, at the end of the reaction, the reactor was cooled to room temperature under

nitrogen flow and prepared for execution of the other experiments. The procedures described above were repeated for the 6 CuCl₂/SiO₂ and 3 CuCl₂/SiO₂.

3. RESULTS AND DISCUSSION

3.1 Catalyst syntheses and characterization

The results of the thermogravimetric analyses showed that the decomposition of the tetraamminecopper(II) sulfate complex of the samples containing 3 and 6 % copper occurred in two distinct regions, as seen in the graphs of Figure 2.

In the non-calcined sample with 3 % copper, the first region, from approximately 298 to 450 K, there

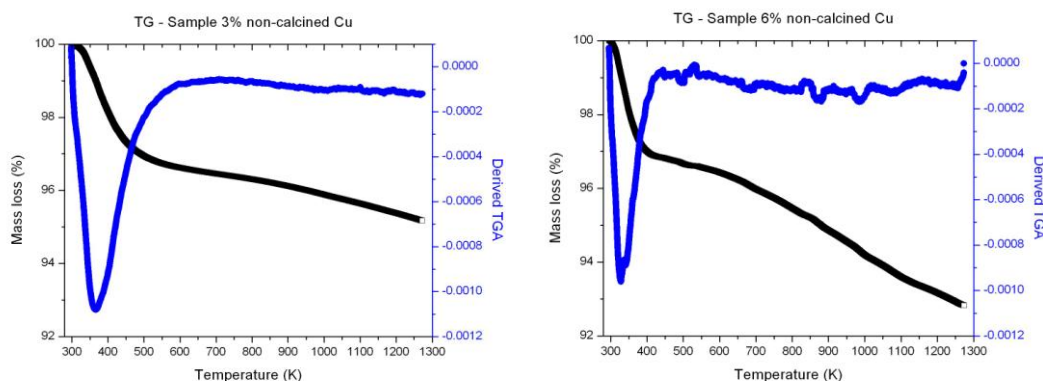


Figure 2. TG analysis of the non-calcined sample with 3 % and 6 % copper.

is a mass change that can be attributed to the water adsorbed in the material, whereas in the second region, from 450 K, the mass loss can probably be attributed to the breaking of the tetraamminecopper(II) sulfate complex bonds. It is also observed that there were mass losses of 3 % and 2 % in the first and second region, respectively.

In the non-calcined sample with 6 % copper, in the first region, from approximately 298 to 400 K, there was a mass variation that can also be attributed to the water adsorbed in the material, whereas in the second region, from 400 K, the mass loss can probably be attributed to the breaking of the tetraamminecopper(II) sulfate complex bonds. Higher mass loss was observed for the sample with 6 % copper, in the first and second regions, whose percentages were around 3 % and 5 %, respectively.

The results of the thermogravimetric analyses indicated that the mass loss of the copper oxide of the samples with copper contents of 3 and 6 %

Table 3. XRF analyses of the samples with 3 and 6 % copper.

Material	Cu (%)	Si (%)	O (%)	Cl (%)	Impurities (%)
3 CuCl ₂	3.08	43.24	50.31	2.97	0.40
6 CuCl ₂	5.89	43.39	47.87	5.46	0.39

occurred in two distinct temperature ranges, in accordance with the graphs of Figure 3.

In the calcined sample with 3 % copper, the first region, from approximately 298 to 375 K, there was a mass variation that can be attributed to the water adsorbed in the material, whereas in the second region, from 375 K, the mass loss probably can be attributed to the breaking of the copper oxide bonds. There were mass losses of 2.5 % and 4.5 % in the first and second regions, respectively. In the sample with 6 % copper, the results were similar to those of the sample with 3 %.

The mass loss did not exceed 7 % in any of the calcined or non-calcined samples. In addition, the derivatives relative to the thermogravimetric analyses showed just one well-defined endothermic peak, which confirms that the first regions of each analysis correspond to dehydration steps, and the absence of other peaks indicates that the samples are thermally stable up to a temperature of 1,300 K. The impregnation of the metal in the supported samples with metal loads of 3 and 6 % copper was effective according to the results shown in Table 3, obtained from the X-ray fluorescence (XRF) analyses.

In the synthesized samples, the maximum impurity percentage was 0.40 %, demonstrating the efficiency of the washing step during preparation. The experimental error obtained was 2.67 % for the sample with a metal load of 3 % and 1.83 % for the sample with a metal load of 6 %, showing that the impregnation process of copper onto silica can be used to prepare catalysts for the oxychlorination of methane. The chemical composition of the catalyst samples (relative to silicon and oxygen) showed similar percentage. Figure 4 (A, B and C) shows the images, obtained by SEM, of the support (silica) and the 3 CuCl₂/SiO₂ and 6 CuCl₂/SiO₂ catalyst samples, respectively.

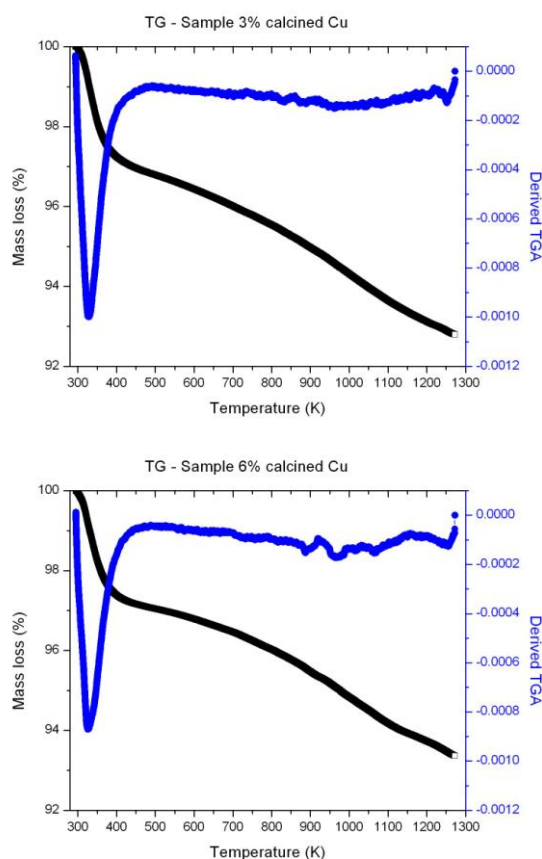
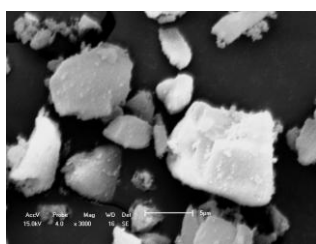


Figure 3. TG analysis of the calcined sample with 3 % and 6 % copper.



(A) - support (silica)

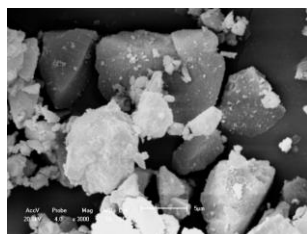
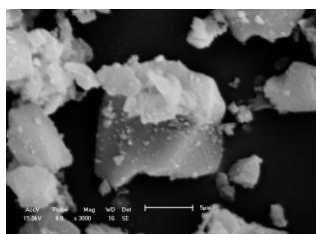
(B) - 3 CuCl₂/SiO₂(C) - 6 CuCl₂/SiO₂

Figure 4. SEM of support (A), 3 CuCl₂/SiO₂ (B), and 6 CuCl₂/SiO₂ (C).

The SEM photographs of the CuCl₂/SiO₂ catalyst obtained in the experiments of [Zhang et al. \(2009\)](#) were similar to those obtained in this study. As expected, these images showed that the particles are amorphous and that the support, after impregnation of copper and chlorination, showed no morphological changes under the conditions examined by SEM. Moreover, it was not possible to identify nor classify particles of copper or other elements or even detect any metallic dispersion. From the results of the exact chemical analysis of the 3 CuCl₂/SiO₂ and 6 CuCl₂/SiO₂ catalyst samples via SEM-coupled EDS, it was observed that copper was apparently distributed in the samples, according to Figure 5 (A and B). The exact results of the chemical composition analyses were confirmed by X-ray fluorescence (XRF).

Table 4 shows the results of the specific area and specific pore volume analyses provided by the BET technique for the support and catalyst samples.

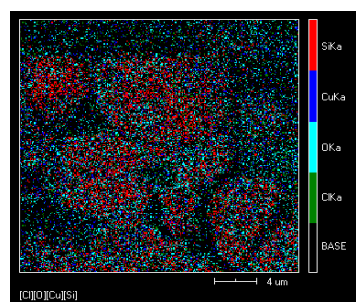
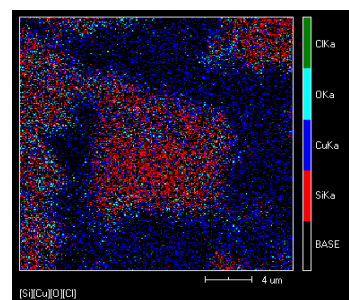
(A) 3 CuCl₂/SiO₂(B) 6 CuCl₂/SiO₂

Figure 5. Exact chemical analysis of 3 CuCl₂/SiO₂ and 6 CuCl₂/SiO₂ by SEM-EDS.

It can be observed that the specific areas of the catalyst samples were smaller than the support area, decreasing as the copper content increased. Therefore, it is possible to assume that the impregnation method used caused the blockage of the support pores. According to [Guerreiro et al. \(1997\)](#), this may be due to long contact time with the [Cu(NH₃)₄]⁺² solution at the high pH used to perform the ion exchange. The specific pore volume of the samples was the same. Differently, the specific volume of the support was reduced to 8 %, which supports the evidence of the hypothesis of pores' blockage.

Figure 6 (A and B) shows the TPR profiles of the samples. The graphs confirm the formation of copper oxide during the calcination process at 773

Table 4. Specific area and specific pore volume of the support and the catalyst via the BET technique.

Material	Specific area (m ² /g)	Specific pore volume (cm ³ /g cat.)
Silica	179.14	0.26
3 CuCl ₂	175.85	0.24
6 CuCl ₂	166.37	0.24

K for 3 hours. Reduction peaks are observed at 434 and 631 K for the sample with 3 % copper, and at 439 and 634 K for the sample with 6 % copper.

It can be observed that the formation temperatures of the sample with 6 % copper were higher when compared with those of the 3 % sample. This variation is due to enhanced interactions of the copper atoms caused by the increased density of the catalytic sites, in addition to the metal/support interactions, which have much lower intensities.

The total hydrogen consumption was 0.43 mL for the sample with 3 % copper and 0.53 mL for the 6 % sample. In this characterization, it was expected that the hydrogen volume consumed for the sample with 6 % would be double that of the sample with 3 %. This did not occur, probably due to the lack of uniformity in calcination, which means that the sample should be calcined for longer (12 hours) and at a higher temperature (700 K).

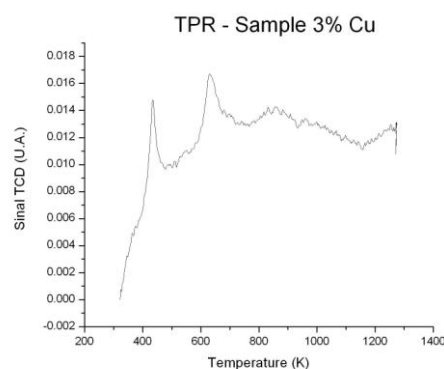
The results also indicate that the TPR profiles of the CuO/SiO₂ samples displayed more than one reduction peak, which can be attributed to the existence of more than one kind of copper, consistent with research results reported by Shimokawabe et al. (1983), Guerreiro et al. (1997), Liu et al. (2006), and Zhu et al. (2008). The finding of more than one reduction peak suggests that the Cu⁺² species had been reduced in stages until the Cu⁰ species, that is, Cu⁺² to Cu⁺¹, and then Cu⁺¹ to Cu⁰, as proposed by Shimokawabe et al. (1983).

3.2 Catalyst tests

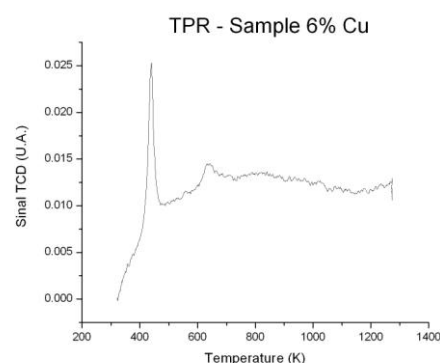
3.2.1 Influence of copper content and temperature

Table 5 shows the methane conversions of the catalyst samples with metal loads of 3 and 6 % copper at 673 and 773 K. The methane conversion obtained with the 3 CuCl₂/SiO₂ catalyst at 673 K was 9.8 % in the initial stages, decreasing with time. After 135 minutes of reaction, the conversion was reduced to nearly zero, indicating a probable poisoning of the catalyst's active sites.

At the same temperature, the 6 CuCl₂/SiO₂ catalyst enabled a methane conversion of 16.3 % in the first moments, but by the end of the reaction (after 135 min) the conversion was reduced to 12.7



(A) 3 CuCl₂/SiO₂



(B) 6 CuCl₂/SiO₂

Figure 6. TPR profile of the CuO/SiO₂ sample with 3 % and 6 % copper.

%, indicating that the increase in copper content seems to minimize the catalyst activity loss, keeping it fairly stable during the reaction. When the catalyst samples were tested at a temperature of 773 K, the methane conversion for the samples with 3 and 6 % copper were similar.

Comparing the results of the experiments at temperatures of 673 and 773 K, it is possible to observe that, regardless of the copper content impregnated, methane conversion was reduced as the temperature of the reaction medium increased. This result may be an evidence of catalyst sintering at high temperatures. According to Garcia and Resasco (1987), increasing the

Table 5. Methane conversion.

Catalyst	Methane conversion (%)	Reaction Temperature (K)
3 CuCl ₂	9.8	673
6 CuCl ₂	16.3	673
3 CuCl ₂	3.8	773
6 CuCl ₂	5.0	773

reaction temperature in catalytic oxychlorination causes an increase in the CuCl_2 volatility, inducing loss of catalytic activity. This fact may also help to explain why lower methane conversion is effected at higher reaction temperatures.

It has been confirmed that the copper load and the reaction temperature affect the catalytic activity in the methane oxychlorination reaction. Therefore, in this study, factors such as CuCl_2 volatility, small size of the catalytic bed (which reduce the residence time of the reaction components), probable formation of preferential channels in the bed (impairing the interaction between the bed and the reagent gases), and the catalyst's own deactivation may have contributed to the low methane conversions obtained in the oxychlorination process.

4. CONCLUSIONS

From the characterization results, it can be stated that the impregnation method via ion exchange in a basic medium, applied in $\text{CuCl}_2/\text{SiO}_2$ catalyst synthesis with variable copper content, to be applied in the oxychlorination of methane, proved to be satisfactory once the presence of copper in the structure of the synthesized material was confirmed. It was found that increased copper content leads to a reduction in the catalyst's specific area. The experimental errors relative to the nominal values of the metal were less than 3 %.

According to the results of the catalytic tests, it appears that both the amount of impregnated copper and the reaction temperature exert an important influence on the conversion of methane. The 6 $\text{CuCl}_2/\text{SiO}_2$ catalyst sample provided a better conversion at a temperature of 673 K.

5. REFERENCES

- Brunelle, J. P. Preparation of catalysts by metallic complex adsorption on mineral oxides. **Pure and Applied Chemistry**. v. 50, n. 9/10, p. 1211-1229, 1978. [doi:10.1351/pac197850091211](https://doi.org/10.1351/pac197850091211)
- Garcia, C. L.; Resasco, D. E. Promoter action of KCl on $\text{CuCl}_2/\text{SiO}_2$ catalysts used for the oxyhydrochlorination of methane. **Applied Catalysis**. v. 29, p. 55-66, 1987. [doi:10.1016/S0166-9834\(00\)82606-8](https://doi.org/10.1016/S0166-9834(00)82606-8)
- Garcia, C. L.; Resasco, D. E. Effects of the support and the addition of a second promoter on potassium chloride-copper II chloride catalysts used in the oxychlorination of methane. **Applied Catalysis**. v.46, p. 251-267, 1989. [doi:10.1016/S0166-9834\(00\)81121-5](https://doi.org/10.1016/S0166-9834(00)81121-5)
- Guerreiro, E. D.; Goriz, O. F.; Rivarola, J. B.; Arrúa, L. A. Characterization of Cu/SiO_2 catalysts prepared by ion Exchange for methanol dehydrogenation. **Applied Catalysis A: General**. v. 165, p.259-271, 1997. [doi:10.1016/S0926-860X\(97\)00207-X](https://doi.org/10.1016/S0926-860X(97)00207-X)
- Liu, J.; Lu, X.; Zhou, G.; Zhen, K.; Zhang, W.; Cheng, T. Effect of KCl on $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst for oxychlorination of ethane. **Reaction Kinetics and Catalysis Letters**. v. 88, n. 2, p. 315-323, 2006. [doi:10.1007/s11144-006-0067-6](https://doi.org/10.1007/s11144-006-0067-6)
- Perego, C.; VILLA, P. Catalyst preparation methods. **Catalysis Today**. v. 34, p. 281-305, 1997. [doi:10.1016/S0920-5861\(96\)00055-7](https://doi.org/10.1016/S0920-5861(96)00055-7)
- Reddy, U. V.; Cheendipudi, V. L.; Bankupalli, S.; Kotra, V. Recovery of chlorine from anhydrous hydrogen chloride. **International Journal of Chemical Reactor Engineering**. v. 6, n. A97, 2008.
- Shimokawabe, M.; Takezawa, N.; Kobayashi, H. Temperature programmed reduction of copper-silica catalysts prepared by ion exchange method. **The Chemical Society of Japan**. v. 56, n. 5, p. 1337-1340, 1983. [doi:10.1246/bcsj.56.1337](https://doi.org/10.1246/bcsj.56.1337)
- Zhang, T.; Troll, C.; Rieger, B.; Kintrup, J.; Schlüter, O. F. K.; Weber, R. Reaction kinetics of oxychlorination of carbon monoxide to phosgene based on copper II chloride. **Applied Catalysis A: General**. v. 357, p.51-57, 2009. [doi:10.1016/j.apcata.2008.12.035](https://doi.org/10.1016/j.apcata.2008.12.035)
- Zhu, W.; Wang, L.; Liu, S.; Wang, Z. Characterization and catalytic behavior of silica-supported copper catalysts prepared by impregnation and ion-exchange methods. **Reaction Kinetics and Catalysis Letters**. v. 93, n. 1, p. 93-99, 2008. [doi:10.1007/s11144-008-5178-9](https://doi.org/10.1007/s11144-008-5178-9)