Versatile mesoporous carbonaceous materials for acid catalysis

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Starbon mesoporous materials were synthesized after pyrolysis of expanded starch and subsequently functionalised with sulfonated groups, providing highly active and reusable materials in various acid catalysed reactions.

A new family of mesoporous carbonaceous materials named Starbons® has been recently discovered in our group.[1] These materials are directly produced from high surface area forms of starch and other expanded polysaccharides after pyrolysis at different temperatures. Mesoporous forms of the polysaccharide are needed to generate the Starbons® and high surface area starches have been found to be more stable upon storage for extended periods of time than any other high surface area polysaccharides (*e.g.* cellulose). Moreover, Starbons® can be directly prepared from the parent material (mesoporous expanded starch[2]) in a simpler and less wasteful process than other mesoporous forms of carbon.[3] The most extraordinary characteristics of these materials are a high degree of mesoporosity as well as easily tunable surface properties, from more starch-like to more graphite like, depending on the pyrolysis temperature. Materials have been found to be stable in a wide range of conditions, including boiling toluene and water and even in acid and basic solutions (high temperature Starbons®). Starbons® can be produced in different forms such as powders and monoliths, thus extending their range of useful applications. We have functionalised the Starbons® with acidic groups and tested the solid acid's activity in various acid catalysed reactions under thermal or microwave conditions.

Starbons® were synthesized as recently reported in the literature.[1] Material carbonised at 400 °C (herein after referred to as Starbon®-400) was chosen for its ideal hydrophilicity/hydrophobicity ratio and was subsequently functionalised. Starbon®-400 was suspended in H_2SO_4 (99.999% purity, 10 mL acid per g material) and heated for 4 h at 80 °C. After sulfonation, the solid acid was washed with distilled water until the washings were neutral, conditioned in boiling toluene (150 °C, 4 h) and water (100 °C, 3 h) and finally oven dried overnight (100 °C) before being tested in the catalytic reactions. Sulfonated material was denoted as Starbon®-400-SO_3H. Products were analysed by GC using an Agilent 6890 N GC model equipped with a 7683B series autosampler. Response factors of the different reaction products were determined with respect to the starting material in each reaction using known compounds in calibration mixtures of specified compositions.

The SO_3H loading in sulfonated Starbon®-400 was found to be 0.5 mmol g^{-1} and 0.3 mmol g^{-1} for the SO_3H sulfonated commercial DARCO® as measured by TG-IR.

We first tested our sulfonated Starbon® in the esterification of different organic acids in water (Table 1). Esterification reactions are one of the most useful transformations for organic acids,[4] especially for a dicarboxylic acid since the diester can be used as an intermediate in the manufacture of polymers, fine chemicals, perfumes, plasticizers and solvents.[5,6]

The drive towards greener process chemistry has resulted in some research reports of the partial or even complete replacement of organic solvents with water in a few organic reactions but to our knowledge there are no reports on esterification of organic acids in water. Indeed, esterifications have been reported as very sensitive to water environments due to different equilibrium steps in which water is involved.[7] However, we can expect to increase the reaction rates by altering the local water concentration in the active centre of the solid acids through careful adjustment of the local surface properties.

Table 1 summarises the conversion and selectivity values obtained for the esterification reaction of different diacids, under similar conditions, employing various solid acids. Four different substrates (succinic, fumaric, levulinic and itaconic acid) were screened in the esterification reaction in aqueous ethanol, yielding a very high conversion and selectivity to their respective esters. The rates of esterification of diacids (succinic, fumaric and itaconic) for our Starbon® material were found to be between 5 and 10 times higher than any commercial alternative solid acid catalyst (zeolites, sulfated zirconias, acidic clays, *etc.*). A diester selectivity improvement (from 35–50% range for the majority of the solid acids to >90% for Starbon®-400 at conversion levels of *ca.* 90%) was also obtained. Starbon® acid also exhibited a superior performance in the esterification reaction of the different acids screened compared to microporous commercial sulfonated carbons (DARCO® and NORIT®, Table 1), not only in terms of conversion but also in terms of selectivity to the diester (at conversion values of *ca.* 90%, selectivity to the diester was 35% for sulfonated DARCO® compared to the 90% of Starbon®) .

We then moved on to another acid catalysed reaction, the liquid-phase acylation of alcohols under microwave conditions. Acylation of aromatic alcohols is one of the most frequently used transformations for the synthesis of aromatic ketones, important intermediates in the production of pharmaceuticals, dyes, agrochemicals and fragrances.[8,9] Furthermore, the use of acetic acid (HAc) instead of the corrosive acetyl chloride or the lachrymator acetic anhydride provides many advantages from both economical and environmental points of view. Data is summarised in Table 2 and Fig. 1.

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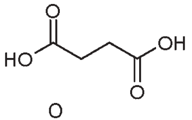
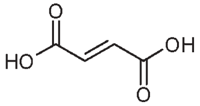
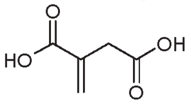
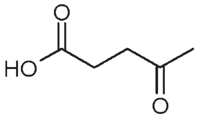
Table 1 Esterification of different organic acids over Starbon®-400-SO_3H in aqueous ethanol[a]

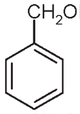
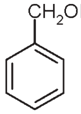
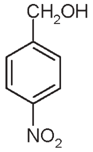
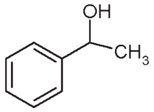
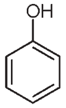
Acid	Structure	Run	Time/min	Conversion/mol%	Diester selectivity/mol%
Succinic		Blank	500	25	<10
		NORIT®		72	25
		DARCO®		81	28
		Starbon®		>99	>99
Fumaric		Blank	1000	<5	—
		DARCO®		83	70
		Starbon®		>99	90
Itaconic		Blank	1440	<10	—
		Starbon®		81	75
Levulinic		Blank	365	<5	>99[b]
		DARCO®		24	>99[b]
		Starbon®		85	>99[b]

[a] 1 mmol acid, 30 mmol EtOH, 50 mmol H_2O, 0.1 g Starbon-400-SO_3H, 80 °C. [b] The monoester was the only product obtained.

The acylation reaction performed under microwave conditions provided very good results, in terms of conversion and selectivity (Table 2), for a wide range of substrates screened in the reaction, in a very short period of time (less than 10 min). The blank reaction (no catalyst) gave a very poor reaction conversion compared to the Starbon® catalysed one (see Table 2, blank entry).

Moreover, several catalysts were also evaluated in the acylation reaction in order to compare results with those of Starbon®. Fig. 1 summarizes the catalytic activity of the main materials tested in the acylation of benzyl alcohol with acetic acid. The Starbon®-400-SO_3H catalysed benzyl alcohol acylation reaction rate was found to be between 5 and 10 times greater than any of the reactions with commercial catalysts [microporous beta-25 zeolite (SiO_2/Al_2O_3 ratio 25), mesoporous Al-MCM-41 and acidic Montmorillonite KSF] and twice as fast as similar sulfonated microporous carbonaceous materials (Fig. 1).

Table 2 Alcohol acylation with acetic acid over Starbon®-400-SO_3H under microwave conditions[a]

Entry	Alcohol	Time/s	Conversion/ mol%	Ester selectivity/ mol%
Blank		45	—	—
1		45	>99	>97
2		60	>99	>98
3		60	>99	>98
4		600	45	>99

[a] 2 mmol alcohol, 2 mmol HAc, 0.1 g Starbon-400-SO_3H, 300 W, 130 °C.

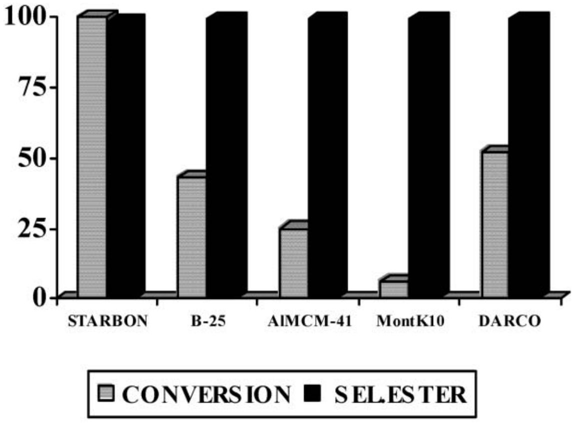


Fig. 1 Benzyl alcohol acylation with acetic acid over different solid acids (2 mmol benzyl alcohol, 2 mmol HAc, 0.1 g cat., 300 W, 130 °C, 45 s).

Finally, our materials were tested in the liquid-phase alkylation of different aromatic substrates with benzyl chloride under microwave conditions. The alkylation of aromatics is of particular importance in chemical manufacturing.[10,11] Results are shown in Table 3 and Fig. 2.

Sulfonated Starbon® afforded the alkylated compounds in very good yields and selectivity, where only either the *o*- or *p*- monoalkylated products were found (Table 3) except for the *m*-xylene alkylation, in which a *p*-/*o*- 3 : 2 ratio mixture was found. The Starbon®-400-SO_3H rate of reaction was at least comparable with that of beta-25 zeolite and much higher than any of the other catalysts tested, including sulfated zirconias (SZr) and mesoporous Al-MCM-41 materials. Interestingly, sulfonated DARCO® provided attractive activities compared to commercial zeolites and our Starbon® acids (Fig. 2).

To ensure the heterogeneous nature of the materials, a hot filtration test (typically half way through every reaction in which

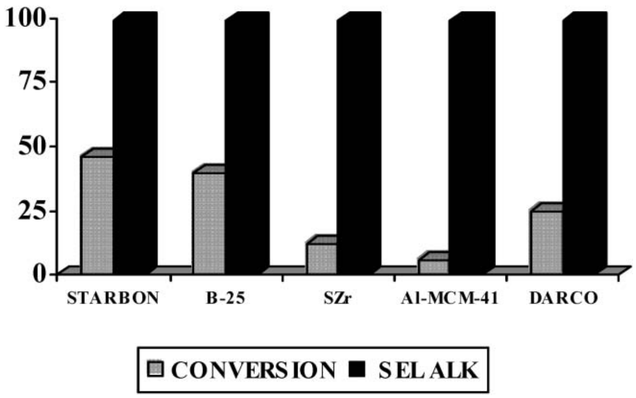
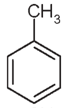
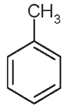
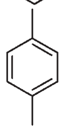
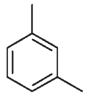
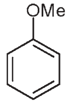


Fig. 2 *m*-Xylene alkylation with benzyl chloride over solid acids (5 mmol *m*-xylene, 2 mmol benzyl chloride, 0.1 g cat., 300 W, 150 °C, 900 s).

Table 3 Aromatic alkylation with benzyl chloride over Starbon®-400-SO_3H under microwave conditions[a]

Entry	Substrate	Time/s	Conversion/ mol%	Alkylation selectivity/ mol%
Blank		900	<5	>99 (*p*-)
1		900	>95	>99 (*p*-)
2		900	75	>99 (*o*-)
3		1800	82	>99 (*o*-, *p*-)
4		1800	>90	>99 (*p*-)

[a] 5 mmol substrate, 2 mmol benzyl chloride, 0.1 g Starbon-400-SO_3H, 300 W, 150 °C.

the materials were tested) was performed. The hot filtration test proved that the Starbon acids were behaving in a truly heterogeneous manner and no catalytic activity could be attributed to any leached species in the solution.

The highly active sulfonated Starbon® catalyst was easily recovered from the reaction mixture whereupon the reaction rates return to the background values, irrespective of the reaction performed. Starbon® acids reuse was simple and straightforward. Materials were filtered from the reaction mixture (after completion), washed with acetone at room temperature and subsequently oven dried at 100 °C overnight before another reaction was conducted. The recovered Starbon® could be added to fresh substrate solutions giving almost identical behaviour (for at least 3 reuses) to that observed in the original reaction (*i.e.* 98% conversion, >99% selectivity to the diester in the esterification of succinic acid after 3 reuses). Thus the catalyst is stable as well as active under a wide range of conditions.

Starbon® acid is a renewable, sustainable and environmentally compatible catalyst that can easily be obtained from biomass and has proven to be very effective for several acid catalysed reactions. Rates of reaction are generally considerably higher than those obtained with commercial solid acids. The hydrophilicity/hydrophobicity of the Starbons® can be tuned and optimised for enhanced performance in many applications.

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Notes and references

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