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Zirconia-Supported Tungstophosphoric Heteropolyacid as Heterogeneous Acid Catalyst for Biodiesel Production

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Graphical Abstract



 $R^4COOH+CH_3OH \Leftrightarrow H_2O+R^4COOCH_3$

Highlights

- Sol-gel/Hidrothermal method is efficient for the immobilization of HPA on zirconia
- The presence of the HPA leads to significant modifications on zirconia
- Supported HPA on zirconia are suitable catalysts for esterification.
- Leaching and the porosity blockage cause a reduction of the catalytic activity.

Abstract: A series of materials based on the immobilization of the 12-tungstophosphoric heteropolyacid over zirconia supports have been prepared and applied as heterogeneous acid catalysts in the esterification of palmitic acid with methanol as a model reaction for the preliminary stage of the biodiesel production. The title materials have been obtained through the sol-gel method combined with a subsequent hydrothermal treatment at mild conditions, which affords catalysts with larger porosity and higher thermal and chemical stability under the esterification reaction conditions than other preparative approaches. Generating the zirconia support by hydrolysis of an alkoxyde precursor in the presence of the heteropolyacid leads to materials with homogeneously well-dispersed clusters, as well as to an increasing contribution of the tetragonal ZrO_2 crystalline phase, a decreasing size of the nanoparticles and larger microporous volumes as the loading of the Keggin-type species increases. The 12-tungstophosphoric acid retains its catalytic activity in the esterification of palmitic acid with methanol at 60 °C upon immobilization over zirconia and conversions even higher than those

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