31º ENCONTRO DE QUÍMICA DA REGIÃO SUL
A QUÍMICA COMO PROPULSORA DE NOVOS ECOSSISTEMAS DE INOVAÇÃO
19 A 21 DE NOVEMBRO
Campus Toledo
Unioeste

Área: FIS

MnS on Carbonaceous Support as Catalyst for PET Depolymerization

Daniel Fernandes Baio (IC),[1] Thelma Sley Pacheco Cellet (PQ),[1] Guilherme Miranda Pereira (PQ)[1]

tspcellet2@uem.br; danbaio@hotmail.com

[1]*Departamento de Ciências, Universidade Estadual de Maringá - UEM*

Keywords: *PET Glycolysis, Polyethylene terephthalate, Catalysis, Carbonaceous Support, Kapok.*

Highlights

- MnS on C support were prepared from kapok fibers by pyrolysis.
- Materials were able to catalyze PET glycolysis with 100% of efficiency.
- Catalysts yielded 68% of BHET and showed great recyclability.

Resumo/Abstract

With the proliferation of polyethylene terephthalate (PET) use, waste accumulation has become a problem for society. PET is a material that is naturally difficult to degrade, thus recycling is the most promising option to reduce its environmental impact. PET recycling can be carried out using several methods, with chemical processes being the most established, since it leads to depolymerization into monomers. Chemical recycling is essentially slow without a catalyst and the efficiency is directly related to the catalyst used. Homogeneous catalysis based on metal-derived compounds is effective, however due to their high solubility in solvents, product purification becomes complicated, and its use also increases the risk of environmental contamination. A promising alternative is to immobilize these metal species on solid supports enabling catalyst separation and recovery from the reaction mixture. Hybrid Mn-C catalysts were obtained by pyrolysis of kapok fibers (*Ceiba speciosa*) collected on the UEM campus. The fibers were dried, deseeded, and boiled in distilled water to remove impurities, then wet-impregnated to form three precursors: P1 ($MnSO_4$), P2 ($MnSO_4$ + H_3BO_3), and P3 ($MnSO_4$ + H_3BO_3 + melamine). After drying, the impregnated fibers were pyrolyzed in a tube furnace under N_2 (50 mL min^{-1}) using a two-step profile: 200 °C (30 min) followed by 800 °C (30 min). The resulting hybrid Mn/C catalysts were designated D1–D3 (from P1-P3) and characterized by X-ray diffraction (XRD), Raman spectroscopy and Thermogravimetric analysis (TGA). XRD reveals MnS as the dominant crystalline phase in D1-D3, with $2\theta \approx 29.5°$, 34.1°, and 49.1° (PDF 72-1534). D2 and D3 also exhibit weak peaks at 30.9° and 33.0°, ascribed to Mn_3O_4 (PDF 03-065-2776). These results indicate that $MnSO_4$ decomposes mainly to MnS during pyrolysis, with minor Mn_3O_4 forming in selected samples. Raman spectra display bands at ~1350 cm^{-1} and ~1585 cm^{-1} known as the D and G bands of carbonaceous materials, ascribed to the breathing of sp^2 rings and the in-plane E_{2g} stretching of sp^2 C-C bonds, respectively. Comparing band intensities, I_D/I_G increases from D1 to D2 and D3, indicating greater disorder/defect density and reduced graphitic order induced by these additives during pyrolysis. Catalytic performance was evaluated by PET conversion and BHET yield. With 1.5% catalyst loading for 2 h, all materials achieved 100% PET conversion, but the BHET yields were 62%, 65% and 58% for D1, D2 and D3, respectively. Differential scanning calorimetry confirmed BHET as the main product via its ~110 °C melting peak. BHET yield correlated with MnS content obtained from TGA (D1: 39%, D2: 42%, D3: ~30%), aligning with D2's higher yield. D1 was selected for optimization due to its simpler composition and elevated activity. At 1.5% loading, BHET yield increased from 62% (2 h) to 68% (3 h) and slightly decreased at 4 h, indicating equilibrium at 3 h. At 3 h, optimum yield (68%) occurred at 1.5% catalyst; 0.75% gave 62%, while 3.0% and 4.5% lowered yields (53%, 48%) due to equilibrium shifts and/or oligomer formation. Under the optimal condition (3 h, 1.5%), complete PET conversion and stable BHET yields (~68%) were maintained over three cycles, confirming catalyst robustness. The results demonstrate the viability of kapok as a sustainable precursor for catalysts used in PET chemical recycling, contributing to environmentally responsible plastic-waste reuse.

Agradecimentos/Acknowledgments

The authors thank CNPq, UEM and FA for financial support, and the SBQ-Sul committee for organizing the event.