In situ XRD study of the stability of zeolitic imidazolate frameworks as catalysts for CO_2 cycloaddition to epoxides

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Resumo/Abstract

RESUMO – Este trabalho avaliou a estabilidade de dois materiais do tipo ZIF-67 (redes zeolíticas de imidazolato) sintetizados a partir de duas fontes diferentes de cobalto: acetato e nitrato. Ambas as amostras foram caracterizadas ex situ por difração de raios X (DRX), microscopia eletrônica de varredura (MEV) e fisissorção de N_2. A caracterização in situ foi realizada na linha PAINEIRA do síncrotron Sirius, utilizando uma célula capilar, na qual as amostras foram analisadas por DRX em condições similares às da reação de cicloadição de CO_2 em epóxidos (sob atmosfera de CO_2, na presença de óxido de propileno e sob aquecimento). As análises in situ demonstraram que ambas as amostras sofreram perda de cristalinidade nas condições reacionais, sendo que a amostra sintetizada com nitrato de cobalto apresentou maior estabilidade estrutural em comparação à amostra sintetizada com acetato de cobalto, que sofreu amorfização e recristalização durante o aquecimento em condições de reação.
Palavras-chave: ZIF-67, estabilidade estrutural, cicloadição de CO_2 em epóxidos.

ABSTRACT – This work evaluated the stability of two ZIF-67 materials (zeolitic imidazolate frameworks) synthesized from two different cobalt sources: acetate and nitrate. Both samples were characterized ex situ by X-ray diffraction (XRD), scanning electron microscopy (SEM), and N_2 physisorption. In situ characterization was performed on the PAINEIRA beamline of the Sirius synchrotron, using a capillary cell in which the samples were analyzed by XRD under reaction conditions similar to those of the CO_2 cycloaddition reaction to epoxides (under a CO_2 atmosphere, in the presence of propylene oxide, and under heating). The in situ analyses showed that both samples underwent crystallinity loss under reaction conditions. However, the sample synthesized using cobalt nitrate exhibited higher structural stability compared to the one synthesized with cobalt acetate, which underwent amorphization and recrystallization during heating under reaction conditions.
Keywords: ZIF-67, structural stability, CO_2 cycloaddition to epoxides.

Introduction

The high consumption of fossil fuels has led to a significant increase in atmospheric CO_2, a major contributor to the greenhouse effect. To mitigate its presence in the atmosphere, CO_2 can be used as a carbon source in the cycloaddition reaction with epoxides to generate cyclic carbonates, which can be used as polar aprotic solvents, and polycarbonate precursors (1). Among the wide variety of materials that can be used as catalysts in the CO_2 cycloaddition reaction, zeolitic imidazolate frameworks (ZIFs), a subclass of metal-organic frameworks (MOFs), have been extensively studied due to their high porosity and utilization in the absence of solvent or co-catalyst (2). ZIF- 67 has a 3D framework and is built by connecting Co^{II} ions to 2-methylimidazole (2-MIM) linkers, showing a sodalite (SOD) topology (3). ZIF-67 has been reported as an effective catalyst in the CO_2 cycloaddition reaction with epoxides, showing high selectivity and yield to cyclic carbonates. However, recent studies have shown that its stability after recycling reactions was lower than previously anticipated (4,5). Additionally, its stability could depend on the crystal size of the ZIF (6). Thus, this work aimed to evaluate the stability of two ZIF- 67 samples (synthesized using different cobalt salts to achieve distinct crystal sizes) under reaction conditions similar to those applied in the CO_2 cycloaddition with propylene oxide.

Experimental

ZIF-67 samples were synthesized by mixing an aqueous solution of $(CH_3COO)_2Co\cdot 4H_2O$ (Z67-A) or $Co(NO_3)_2\cdot 6H_2O$ (Z67-N) with an aqueous solution of 2-methylimidazole (2-MIM) in a 1:40:555 (Co:2-MIM:H_2O) molar ratio at room temperature for 3 h. The solids were then filtered, washed until pH 7, and dried at 60 °C. All catalysts were characterized by ex situ techniques such as XRD, N_2 physisorption and SEM. Additionally, the samples were characterized by in situ XRD at the PAINEIRA beamline of the Sirius synchrotron. The samples were placed in a capillary cell, filled with propylene oxide, and pressurized with CO_2 up to 2 bar. Then, the cell was heated up to 100 ºC at a 5 ºC/min ramp, and kept at 100 ºC for 15 min. After that, the catalytic cell was cooled down to 35 ºC. XRD diffractograms were acquired in situ using an acquisition time of 60 s at a 25.53 keV energy, which was subsequently converted to the Cu Kα radiation energy for comparative purposes with literature data.

Results and Discussion

Ex situ XRD showed that both samples crystallized solely in the SOD topology. The use of different salts as cobalt precursors resulted in particles with a similar truncated rhombic dodecahedral shape, although with substantially different crystal sizes. The sample synthesized with cobalt nitrate (Z67-N) showed crystal sizes of approximately 250 nm, in contrast to the sample synthesized with cobalt acetate (Z67-A), which displayed crystal sizes of about 750 nm.

The porosity of the samples was assessed by N_2 physisorption. Both samples displayed type I isotherms, typical of microporous materials. The BET specific surface areas of samples Z67-A and Z67-N were 1850 and 2055 m^2/g, respectively. The higher BET specific surface area of the sample Z67-N is most likely due to its lower crystal size.

Recently, it has been demonstrated that ZIF-67 exhibits a loss in crystallinity after being utilized as a catalyst in CO_2 cycloaddition reactions with epoxides, and its stability is dependent on the initial morphology, crystal size, and porosity (4,5). To gain further insights into the loss of crystallinity during CO_2 fixation reactions, both Z67-A and Z67-N were analyzed in situ by XRD at the PAINEIRA beamline of the Sirius synchrotron. Figure 1 shows the diffractograms of Z67-N under different environments. When propylene oxide (PO) was added to the reaction cell at room temperature and the pressure was increased up to 2 bar of CO_2, an elevation of the baseline was observed between 15 and 25º of 2θ in the diffractogram, which is attributed to the presence of liquid PO inside the cell. After increasing the temperature up to 100 ºC, the PO vaporized, and the baseline returned to a flat profile. After 15 min at 100 ºC, the temperature was reduced, and the diffractogram collected (after reaction) showed a significant reduction in intensity, indicating a loss of crystallinity.

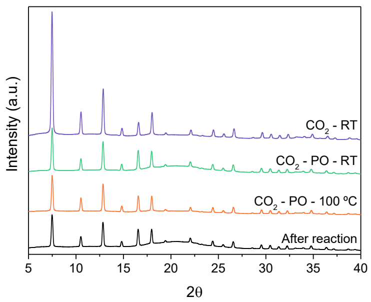

Figure 1. In situ XRD diffractograms measured under CO_2 fixation reaction conditions for sample Z67-N.

The Z67-A sample was measured at the same reaction conditions (Figure 2); however, this sample experienced a greater loss of crystallinity after being applied as a catalyst (after reaction). Interestingly, during the in situ heating process, the Z67-A sample underwent amorphization at 40 ºC, followed by recrystallization at 90 ºC (Figure 3), a behavior that was not observed for Z67-N. This amorphization/recrystallization process indicates that Z67-A has lower stability under reaction conditions, which could affect its catalytic properties.

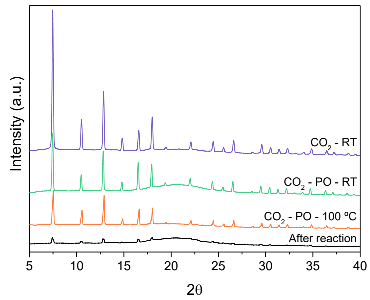

Figure 2. In situ XRD diffractograms measured under CO_2 fixation reaction conditions for sample Z67-A.

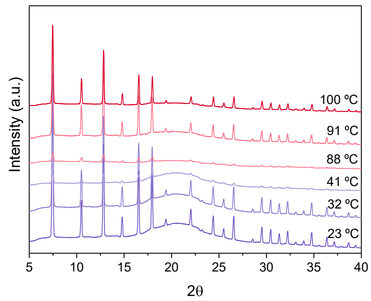

Figure 3. In situ XRD diffractograms collected during heating under reaction conditions for sample Z67-A.

Conclusions

The stability of ZIF-67 catalysts under reaction conditions depends on the cobalt source used in its synthesis. In situ XRD measurements during heating in the presence of CO_2 and propylene oxide showed that the sample prepared using cobalt nitrate exhibited higher structural stability than the sample prepared using cobalt acetate.

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