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Friedel-Crafts Acylation of Ferrocene Catalyzed by Solid Superacid, Silica-supported Polytrifluoromethanesulfosiloxane

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Abstract: Solid superacid, silica-supported polytrifluoromethanesulfosiloxane (SiO_2-Si-SCF_3) was firstly used in the Friedel-Crafts acylation of ferrocene as a novel catalyst. IR spectra, WAXD and specific surface area of the superacid SiO_2-Si-SCF_3 were also investigated.

Keyword: Friedel-Crafts acylation, ferrocene, solid superacid catalyst, silica-supported polytrifluoromethanesulfosiloxane.

Friedel-Crafts type acylation of ferrocene is of particular value owing to the importance of ferrocene ketones and keto acids, which could be used widely in various fields, such as enatioselective and asymmetric synthesis[1,2], pharmaceutical preparation[3] and organometallic catalyst[4].

The conventional method for the Friedel-Crafts acylation is carried out with stoichiometric amount of classic Lewis acids catalysts $AlCl_3$, BF_3 and $SnCl_4$, *etc*. However, these commonly used homogeneous acid catalysts pose several problems such as high toxicity, difficulty in separation and recovery of spent catalyst.

In this paper, we reported the use of an inorganic polymer, silica-supported polytrifluoromethanesulfosilocane solid superacid (SiO_2-Si-SCF_3) as a new catalyst in the acylation of ferrocene with different acyl chloride. It was found that the catalyst SiO_2-Si-SCF_3 possesses the advantages of high stability, easy separation and regeneration. Moreover, the acylation reaction was accomplished in mild conditions, avoiding side reaction. IR spectra, WAXD and specific surface area of the superacid SiO_2-Si-SCF_3 were also investigated[8].

SiO_2-Si-SCF_3 was prepared as the reported literature[5-7]: 8 g of fumed silica powder, 4 mL of deionized water, 4 mL of trifluoromethanesulfonic acid were added to 40 mL of ethanol. After refluxing for 2 h with stirring and removing solvent, the remained product was heated at 200 ℃ for 4 h, then the gray-brown catalyst SiO_2-Si-SCF_3 was obtained. The synthetic method of Friedel-Crafts acylation of ferrocene with different acyl chlorides is illustrated as follows.

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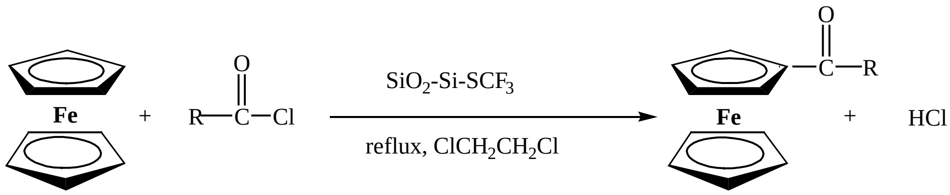
Scheme 1



(R=C_2H_5, C_3H_7, C_4H_9, C_5H_{11}, C_6H_{13}, C_7H_{15})

Table 1 The yield of acylation of ferrocene catalyzed by SiO_2-Si-SCF_3

Run	Acyl chloride	Acylated product	Yield of acylated products (%)
1	Propionyl chloride	Propionyl ferrocene	31.8
2	*n*-Butyryl chloride	*n*-Butyryl ferrocene	3.27
3	*n*-Valeryl chloride	*n*-Valeryl ferrocene	29.1
4	*n*-Caproyl chloride	*n*-Caproyl ferrocene	6.4
5	*n*-Heptyl chloride	*n*-Heptyl ferrocene	10.3
6	*n*-Octyl chloride	*n*-Octyl ferrocene	4.14

Table 2 The activity of the recycled catalyst

Times	Yield of propionyl ferrocene
1	31.8
2	37.4
3	37.8
4	16.6
5 (regenerated)	32.0

A mixture of 0.5 g (2.7 mmol) ferrocene, 15 mL dichloroethane and 0.3 g of the catalyst were heated in a 50 mL three-neck round bottom flask fitted with a reflux condenser and a stirrer. At the reflux temperature, 5.5 mmol acyl chlorides were dropped into the flask. After stirring under reflux for 4 h, the reaction mixture was cooled, then the solid catalyst was filtered, washed with petroleum ether, the filtrate was concentrated and the residue was transferred on a neutral alumina chromatography column, which was eluted with petroleum ether to give the first band of recovered ferrocene then eluted with ether to give the second band of acylated ferrocene as red oil (**Table 1**).

The catalyst SiO_2-Si-SCF_3 can be used repeatedly 3 times without reducing the activities in the acylation of ferrocene with propionyl chloride (**Table 2**). The catalytically activity decreased dramatically after four times reuse, but it can be regenerated simply by calcination at 200 ℃ and showed almost identical activity to the freshly prepared one. In summary, the novel catalyst SiO_2-Si-SCF_3 for acylation of ferrocene was stable in the reaction condition and can be easily separated, regenerated. In comparison with classical Lewis acid catalysts, solid superacid SiO_2-Si-SCF_3 gave unsatisfactory yields in ferrocene's acylation, however, it has the potential as one of the alternatives of conventional Lewis acid and is worth further studying.

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References and Note

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