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Novel solid acid catalyst, bentonite-supported polytrifluoromethanesulfosiloxane for Friedel–Crafts acylation of ferrocene

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Solid acid catalyst, bentonite-supported polytrifluoromethanesulfosiloxane (B-PTFMSS) has been for the first time prepared and used in the Friedel–Crafts acylation of ferrocene with various acyl chlorides. The catalytic activities were influenced by reaction time, reaction temperature, solvent and loaded amount of B-PTFMSS. It was found that the new catalyst B-PTFMSS possessed the advantages of high activities giving similar yield of aliphatic acyl ferrocene (>70%) as conventional Lewis acid catalyst aluminum chloride and it can be used repeatedly and easily regenerated. B-PTFMSS has also been characterized by IR spectra, pyridine adsorbed IR, specific surface area and XRD.

KEY WORDS: bentonite-supported polytrifluoromethanesulfosiloxane; ferrocene; Friedel–Crafts acylation; solid acid catalyst.

1. Introduction

Friedel–Crafts type acylation of ferrocene is of particular value owing to the importance of acylferrocenes which are employed as intermediates for the production of varied functional materials such as functional polymers, charge transfer complexes, chiral catalysts, combustion catalysts for propellants, pharmaceutical treatment, and the like [1–4]. The conventional method of the Friedel–Crafts acylation of ferrocene is carried out with stoichiometric amount of classic Lewis acid such as aluminum chloride, boron trifluoride, etc [5,6]. However, these commonly used acid catalysts pose the drawbacks of high toxicity, tedious work-up procedures and difficulty in separation and recovery. Considerable efforts are being made to find recyclable and environment-friendly catalysts for Friedel–Crafts type acylation reactions. Nafion-H [7], zeolites [8–10], heteropoly acids and their salts [11,12], clays [13,14], and sulfated-doped metal oxides [15] have been reported for the acylation of benzene and its derivatives. However, communication on new type catalyst for acylation of ferrocene is scarce: Choudary and coworkers disclosed that montmorillonite or metal ion exchanged K10 montmorillonite clay was an active and stable catalyst for acylation of ferrocene, but the reaction needs fairly high temperature and long reaction time (generally 150 °C and 24 h)[16]. In this paper, we wish to report our results, showing highly active inorganic polymer, bentonite-supported polytrifluoromethanesulfosiloxane (B-PTFMSS) solid acid catalyst in the acylation of ferrocene with different acyl chlorides. The main variables affecting the performance of the catalyst have been investigated. B-PTFMSS has also been characterized by IR spectra, pyridine adsorbed IR, specific surface area and XRD.

2. Experimental

2.1. Catalyst

The catalyst B-PTFMSS was firstly prepared as follows:8 g of bentonite, having the formula $[Ca_{0.35}(Al,Mg,Fe)_1(Si,Al)_5O_{20}(OH)_4.nH_2O]$ and originating from the eastern suburb of Huhhot, Inner Mongolia, and 4 mL *ortho*-ethyl silicate, 4 mL of deionized water, 4 mL of trifluoromethanesulfonic acid and 80 mL ethanol were placed in a 250 mL three-neck round bottom flask equipped with a magnetic stirrer and a condenser. After stirring under reflux for 2 h, the solvent was distilled off, the remained solid was calcined at 200 °C for 4 h and 10.4 g of gray catalyst B-PTFMSS was obtained. The procedure of preparation was inspired by the reported method [17,18].

2.2. Chemicals

Acyl chlorides were synthesized according to ref.[19], trifluoromethanesulfonic acid was purchased from Acros and other reagents were commercial products from Shanghai and used as received.

2.3. Catalyst characterization

The catalyst B-PTFMSS have been characterized by XRD (using a Japanese D/MAX-III XRD diffractometer with a Fe target and Kα radiation), specific surface

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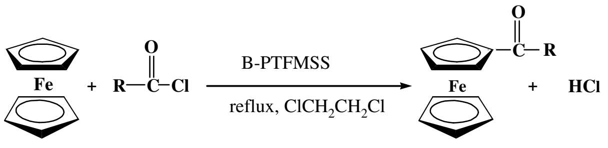
area (determined on an American Micromeritics ASAP2010 instrument) and IR spectra (performed on an American Nicolet Nexus FT-670 spectrophotometer). Catalyst sample for pyridine adsorbed FTIR had been pretreated in vacuum for 15 min, then the adsorption of pyridine vapor was performed for 0.5 h and subsequent evacuation for 15 min at 100 °C to remove physically adsorbed pyridine.

2.4. *Acylation of ferrocene*

The synthetic route of Friedel–Crafts acylation of ferrocene with different acyl chlorides over B-PTFMSS is shown in scheme 1.



(R=C_2H_5, C_3H_7, C_4H_9, C_5H_{11}, C_6H_{13}, C_7H_{15}, $ClCH_2CH_2CH_2$, Fc, Ph)

Scheme 1.

A mixture of ferrocene (0.5 g, 2.7 mmol), B-PTFMSS (0.3~0.5 g) as catalyst and solvent were heated under reflux with a magnetic stirrer. Then acyl chlorides (5.5 mmol) were added into the mixture. After 4 h the mixture was cooled and the solid catalyst was filtered off, 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 and eluted with ether to give the second band of acylated ferrocene as red oil (confirmed by IR) which solidified to dark-red crystals after freezing and recrystallization.

3. Results and discussion

3.1. *Catalyst characterization*

The X-ray diffraction of the catalyst B-PTFMSS and its supporter bentonite was measured and from that it is inferred that the crystallinity of catalyst was changed as compared with bentonite (figure 1). Physico-chemical properties of B-PTFMSS and bentonite are given in table 1 and figure 2 shows IR of B-PTFMSS, from which following observations are made:

the colour of B-PTFMSS have been changed from bentonite;
its surface area are enhanced;
its IR data show different absorptions.

All above reveal that the acid polymer adsorbates on the bentonite supporter not only determine the activities of the catalyst, but also contribute to the differences of its surface structure from the bentonite.

Pyridine adsorbed IR was used to study the nature of acid sites on catalyst B-PTFMSS (figure 3). Brønsted acidity of B-PTFMSS was proved by the appearance of a band at 1544 cm^{-1} and Lewis acidity at 1490 cm^{-1}.

3.2. *Acylation of ferrocene with various acyl chlorides*

Aclyation of ferrocene with different acyl chlorides over the catalyst B-PTFMSS is presented in table 2. Results showing the activities of acyl chlorides increase in the following order: aromatic acyl chlorides (~20% conversion) < chlorobutyryl chloride (~30% conversion) ≪ long chain acyl chloride (70%~80% conversion).

3.3. *Effect of time-on-stream*

Kinetic curve (ferrocene conversion versus time plot) for the acylation of ferrocene with butyryl chloride over B-PTFMSS is illustrated in figure 4 which presents that the conversion of ferrocene or the yield of butyryl ferrocene is greatly affected by the reaction time. In the range of 0.5–4 h, the conversion of ferrocene increases

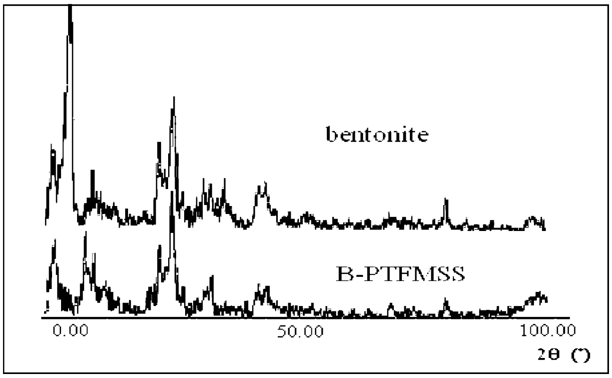


Figure 1. The XRD of bentonite and B-PTFMSS.

Table 1
Physico-chemical properties of bentonite and B-PTFMSS

Material	Color	Specific surface area (m^2 /g)	Activities in the acylation of ferrocene	IR absorption (cm^{-1})
Bentonite	Light pink	50.75	Inactive	3631, 3447, 1632, 1054, 786, 525, 470
B-PTFMSS	Dark grey	83.20	Highly active	3481, 3449, 1638, 1253,1186, 1065, 1036, 795, 646, 574, 520, 468

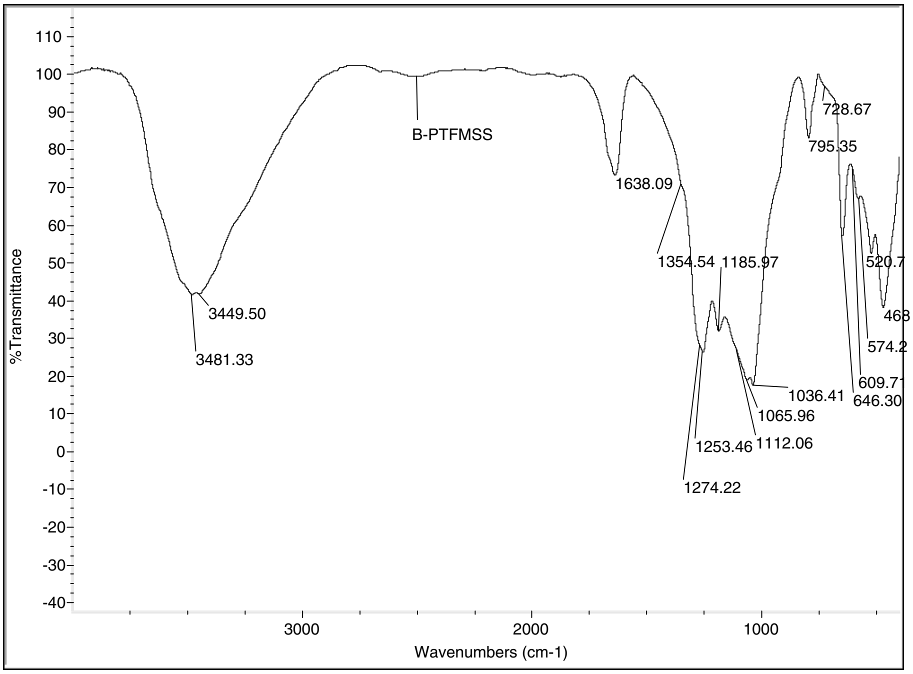


Figure 2. FTIR of B-PTFMSS.

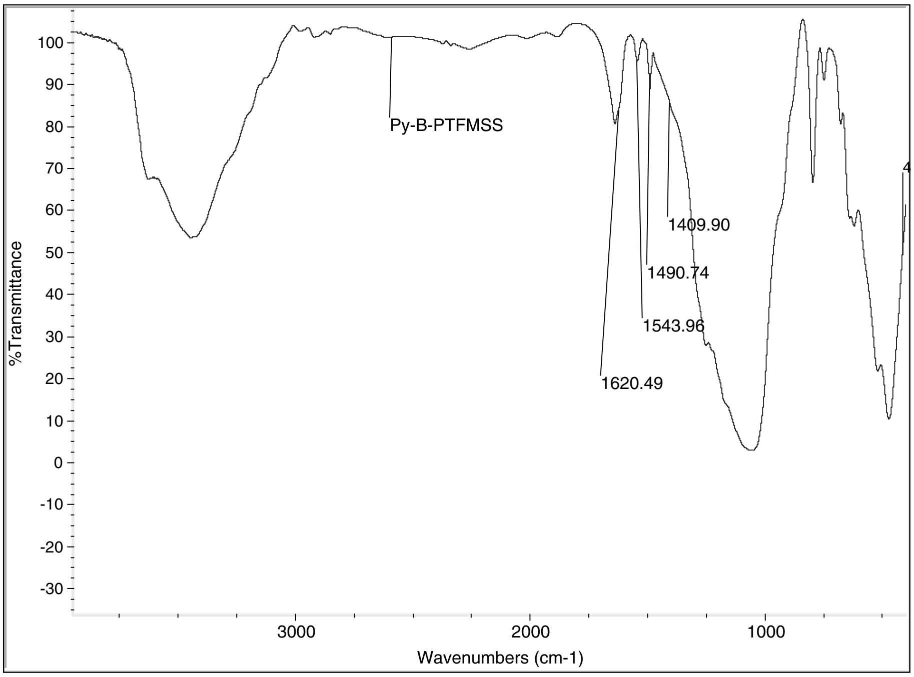


Figure 3. Pyridine adsorbed FTIR of B-PTFMSS.

greatly from 2.45 to 81.3%. When the reaction time continues from 4 to 8 h, the conversion keeps stable around 70~80%, and in the range of 8 to 10 h, the conversion enhanced to 97.9%. Generally, the conversion and yield have a increasing tendency with the extending of times.

3.4. Effect of temperature and solvent

From table 3, it can be seen that the temperature and solvent play big roles in the acylation of ferrocene with butyryl chloride over the B-PTFMSS. From 35 °C to 80 °C, the conversion of ferrocene keeps growing with

Table 2
B-PTFMSS catalyzed acylation of ferrocene with acyl chloride

entry	Acyl chloride	Acylated product	Yield of acylferrocene (%)	Conversion of ferrocene (%)	IR of aclyated product (cm^{-1})
1	Propionyl chloride	Propionyl ferrocene	58.4	72.5	3094, 2971, 2935, 2902, 1668
2	*n*-Butyryl chloride	*n*-Butyryl ferrocene	70.1	81.3	3096, 2962, 2932, 2873, 1667
3	*n*-Valeryl chloride	*n*-Valeryl ferrocene	75.2	79.8	3096, 2957, 2932, 2871, 1669, 732
4	*n*-Caproyl chloride	*n*-Caproyl ferrocene	71.2	73.6	3096, 2955, 2929, 2862, 1655, 724
5	*n*-Heptyl chloride	*n*-Heptyl ferrocene	70.3	72.8	3095, 2954, 2972, 2856, 1668, 728
6	*n*-Octyl chloride	*n*-Octyl ferrocene	75.5	82.5	3097, 2955, 2926, 2855, 1669, 724
7	4-Chlorobutyryl chloride	4-Chlorobutyryl ferrocene	18.0	28.7	3097, 2956, 2915, 2887, 2863, 1667, 816
8	Ferrocenoyl chloride	Diferrocenylmethanone	8.1	22.9	3122, 3095, 2962, 2923, 2859, 1609, 810
9	Benzoyl chloride	Benzoyl ferrocene	8.3	21.1	3113, 3090, 3064, 2962, 2923, 1625, 1600,720, 694

Ferrocene: 2.7 mmol (0.502 g); acyl chloride: 5.5 mmol; B-PTFMSS: 0.3 g; solvent: 1,2-dichloroethane 40 mL; reflux temperature: 80 °C; reaction time: 4 h.

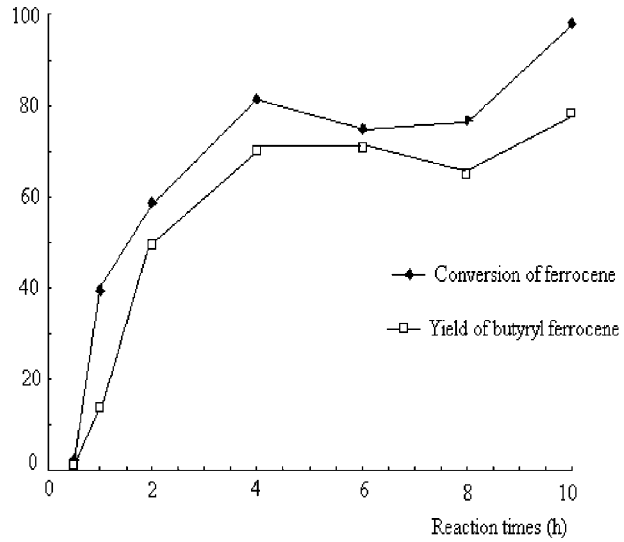


Figure 4. The influence of reaction time on acylation of ferrocene with butyryl chloride Ferrocene:2.7 mmol (0.502 g); butyryl chloride: 5.5 mmol (0.67 mL); catalyst B-PTFMSS: 0.3 g; solvent: 1,2-dichloroethane 40 mL; reflux temperature: 80 °C.

Table 3
The influence of temperature and solvent on acylation of ferrocene with butyryl chloride

Reaction temperature (°C)	Solvent	Conversion of ferrocene (%)
35	*n*-Pentane	13.4
38	Dichloromethane	23.7
68	*n*-Hexane	26.3
80	1,2-Dichloroethane	81.3
120	*n*-Octane	27.8

Ferrocene: 2.7 mmol (0.502 g); butyryl chloride: 5.5 mmol (6.7 mL); B-PTFMSS: 0.3 g; reaction time: 4 h

Table 4
The effect of the amount of catalyst

Weight of catalyst B-PTFMSS (g)	Conversion of ferrocene (%)
0.1	80.1
0.3	81.3
0.5	48.3

Ferrocene: 2.7 mmol (0.502 g); butyryl chloride: 5.5 mmol (6.7 mL); solvent: 1,2-dichloroethane 40 mL; reflux temperature: 80 °C; reaction time: 4 h

the increase of temperature, while the temperature reaches 120 °C the activity decreased dramatically due to the low polarity of the alkane solvent of *n*-octane, which indicates that the higher the reaction temperature, the better the catalyst performs and the acylation reactions occur unreadily in nonpolar solvent where acyl carbonium ions are difficult to form.

3.5. *Effect of the amount of catalyst*

The effect of the amount of catalyst used in the reactor on the conversion of ferrocene is showed in table 4. It can be seen when the amount of B-PTFMSS is 0.1 g and 0.3 g, the conversion of ferrocene is 80.1% and 81.3%, respectively. While the weight of catalyst is 0.5 g, the conversion decreases to 48.3% probably because of the adsorption of acylated products on the excess catalyst.

3.6. *Recycle of catalyst*

The catalyst B-PTFMSS can be used repeatedly and the used one showed similar even enhanced activities in the acylation of ferrocene with butyryl chloride after recycled once and twice. The results of recycling catalyst for the acylation of ferrocene are presented in table 5. The catalytically activity decreased slightly after the catalyst B-PTFMSS was used four times, which showed little activity after recycled five times. B-PTFMSS can be regenerated simply from the reaction solution through filtration then calcined at 200°C.

Table 5
Recycling the catalyst in the acylation of ferrocene with butyryl chloride

Using times of B-PTFSS	Conversion of ferrocene (%)
1	81.3
2	73.3
3	86.4
4	47.1
5	29.5
6	7.7

4. Conclusions

In summary, the solid superacid, B-PTFMSS, is a highly active catalyst in the Friedel–Crafts acylation of ferrocene by acyl chlorides to give corresponding acylferrocenes in mild condition. Unlike soluble Lewis acids, the solid catalyst here do not produce any effluents and can be easily separated and recycled many times. Meanwhile, the catalyst is stable and no side products were observed in the process of acylation reaction. As the clay bentonite is cheap, the catalyst B-PTFMSS is not only eco-friendly but also has the potential of economically application.

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