

## NiO and ZrO<sub>2</sub> impregnation in KIT-6 by excess solvent and mechanochemistry: A comparison

Jesyka Macêdo Guedes<sup>a,\*</sup>, Fernando Rodrigo Dantas Fernandes<sup>b</sup>,  
Adriana Paula Batista dos Santos<sup>c</sup>, Miguel Martins dos Santos Neto<sup>c</sup>,  
Alexandre Magno Rodrigues Teixeira<sup>d</sup>, Emmanuel Silva Marinho<sup>a</sup>,  
Jane Eire Silva Alencar de Menezes<sup>a</sup>, Kaio Gráculo Vieira Garcia<sup>e</sup>, Anne Gabriella Dias Santos<sup>c</sup>,  
Hélcio Silva dos Santos<sup>f</sup>

<sup>a</sup> State University of Ceará, Department of Science and Technology, Fortaleza, Brazil

<sup>b</sup> Federal University of Rio Grande do Norte, Department of Chemistry, Natal, Brazil

<sup>c</sup> State University of Rio Grande do Norte, Department of Chemistry, Mossoró, Brazil

<sup>d</sup> Regional University of Cariri, Department of Biological Chemistry, Crato, Brazil

<sup>e</sup> Federal University of Ceará, Department of Soil Sciences, Fortaleza, Brazil

<sup>f</sup> State University of Acaraú Valley, Department of Science and Technology, Sobral, Brazil

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### ABSTRACT

Metal oxides have been widely used in heterogeneous catalysis. One of the most used methods currently to impregnate metallic oxides in inorganic supports is the wet method, however, this has some disadvantages. In this work, the impregnation of NiO and ZrO<sub>2</sub> in KIT-6 was carried out by the excess solvent and mechanochemical method to compare the most advantageous method. The obtained materials were characterized by X-ray diffraction analysis (XRD), X-ray fluorescence spectrometry (XRF), scanning electron microscopy (SEM) and N<sub>2</sub> adsorption and desorption. The results revealed that the impregnation did not modify the typical structure of the support. Moreover, the insertion of the oxides promoted a decrease in the specific area and in the total volume of pores. The catalysts showed similar characteristics for both methods. However, when considering time and other subsequent steps, the mechanochemical method was considered more advantageous.

### 1. Introduction

Metal oxides are excellent catalysts and can be impregnated into rigid porous structures to improve their structural and textural characteristics [1]. Ordered mesoporous silicas, such as KIT-6, are a promising option due to their cubic structure, high thermal stability, micropore system interconnecting the mesopores and high specific area [2].

Among the most used impregnation methods, wet impregnation stands out, which occurs in the presence of a solvent. However, this method requires an additional step of drying the material, implying a longer synthesis time. In contrast, mechanochemical impregnation (solvent-free) is promoted by mechanical force and frictional heating, occurs in a single step and is considered faster [3]. This study proposed for the first time to compare these two methods in impregnation of NiO and ZrO<sub>2</sub> in KIT-6, evaluating the structural and textural properties of

the obtained catalysts.

### 2. Material and methods

#### 2.1. Support synthesis - KIT-6

The synthesis of KIT-6 was carried out under acidic conditions by the hydrothermal method proposed by Kleitz et al. [4]. First, concentrated 37% HCl solution (7.6 ml) and Pluronic P123 (4.9 g) were dissolved in distilled water (176.4 ml). After 6 h, n-butanol (6 ml) was added. After 1 h, tetraethyl Orthosilicate (11.4 ml) was added, and this mixture remained for 24 h under the same conditions. Then, the resulting gel was aged in a Teflon autoclave at 100 °C for another 24 h. Next, the precipitated product was cooled, filtered, washed with an alcoholic solution of HCl (2%), dried at 100 °C for 12 h, and finally calcined in a

\* Corresponding author at: State University of Ceará, Department of Science and Technology, Ave. Dr. Silas Munguba, 1700, 60.714-903 Fortaleza, Brazil.

E-mail address: [jesyka.mg@gmail.com](mailto:jesyka.mg@gmail.com) (J. Macêdo Guedes).

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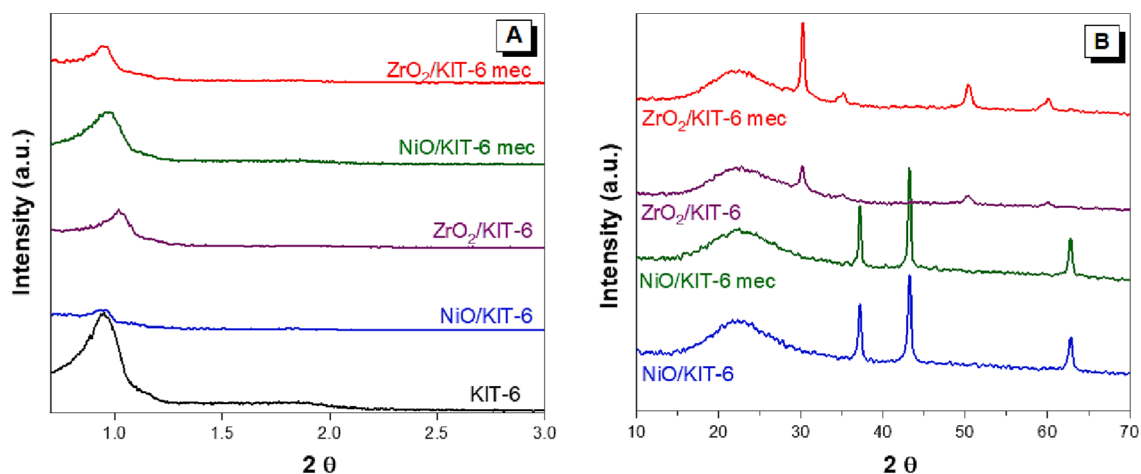


Fig. 1. XRD. Small angle (A) and Large angle (B).

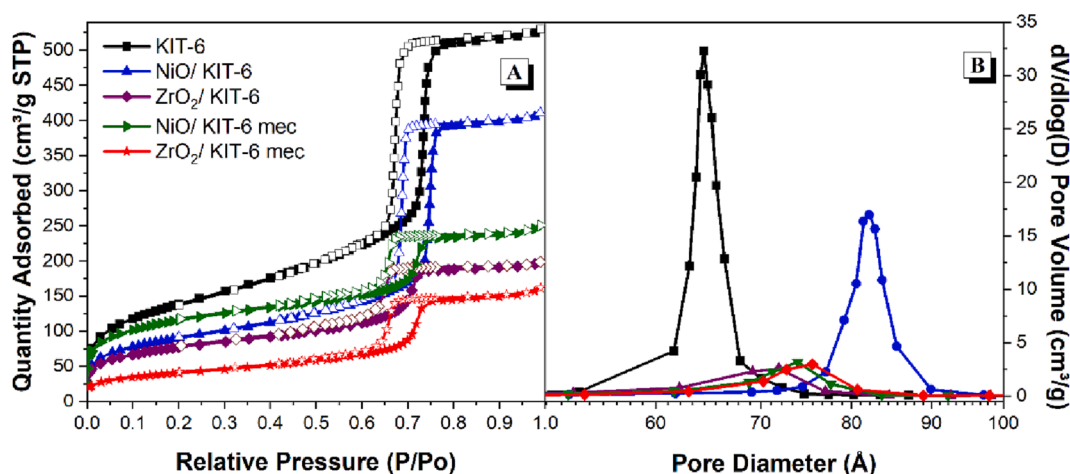


Fig. 2. N<sub>2</sub> Adsorption-desorption isotherms (A) and Average pore diameter (B).

Table 1

Summary of textural properties, values of interplanar distances ( $d_{(211)}$ ) and unit cell parameters ( $a_0$ ).

Sample	$S_{\text{BET}}$ (m <sup>2</sup> /g) <sup>a</sup>	$V_{\text{T}}$ (cm <sup>3</sup> /g) <sup>b</sup>	$d_{\text{p}}$ (nm) <sup>c</sup>	$d_{(211)}$ (nm)	$a_0$ cubic (nm)
KIT-6	501	0.99	6.4	8.7	21.4
NiO/KIT-6	323	0.63	8.2	9.3	22.78
ZrO <sub>2</sub> /KIT-6	276	0.31	7.1	8.7	21.31
NiO/KIT-6 mec.	410	0.39	7.3	9.2	22.55
ZrO <sub>2</sub> /KIT-6 mec.	149	0.25	7.5	9.1	22.31

<sup>a</sup>  $S_{\text{BET}}$  = Specific surface area calculated by the BET method; <sup>b</sup>  $V_{\text{T}}$  = Total pore volume calculated by the BHJ method in  $p/p_0 = 0.98$ ; <sup>c</sup>  $d_{\text{p}}$  = Pore diameter calculated by the BHJ method.

muffle at 550 °C with a heating ramp of 10 °C min<sup>-1</sup> for 6 h.

## 2.2. Support impregnation

10% of oxide about the mass of the support was impregnated, using the same precursors (0.224 g of NiCl<sub>2</sub> and 0.14 g of ZrO(NO<sub>3</sub>)<sub>2</sub>) for both processes. The materials impregnated by excess solvent were named NiO/KIT-6 and ZrO<sub>2</sub>/KIT-6, while the materials impregnated by mechanochemistry were named NiO/KIT-6 mec and ZrO<sub>2</sub>/KIT-6 mec. All materials were calcined at 550 °C for 6 h with a heating ramp of 10 °C

min<sup>-1</sup>.

## 2.3. Impregnation by excess solvent

The oxide source was dissolved in distilled water, and after dissolution, the support was added, this mixture remained under constant agitation at 70 °C until a gel was formed. After that, the mixture was placed in an oven for 12 h at 70 °C [5].

## 2.4. Mechanochemical impregnation

Mechanochemical impregnation was carried out in a ball mill with a 250 ml reaction chamber, 8 mm stainless steel spheres and processing at 350 rpm for 20 min, using 14 spheres [6].

## 2.5. Catalysts characterization

The XRD was carried out using the Rigaku - Mini Flex II equipment. The XRF by the Bruker S2 Ranger device. The N<sub>2</sub> adsorption/desorption isotherms were determined using Micromeritics ASAP 2020. And the SEM was performed on the MIRA3 FERG equipment. More details are described in [Supplementary Material](#).

## 3. Results and discussion

The low-angle XRD diffraction peaks in [Fig. 1a](#) show three Miller

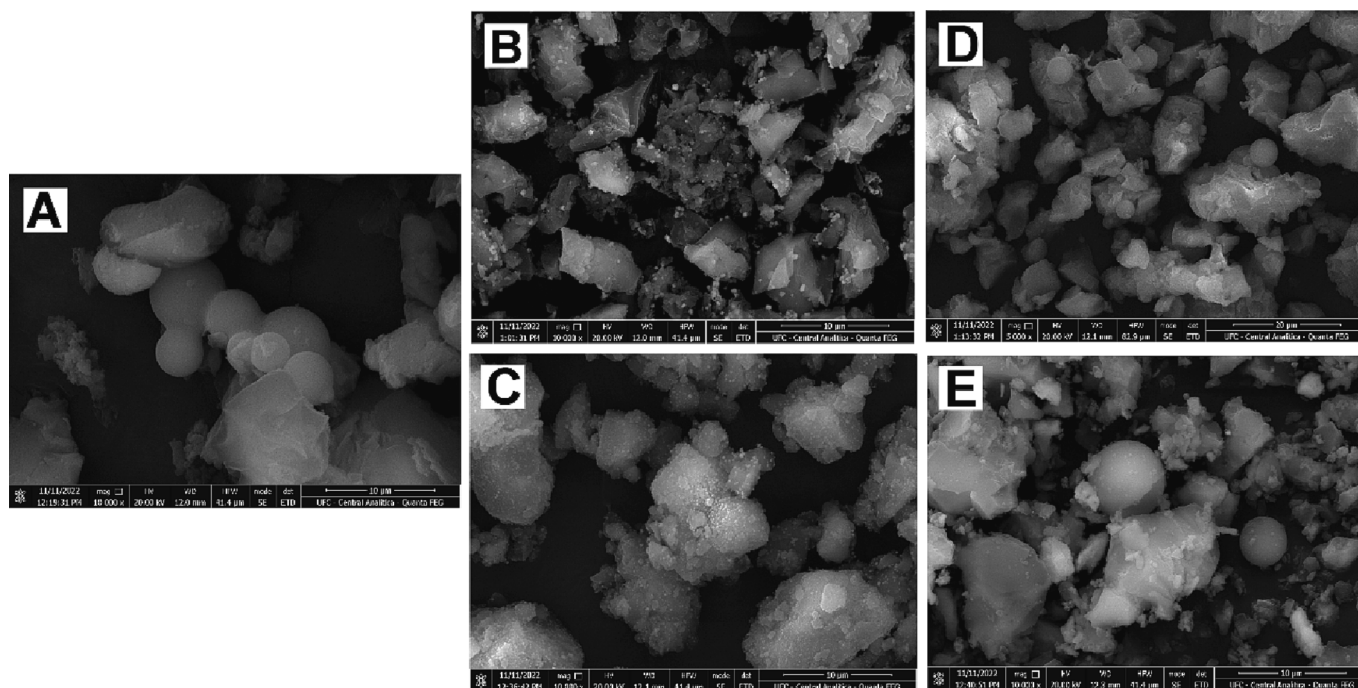


Fig. 3. SEM images. KIT-6 (A), NiO/KIT-6 (B), NiO/KIT-6 mec (C); ZrO<sub>2</sub>/KIT-6 (D) and ZrO<sub>2</sub>/KIT-6 mec (E).

indices characteristic of the mesoporous structure of KIT-6 (211) (220) and (332), indicating uniform pore distribution and space group *Ia3d* [7]. The diffractogram profile indicates that the oxides' impregnation did not significantly modify the support structure, maintaining the characteristics of KIT-6.

In Fig. 1b, the materials impregnated with NiO show diffraction peaks at (111), (200) and (220), indicating the presence of the cubic polycrystalline phase of nickel oxide. The materials impregnated with ZrO<sub>2</sub>, on the other hand, exhibit diffractograms with a monoclinic phase, according to the crystallographic record (JCPDS-83-0943).

The XRF results confirm the presence of oxides in KIT-6, with percentages of 14% for NiO/KIT-6 and 20% for NiO/KIT-6 mec, values above those calculated, possibly due to the non-uniform distribution of the oxide about the support. The percentages for ZrO<sub>2</sub>/KIT-6 and ZrO<sub>2</sub>/KIT-6 mec were 6% and 9%, respectively, lower values than those calculated. This may be due to the size of the oxide formed, making it difficult to impregnate the support.

The N<sub>2</sub> adsorption/desorption isotherms (Fig. 2) of all materials are type IV, typical of mesoporous materials, and variations in hysteresis loops indicate changes in pore morphologies, the alteration of the H1 hysteresis loop (a) of the support before mechanochemical impregnation for H2 (b) indicates deposition of oxides inside the pores. The isotherm profile confirms that all materials have an orderly and uniform pore distribution maintained after impregnation [8,9].

The textural properties of the materials are listed in Table 1. It is possible to observe that the specific areas (*S*<sub>BET</sub>) and the total pore volume (*V*<sub>T</sub>) decrease with the impregnation of the oxides, indicating that the metallic oxides are dispersed on the surface of the mesoporous silica. On the other hand, the average pore diameter increases after impregnation, indicating that the oxides are inside the smaller mesopores, shifting the distribution profile to larger pore diameters, a fact related to the decrease in the total pore volume [10,11].

Table 1 shows the (*d*<sub>211</sub>) and (*a*<sub>0</sub>) values of the obtained catalysts. Due to the contraction of the unit cell, there was a small displacement to larger angles with the impregnation of metallic oxides in the support. The unit cell parameter (*a*<sub>0</sub>) of the plane (211) for the pure support was smaller when compared to the impregnated materials, this may indicate that the pores of the material were affected due to the presence of oxides

inside the pores [12].

SEM images (Fig. 3) of all catalysts show compacted, rock-like morphology with irregular shapes and sizes [12]. It is possible to identify that the catalysts impregnated with NiO present some agglomerates of irregularly shaped fragments in the interparticle space, demonstrating that the oxide is not uniformly distributed in the pores, which explains the textural properties result. A similar behavior was observed by Lacoste et al. [13].

#### 4. Conclusions

The characterization techniques confirm that the KIT-6 support and the catalysts impregnated with nickel and zirconium oxides by both methods were successfully obtained. This study also demonstrated that the analyzed catalysts have good structural and textural characteristics. However, when considering the percentage of oxide present in the catalysts, time and subsequent steps, the mechanochemical method can be more advantageous than the excess solvent method, making it a promising alternative for impregnating metal oxides in inorganic supports.

#### Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Jesyka Macedo Guedes reports financial support was provided by Foundation for Scientific and Technological Development and Support of Ceará. Jesyka Macedo Guedes reports a relationship with Foundation for Scientific and Technological Development and Support of Ceará that includes: funding grants.

#### Data availability

Data will be made available on request.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matlet.2023.134512>.

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