

Rice Husk Ash Modified with Vanadium Pentoxide

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Abstract: Rice husk collected in Barreiras City, Bahia, Brazil was converted to rice husk ash (RHA) by acidic or basic leaching, followed by calcination. The resulting RHA was modified with vanadium pentoxide (2, 5, or 10 mass% of V₂O₅). The modified RHA samples were characterized by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). RHA exhibited FTIR bands associated with silica. After modification of acid-leached RHA with vanadium, the XRD data indicated the formation of V₂O₅ phases. Base-leached RHA modified with vanadium pentoxide showed the presence of the V₂O₅ phase only in the sample containing 10 mass% V₂O₅. The FTIR data indicated the formation of cristobalite, where bands associated with Si-O-V interactions were observed only for the sample with 10 mass% V₂O₅ prepared with acid-leached RHA.

Keywords: catalysts; rice husk ash; vanadium pentoxide

1. INTRODUCTION

Several studies have focused on the application of rice husk, motivated by its versatility, to add value and simultaneously ameliorate rice husk disposal issues [1]. Rice is widely produced in many countries, with a global production of 478.65 million tons of processed rice in 2015–2016. Brazilian production in the same period was 10.6029 million tons of processed rice, resulting in massive generation of rice husk [2, 3].

Rice husk is a by-product of rice processing; thus, the agribusiness provides a stable source of rice husk. Rice husk is rich in organic matter and silica, which upon pyrolysis can produce an ash rich in silica (over 90 mass%). Rice husk can produce amorphous materials when combusted below 800 °C [4, 5]. Silica from rice husk is commonly obtained by combustion of the husk or by acid or base leaching, followed by calcination [6]. Due to its composition, rice husk has been utilized in several applications for generation of thermal energy, producing adsorbents and materials for cement and concrete, and production of silica for use in the synthesis of catalysts (e.g., zeolites, MCM-41, and supported oxides) and other silicon-based

materials [7–10].

Catalysts containing vanadium pentoxide are attractive because of their high activity and selectivity in many catalytic processes, especially industrial processes involving oxidation reactions. The catalytic activity of supported vanadium pentoxide results from the species formed on the surface, the distribution and quantity of these species, and the properties of the support [11].

This study aims to prepare rice husk ash (RHA) by leaching, followed by modification with vanadium pentoxide and characterization of the material.

2. MATERIAL AND METHODS

2.1. Synthesis of catalysts

2.1.1. Preparation of rice husk ash

Rice husk samples were collected from Tio Mário Rice Milling Company, located in Barreiras city, Bahia, Brazil. The rice husk was washed with distilled water at ambient temperature, dried, and then leached with HCl (0.1 mol/L) solution or NaOH (0.1 mol/L)

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solution at 100 °C for 2 h in an autoclave in a Teflon beaker; the mass ratio was 2:1 (rice husk:solution). The materials were then washed with distilled water, dried at 100 °C for 2 h and calcined at 600 °C for 2 h at a heating rate of 10 °C/min, thus generating RHA.

2.1.2. Rice husk ash modified with vanadium pentoxide

RHA was modified with 2, 5, or 10 mass% of vanadium pentoxide by the combustion method with urea. A mixture of rice husk ash, urea, and ammonium metavanadate, with a urea:vanadium molar ratio of 3:1, was macerated and burned in a muffle furnace (EDG 3P) at 500 °C with the door partly closed. After 15 min, the material was cooled, pulverized, and calcined in sequence at 500 °C for 2 h then at 600 °C for 1 h.

2.2. Material characterization

2.2.1. X-ray diffraction (XRD)

X-ray diffraction (XRD) analysis of the samples was performed with an X-ray diffractometer (Rigaku Ultima IV) using Cu-K α irradiation (1.5418 Å) at 2 θ angles ranging from 2 to 60° with a scanning speed of 0.02 s/step. The crystalline phases were identified by comparison with equipment library standards. The average size of the crystallites was determined qualitatively using the Scherrer equation (**Equation 1**).

$$d = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

Where d is the average crystallite size (nm); k is the shape factor (0.89); λ is the wavelength (0.15406 nm for the Cu-K α radiation); β (in radians) is the FWHM (full width at half maximum) of the main peak.

2.2.2. Fourier transform infrared spectroscopy (FTIR)

The FTIR spectra of the samples were obtained at 4 cm⁻¹ resolution from 16 scans of KBr pellets containing 1 mass% of the samples. The analyses were performed under ambient conditions using a Perkin Elmer spectrophotometer (Spectrum Two).

3. RESULTS AND DISCUSSION

3.1. X-ray diffraction

Figure 1 shows the X-ray diffraction patterns of the sample materials prepared using RHA obtained by acid leaching. The pattern for pure RHA was consistent with that of amorphous materials due to the low temperature used for RHA preparation. On the other hand, the samples of RHA modified with vanadium pentoxide showed peaks associated with the formation of vanadium pentoxide, identified with the aid of the equipment library (pdf card: 00-009-0387). These peaks of the V₂O₅/RHA samples with low vanadium concentration suggest minimal interaction of the vanadium pentoxide species with RHA and/or agglomeration of these species on RHA.

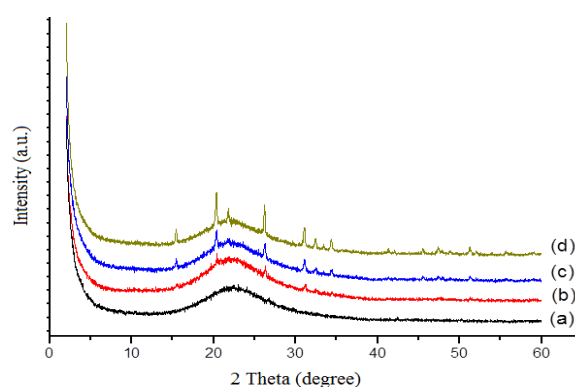


Figure 1. XRD patterns of: (a) RHA 600 and (b) 2, (c) 5, and (d) 10 mass% V₂O₅/RHA. RHA was obtained by acid leaching.

The X-ray patterns of pure RHA and the modified materials prepared with use of RHA obtained by basic leaching are shown in **Figure 2**.

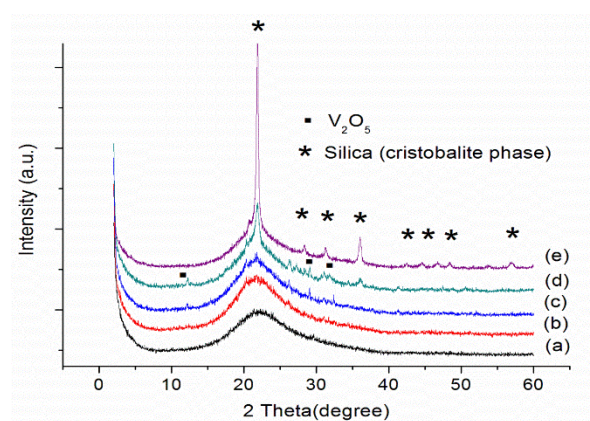


Figure 2. XRD patterns of: (a) RHA 600 and (b) 2, (c) 5, (d) 10 mass% of V₂O₅/RHA and (e) RHA 700. RHA was obtained by basic leaching.

The pure RHA treated at 600 °C (termed RHA

600) exhibited an amorphous pattern, whereas that treated at 700 °C (RHA 700) showed peaks associated with the formation of silica (cristobalite phase). The samples containing 5 and 10 mass% V_2O_5 showed peaks indicative of poor crystallinity and small amounts of silica. The XRD profiles of the 5 and 10 mass% V_2O_5 /RHA samples showed a few peaks that could be attributed to the V_2O_5 phase, among other peaks. These data indicate the stability of the vanadium species on RHA obtained by basic leaching.

The average sizes of the crystallites, determined qualitatively by application of the Scherrer equation, were on the nanoscale. For pure RHA prepared by basic leaching and the congener modified with V_2O_5 , the crystallite size was around 10 nm. On the other hand, for pure RHA prepared by acid leaching and the counterpart modified with V_2O_5 , the crystallites had an average size of 40 to 80 nm.

3.1. Fourier transform infrared spectroscopy

Figures 3 and 4 show the FTIR spectra of the materials prepared using RHA obtained by acid leaching (Figure 3) and the materials prepared with use of RHA obtained by basic leaching (Figure 4). The FTIR spectra of the solid obtained with acid-leached RHA exhibited FTIR bands at 1098 cm^{-1} (Si-O bonds), 810 cm^{-1} (O-Si-O bonds), 616 cm^{-1} (Si-O bonds,

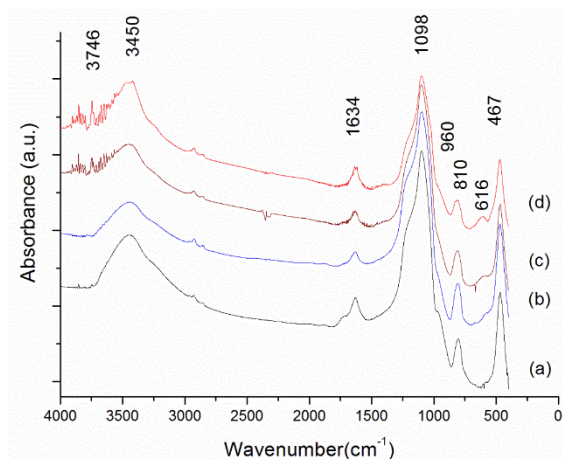


Figure 3. FTIR spectra of: (a) RHA and (b) 2%, (c) 5%, and (d) 10% V_2O_5 /RHA. RHA was obtained by acid leaching.

attributed to cristobalite formation), and 467 cm^{-1} (Si-O-Si bonds), associated with the silica present in RHA [11–13]. FTIR bands associated with -OH groups (the hydroxyl region) [13] were also observed, suggesting the existence of Brønsted acid sites (the FTIR band at

3747 cm^{-1} is associated with isolated Si-OH groups) in the sample prepared with acid-leached RHA. The FTIR bands observed at 960 cm^{-1} , which were more prominent for the 10 mass% V_2O_5 sample, presumably arise from Si-O-V interactions. The band at 1634 cm^{-1} is assigned to physically adsorbed water [11].

The FTIR bands observed in the spectra of the materials prepared using acid-leached RHA were consistent with those of the samples prepared with the use of base-leached RHA. The difference between these materials was the absence of the bands at 3746 and 960 cm^{-1} in the profiles of the materials prepared with base-leached RHA.

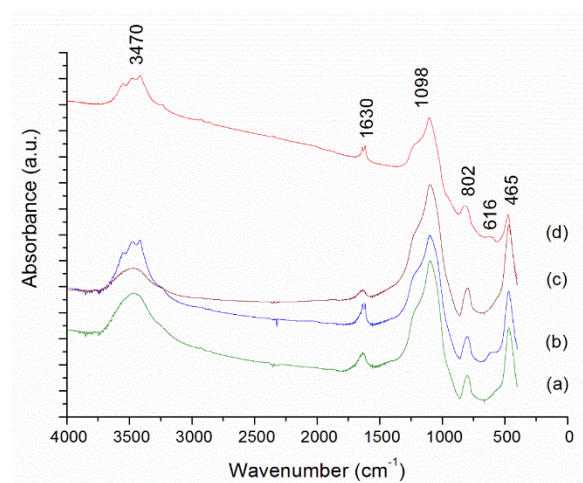


Figure 4. FTIR spectra of: (a) RHA and (b) 2%, (c) 5%, and (d) 10% V_2O_5 /RHA. RHA was obtained by basic leaching.

4. CONCLUSION

V_2O_5 /RHA catalysts prepared with RHA obtained by acid leaching showed greater crystallinity relative to the congeners prepared with RHA obtained by basic leaching. The samples obtained with acid-leached RHA showed the formation of vanadium phases, suggesting minimal interaction and/or low dispersion of the vanadium species. Modified RHA obtained by basic leaching contained vanadium species in higher concentrations and with lower crystallinity, suggesting strong interaction between V_2O_5 and RHA.

FTIR analysis indicated the formation of silica in the samples of pure RHA and RHA modified with vanadium pentoxide, where the FTIR bands were not derived solely from V_2O_5 . However, the acid-leached RHA sample containing 10 mass% V_2O_5 exhibited FTIR bands assigned to possible Si-O-V interactions.

5. ACKNOWLEDGMENTS

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