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Solid superacid, silica-supported polytrifluoromethanesulfosiloxane catalyzed Friedel–Crafts benzylation of benzene and substituted benzenes

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Abstract

A new inorganic polymer, silica-supported polytrifluoromethanesulfosiloxane solid superacid (SiO_2–Si–SCF_3), has been prepared. The acid strength of superacid (Ho < −13.76) is higher than that of 100% H_2SO_4 (Ho = −11.9). It was found that SiO_2–Si–SCF_3 could catalyze Friedel–Crafts benzylation of benzene and substituted benzenes with benzyl alcohol under relatively mild experimental conditions. Reactions are very clean, water is the only by-product of the reaction. The yields amounted to 97–100%, respectively. The selectivity was influenced by catalyst concentration, reaction time and toluene/benzyl alcohol molar ratios.

Keywords: Polytrifluoromethanesulfosiloxane; Friedel–Crafts; Benzylation; Alkylbenzene; Benzyl alcohol

1. Introduction

It has been demonstrated that perfluorinated Resinsulfonic Acid (Nafion-H) was a very active and stable catalyst for catalyze benzylation of benzene and substituted benzenes with benzyl alcohol, but the reaction could not be complete, dibenzyl ether was produced as by-product [1].

Recently, a new inorganic polymer, silica-supported polytrifluoromethanesulfosiloxane solid superacid (SiO_2–Si–SCF_3), has been prepared by a similar method of preparing silica-supported polysulfosiloxane reported in the previous paper [2]. SiO_2–Si–SCF_3 has been found to be more active catalyst than Nafion-H in the benzylation of benzene and substituted benzenes with benzyl alcohol to give diphenylmethane and substituted diphenylmethanes in 97–100% yields, respectively.

2. Experimental

2.1. Preparation of superacid (SiO_2–Si–SCF_3)

The preparation method is as follows: 20 g of fumed silica, 10 ml of *ortho*-ethyl silicate, 10 ml of distilled H_2O, 10 ml of trifluoromethanesulfonic acid and 200 ml of ethanol were placed

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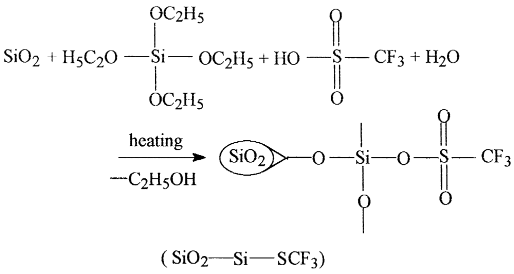


Scheme 1.

in a 500-ml three-neck round bottom flask equipped with a magnetic stirrer. After stirring at 75°C for 2 h, the solvent was distilled off. The solid product was heated at 180°C for 4 h, then 26.6 g of gray SiO_2–Si–SCF_3 was obtained.

The acid strength was measured in a series of sulfuryl chloride solution of Hammett's indicators [3]. A 0.2 g of superacid catalyst, 2 ml of solvent, 0.2 g of Hammett's indicators were placed in a tube, shook and observed the change of color of the catalyst. The acid strength of SiO_2–Si–SCF_3 was $Ho < -13.76$. It was 100 times stronger than that of 100% H_2SO_4 ($Ho = -11.9$).

2.2. Benzylation of benzene and substituted benzenes

A mixture of benzyl alcohol, aromatics and catalyst SiO_2–Si–SCF_3 were heated in a 50-ml three-neck round bottom flask fitted with a reflux condenser and a magnetic stirrer. The reaction flask was placed in a constant temperature bath (±0.5°C). The reaction composition of products was determined by GC using a 2-m column of SE-30.

The procedure of the preparation of SiO_2–Si–SCF_3 may be shown as Scheme 1.

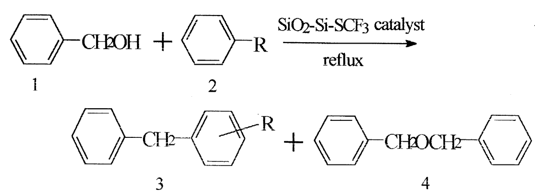
3. Results and discussion

Table 1 shows the benzylation of benzene and substituted benzenes with benzyl alcohol catalyzed by SiO_2–Si–SCF_3. It can be seen (shown as Scheme 2) that in the benzylation of benzene and ethyl benzene with benzyl alcohol, diphenylmethane (3) and ethyl diphenylmethane (3) are obtained in 98% and 97% yields, respectively, and in the benzylation of toluene, 1,2-xylene, 1,3-xylene, 1,4-xylene and anisol with benzyl alcohol to give corresponding substituted diphenylmethanes (3) in 100% yields, respectively, and no any by-products are observed. However, when these benzylation were catalyzed by Nafion-H [1] under the same reaction conditions, the yields of (3) were only 68–93%, and the by-product, dibenzyl ether, was produced in 2–22% yields. It indicates that this new catalyst, SiO_2–Si–SCF_3 is more active and selective than Nafion-H in these reactions.

The influence of reaction time on benzylation of toluene with benzyl alcohol is shown in Table 2. Obviously, the yield of (3) is greatly affected by the reaction time. Namely, in the range of 1.5 to 3 h, the yield of (3) increases from 75% to 100% with the increase of the

Table 1
SiO_2–Si–SCF_3 catalyzed benzylation of benzene and substituted benzenes with benzyl alcohol
Benzyl alcohol: 1 ml (1.045 g, 9.7 mmol); [alkylbenzenes]/[benzyl alcohol] molar ratio = 30:1; catalyst: SiO_2–Si–SCF_3, 10 wt.%; reflux.

Run	R in 2	Time (h)	Product yield (%)	
			3	4
1	H	5	98	0
2	CH_3	3	100	0
3	C_2H_5	3	97	0
4	1,2-CH_3	1.5	100	0
5	1,3-CH_3	1.5	100	0
6	1,4-CH_3	1.5	100	0
7	OCH_3	3	100	0



Scheme 2.

Table 2
Influence of reaction time on benzylation of toluene with benzyl alcohol
Benzyl alcohol: 1 ml (1.045 g, 9.7 mmol); [toluene]/[benzyl alcohol] molar ratio = 30:1; catalyst: SiO_2–Si–SCF_3, 10 wt.%; 110°C.

Run	Time (h)	Product yield (%)	
		3	4
1	1.5	75	0
2	2	89	0
3	3	100	0
4	4	100	0

reaction time. However, when the reaction time increases to 4 h, the yield of (3) is also 100%. And the by-product, dibenzyl ether is not observed in these reactions.

Table 3 shows the influence of the amount of SiO_2–Si–SCF_3 catalyst on benzylation of toluene with benzyl alcohol. It can be seen that when 10 and 8 wt.% of the catalyst (calculated based on the weight of benzyl alcohol used) are used, and the reaction time is 3 h, the yields of (3) amount to 100%, and no by-product, dibenzyl ether (4) is observed. However, somewhat smaller amount of catalyst such as 5 and 3.3 wt.% are used, and the reaction times are 3.5 and 4 h, the yields of (3) decrease to 98% and 83%, and the yields of (4) amount to 2% and 17%, respectively. So, sometimes, the amount of catalyst and reaction time affect the yields of (3) and (4).

Table 3
Influence of the amount of SiO_2–Si–SCF_3 catalyst on benzylation of toluene with benzyl alcohol
Benzyl alcohol: 1 ml (1.045 g, 9.7 mmol); [toluene]/[benzyl alcohol] molar ratio = 30:1; catalyst: SiO_2–Si–SCF_3, 10 wt.%; 110°C.

Run	Catalyst (wt.%)	Time (h)	Product yield(%)	
			3	4
1	10	3	100	0
2	8	3	100	0
3	5	3.5	98	2
4	3.3	4	83	17

Table 4
Influence of toluene/benzyl alcohol molar ratios on benzylation of toluene with benzyl alcohol
Benzyl alcohol: 1 ml (1.045 g, 9.7 mmol); catalyst: SiO_2–Si–SCF_3, 10 wt.%; 110°C.

Run	Toluene:benzyl alcohol molar ratio	Reaction time (h)	Product yield (%)	
			3	4
1	30:1	3	100	0
2	20:1	4	100	0
3	15:1	4	100	0
4	10:1	4	100	0
5	5:1	4	63	37

Table 4 shows the influence of the molar ratios of toluene/benzyl alcohol on the benzylation of toluene with benzyl alcohol. It indicates that in the range of 30:1 to 10:1 of toluene/benzyl alcohol molar ratios, the yields of (3) all amount to 100%, but in the molar ratio of 5:1, the yield of (3) decreases to 63%, and the yield of (4) amounts to 37%. It shows that the molar ratio of toluene/benzyl alcohol is an important factor in the reaction.

4. Conclusions

A new superacid, SiO_2–Si–SCF_3, has been prepared and has been found to catalyze the benzylation of benzene, toluene, ethyl benzene, 1,2-xylene, 1,3-xylene, 1,4-xylene and anisol with benzyl alcohol to give corresponding substituted diphenylmethanes in 97–100% yields, respectively, and no any by-products are observed.

References

[1] T. Yamato, C. Hideshima, G.K.S. Prakash, G.A. Olah, J. Org. Chem. 56 (1991) 2089.
[2] L.M. Tang, Y. Lu, M.Y. Huang, Y.Y. Jiang, Polym. Adv. Technol. 5 (1994) 606.