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Metal silicotungstate salt-catalyzed esterification reaction of benzaldehyde

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Benzaldehyde is naturally produced and primarily found in almonds. Industrially, it can be synthesized through the hydrolysis of benzal chloride and the oxidation of toluene. The presence of the aromatic ring and the aldehyde group renders benzaldehyde a versatile intermediate. Amidst the products of interest are its esters, used in the production of cosmetics, perfumes, polymers, and dyes. Typically, the production of these esters follows two steps: firstly, oxidation to benzoic acid and secondly, esterification with alkyl alcohols. Oxidation usually employs toxic oxidants, such as diazonium salts and N-bromosuccinimide/pyridine. An alternative approach involves the use of hydrogen peroxide, which requires catalytic activation. An example of a class of compounds with wide catalytic activity is the Keggin-type heteropolyacids (HPAs), which are metal-oxygen clusters, where octahedra containing W or Mo surround Si or P tetrahedron. Besides exhibiting a strong Brønsted acidity, the metal doping can provide a Lewis acidity, able to promote oxidation reactions, making them active bifunctional catalysts. In this study, metal salts derived from silicotungstic acid ($M_{4/n}SiW_{12}O_{40}$, onde M= Al^{3+}, Fe^{3+}, Co^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+} e n = nox do metal) were synthesized aiming their application as catalysts in the oxidative esterification of benzaldehyde. The salts were characterized using techniques such as thermogravimetric analysis (TG/DTG), Fourier-transformed infrared spectroscopy (FTIR) coupled with attenuated total reflectance, X-ray powder diffraction (XRD), nitrogen physisorption, scanning electron microscopy, and energy-dispersive X-ray spectroscopy. Through TG/DTG analysis was possible to calculate the number of hydration water molecules. XRD provided the crystallite's size, while FTIR analysis assured that the primary structure of the Keggin anion was maintained during the synthesis of the catalysts. To evaluate the activity of heteropoly salts, catalytic runs were carried out in a three-necked glass reactor (25 mL) equipped with a reflux condenser, maintained under heating and magnetic stirring. Typically, a methanol solution (10 mL) containing benzaldehyde (2.5 mmol) and catalyst (1.0 mol %) was stirred and heated to reaction temperature (323 K). Then, the slow addition of hydrogen peroxide (5.0 mL) started the reaction. Aliquots (1 mL) were periodically collected and analyzed by gas chromatography with flame ionization detection (GC-FID). Initial tests revealed that $Cu_2SiW_{12}O_{40}$ and $Fe_{3/2}SiW_{12}O_{40}$ catalysts were able to achieve at least 90 % conversion with high selectivity, approaching 100 %, for methyl benzoate. The variation of the catalyst amount indicated that even when the lowest catalyst load was used (0.15 mol %), a high conversion (90 %) and maintained ester selectivity. This catalyst was also able to perform the reaction with other alcohols, albeit with lower substrate conversion. Further investigations are ongoing, including the benzaldehyde-to-hydrogen peroxide ratio and catalyst reuse. A promising process is being developed for the one-pot production of esters derived from benzaldehyde which occurs under mild conditions of 323 K, without the need for pressure, using a green oxidant, hydrogen peroxide, in a reaction time of 2 hours.

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References

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