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Solid Acid Catalysts Derived from Modified Kaolinite with Sulfonic/Sulphate Groups for Esterification

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In this study, we are developing a solid acid catalyst from the waste of kaolinite mining, an abundant clay mineral in Brazil, mainly in Minas Gerais and São Paulo. Kaolinite is a hydrated aluminosilicate with $Al_2Si_2O_5(OH)_4$, classified as a 1:1 dioctahedral phyllosilicate. Its crystalline structure comprises alternating layers of octahedral AlO_6 and tetrahedral SiO_4 sheets, forming a stable and organized network [1,2]. This approach involves modifying the structure of kaolinite with sulfate/sulfonic acid groups to create a solid with acidic properties, aiming to use it as a catalyst in the esterification reaction of oleic acid to methyl oleate [3,4]. We prepared two classes of catalysts: one from raw kaolinite (Cau) and another from kaolinite treated at 550°C (metakaolinite, Meta). The solids were impregnated with H_2SO_4 (1.0 mol L^{-1}), washed, and thermally treated at 300°C, 400°C, 500°C, and 600°C, generating the catalysts CauT or MetaT, where T represents the thermal treatment temperature. The catalysts were characterized using TG, FTIR, XRD, XRF, and titration techniques to determine acidic sites. The esterification reactions were then conducted with oleic acid and methanol (molar ratios of 1:5 and 1:10), using the synthesized catalyst (2.5% and 5% w/w) at 100°C for 3 hours. XRD results showed that kaolinite is composed of hematite (Fe_2O_3 - JCPDS-33-664), quartz (SiO_2 - JCPDS-4610-45), goethite (FeOOH - JCPDS-29-713), and kaolinite ($Al_2Si_2O_5(OH)_4$ - JCPDS-14-164). XRF revealed the presence of approximately 23.93% Al, 53.23% Si, 4.95% K, 1.27% Ti, and 8.27% Fe in the sample. Our acidity analysis revealed a significant increase from 0.19 (Cau) to 6.89 (Cau600) mmol g^{-1} in the kaolinite samples and from 0.45 (Meta) to 7.45 (Meta600) mmol g^{-1} in the meta kaolinite samples. This stark increase indicates the profound influence of temperature on the generation of acidic sites. Catalytic tests revealed that the Cau and Cau300 catalysts exhibited low catalytic activity, with conversions below 15%. In contrast, the Cau400 and Cau500 catalysts converted more than 80% of oleic acid to methyl oleate, while the Meta400 and Meta500 catalysts achieved conversions more significantly than 90%. The Cau600 and Meta600 catalysts showed approximately 60% and 70% conversions, respectively. These results demonstrate the potential of the developed catalysts for the esterification reaction, with the Meta400 and Meta500 catalysts showing the highest conversion rates. These results indicate that conversion does not depend solely on the total acidity of the catalyst. The increase in thermal treatment temperature may have caused the aggregation of acidic sites within the material's structure, reducing the availability of essential catalytic sites for the reaction. Therefore, finding an appropriate balance between acidity generation and the maintenance of catalytic site dispersion is crucial to optimize catalyst efficiency [5].

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