Macauba-derived biochar support for FeZn-K catalysts in the CO_2 hydrogenation to olefins

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Resumo/Abstract

RESUMO – A pirólise de biomassa lignocelulósica é uma rota promissora para a produção de suportes carbonáceos aplicáveis em catálise heterogênea. Neste trabalho, o endocarpo de macaúba foi pirolisado a 400 °C e 700 °C com o objetivo de obter suportes de carbono com diferentes propriedades físico-químicas. Os materiais foram aplicados na hidrogenação de CO_2, no contexto da síntese de Fischer–Tropsch modificada para olefinas (CO_2-FTO), como suportes para catalisadores de FeZn-K preparados por impregnação ao ponto úmido.
Palavras-chave: Suportes de carbono, Bio-carvão, Pirólise controlada, Endocarpo de macaúba, Hidrogenação de CO_2.

ABSTRACT - The pyrolysis of lignocellulosic biomass is a promising route for producing carbonaceous supports applicable in heterogeneous catalysis. In this work, macauba endocarp was pyrolyzed at 400 °C and 700 °C to obtain carbon supports with different physicochemical properties. The materials were applied in CO_2 hydrogenation, in the context of the modified Fischer–Tropsch synthesis for olefins (CO_2-FTO), as supports for FeZn-K catalysts prepared by incipient wetness impregnation.
Keywords: Carbon supports, Biochar, Controlled pyrolysis, Macauba endocarp, CO_2 hydrogenation.

Introduction

Catalysis emerges as a promising strategy to convert CO_2 into low-carbon products, which are feedstocks for the chemical industry (1). Modified Fischer–Tropsch synthesis (CO_2-FT) is one of the possible routes, with its efficiency reported in the literature to be associated with the *in-situ* formation of active iron carbide phases (2). In this context, iron catalysts supported on carbon-based materials, such as nanotubes, graphene, and chars, have been explored. The synthesis of biochar via pyrolysis of lignocellulosic biomass is highlighted as an interesting form of carbon-supports production, on which the physicochemical properties are influenced by the pyrolysis temperature (3). Iron catalysts are well known for their higher selectivity towards olefins, especially under alkaline-metals promotion such as potassium (4). Zinc promoted iron catalysts have also been found to increase the catalyst stability (5).

In this context this work aims to evaluate the physicochemical properties of macauba-derived biochars pyrolyzed under different temperatures and evaluate their use as support for FeZn-K catalysts in the CO_2 hydrogenation to olefins.

Experimental

Macauba Pyrolysis

Macauba endocarp samples (40 g) were processed and sieved to 2-4 mm particle size, and pyrolyzed on a vertical quartz tubular reactor located inside of a furnace and coupled on a condenser flask under cold water bath. The temperature on the furnace wall and in the fixed sample bed were controlled and measured respectively. Two temperatures of pyrolysis were chosen based on thermogravimetric analysis, 400 °C right after cellulose and hemicellulose depolymerization and 700 °C, after most of the biomass was decomposed into biochar. Pyrolysis was carried out under 300 mL/min N_2 with the following dynamic heating, including heating rates and soakings, to ensure effective control and minimize temperature peaks: (a) PMC400: RT-130 °C (10 °C/min); 130 °C/1 h; 130-230 °C (10 °C/min); 230 °C/15 min; 230-330 ºC (2.5 °C/min); 330-400 ºC (1 °C/min); 400 °C/1 h; (b) PMC700: RT-130 ºC (10 °C/min); 130 °C/1 h; 130-230 ºC (10 °C/min); 230 °C/15 min; 230-400 ºC (2.5 °C/min); 400-700 ºC (10 °C/min); 700 °C/1 h.

Catalysts preparation

PMC400 and PMC700 biochars were impregnated by incipient wetness with $Fe(NO_3)_3{\cdot}9H_2O$ and $Zn(NO_3)_2{\cdot}6H_2O$ aqueous solution at a 3:1 Fe:Zn molar ratio and 10% Fe/support mass ratio, then dried at 100 °C overnight and calcined for 4 hours at 400 °C under 50 ml/min N_2. KNO_3 aqueous solution was then used to impregnate at 2% K/support mass ratio, dried and calcined under the same conditions. The catalysts were codified as FeZn-K/PMC400 and FeZn-K/PMC700, based on their respective supports.

Catalysts characterization

X-ray diffraction (XRD) patterns were obtained using a Rigaku MiniFlex 600 (6th generation) diffractometer with Cu-Kα radiation source in the range of 15-90°, with a scanning rate of 10°/min and step of 0.01°. Surface areas

were measured at -196 °C via N_2 physisorption using an ASAP 2020 Micromeritics instrument. Raman spectra were obtained by Raman Microscope Xplora Plus with $\lambda = 680$ nm laser in the range 900-2000 cm^{-1}. Attenuated Total Reflectance - Fourier Transform Infrared Spectroscopy (ATR-FTIR) was conducted on a Perkin Elmer Frontier FT-IR/NIR Spectrometer in the range of 4000-600 cm^{-1}.

Catalysts evaluation

Catalytic tests were performed using 500 mg of catalyst in a fixed-bed reactor at 320 °C, 3 MPa, with a H_2/CO_2 molar ratio of 3, and a gas hourly space velocity (GHSV) of 4000 $mL \cdot g\_cat^{-1} \cdot h^{-1}$. Prior to reaction, the catalysts were pretreated in situ at 350 °C for 8 hours under a continuous flow of pure H_2 (50 $mL \cdot min^{-1}$). The reactor effluents were analyzed using a Shimadzu GC-2030 gas chromatograph equipped with a Carboxen 1010 PLOT column, a CP-SIL 5 CB column, and both TCD and FID detectors.

Results and discussions

The biomass pyrolysis temperature control was achieved by a dynamic heating rate until 400 °C or 700 °C. Low temperature pyrolysis leads to low surface area, with PMC400 support achieving <10 m^2/g, whereas high pyrolysis temperatures provide higher BET surface area, with PMC700 = 361 m^2/g.

FTIR and Raman analyses, Figure 1a and 1b indicate a reduction in the quantity of functional groups present on biochar produced at higher temperatures. FTIR analysis for PMC400 identified oxygenated groups such as C=O and C-O, while Raman analysis demonstrated a decrease in the I_D/I_G ratio from 0.9 to 0.84 as temperature increased. This suggests that the defect band becomes less prominent relative to the graphitic band, likely due to the loss of functional groups at elevated temperatures. FTIR for PMC700 will be carried out for comparison.

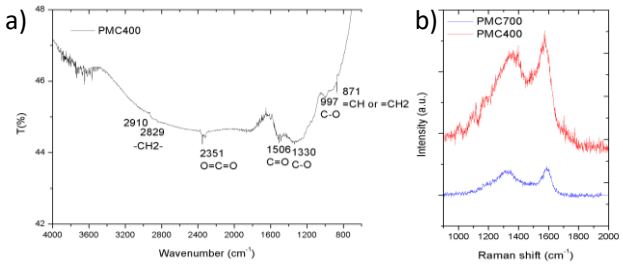

Figure 1. a) FTIR PMC400 b) Raman spectroscopy.

The biochars and catalysts were analyzed using XRD, which indicated the presence of amorphous carbon in the supports and $ZnFe_2O_4$ crystalline phase (PDF#22-1012), as shown in Figure 2.

The catalytic performance after 24 hours on stream is summarized in Table 1 and indicates that FeZn-K/PMC400 yields slightly more olefin products than FeZn-K/PMC700. Triplicates will be still carried out to confirm the statistical difference. The light hydrocarbon (C_2-C_4) O/P ratios are 4.5 for FeZn-K/PMC400 and 4.3 for FeZn-K/PMC700, while the heavy hydrocarbon (C_{5+}) O/P ratios are 3.1 and 0.8, respectively. Literature suggests that a higher O/P ratio may be associated with improved oxide dispersion, leading to higher iron carbide dispersion, potentially facilitated by surface functional groups from the biochar that provide anchoring sites, particularly on biochars pyrolyzed at lower temperatures despite their lower surface area (3). The formation and stability of iron carbide phases, as well as morphology, structure, and reactivity, remain to be more deeply characterized.

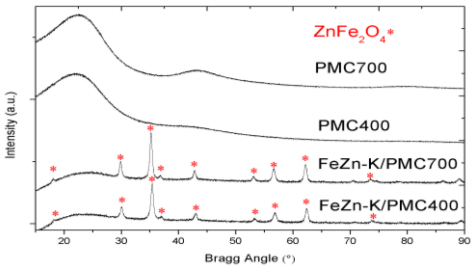

Figure 2. XRD diffractogram for catalysts and supports

Table 1. Catalytic performance of FeZn-K catalysts

Sample	CO_2 Conv (%)	CO Sel (%)	Hydrocarbon distribution (molar%)					O/P	Olefins Yield (%)
			CH_4	C_{2-4}^0	$C_{2-4}^=$	C_{5+}^0	$C_{5+}^=$		
FeZn-K/PMC400	38.3	21	27.2	10.3	46.5	3.9	12.1	3.9	17.7
FeZn-K/PMC700	37.8	17	24.5	9.9	42.6	12.9	10.2	2.3	16.6

Conclusions

The physicochemical properties of the supports, especially affected by pyrolysis temperature, are likely to have influence on the catalyst activity by affecting biochar characteristics. Lower-temperature pyrolysis may increase oxygenated groups in biochar, enhancing iron active phase dispersion and activity towards olefins. Further testing and characterization are required for confirmation.

References

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