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RESEARCH NOTE

A New Solid Acid-Based Route to Linear Alkylbenzenes

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We have investigated the use of sulfated zirconia as a catalyst for the alkylation of benzene with long-chain linear alkenes. Optimum activity was obtained for SZ calcined between 500 to 550°C with subsequent cooling in a desiccator. Spectroscopic pyridine titration of the calcined catalyst shows that SZ is essentially Brønsted in nature under normal reaction conditions. Activity and selectivity are comparable to those of $AlCl_3$. A relationship between catalyst reusability and the pore structure has been observed. Microporous sulfated zirconia was found to be deactivated after the initial reaction, whereas mesoporous sulfated zirconia was reusable. The deactivated catalysts can be regenerated by both solvent extraction and thermal treatment; the latter resulted in complete regeneration of catalyst activity. © 2000 Academic Press

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The alkylation of aromatic substrates is an industrially important synthetic transformation. The preferred alkylating agents are alkenes due to their low cost and ease of availability. However, their use does add to the potential complexity of the system with polyalkylation, dealkylation, and isomerisation giving rise to products other than the normally desired monoalkylaromatic (1). Another important issue in these environmentally conscious days is the choice of acid catalyst (2). Traditionally these reactions have been catalysed by soluble or liquid Brønsted acids such as H_2SO_4 or Lewis acids such as $AlCl_3$ or BF_3. The normal work-up procedure for reactions employing such acids involves a water quench which prevents the acid from being reused and on subsequent neutralisation leads to an aqueous salt waste stream. The introduction of solid acids such as zeolitic materials has removed the need for a quench step, facilitating catalyst reuse through continuous reactions or by separation of the solid phase on work-up. Solid acids are also generally much easier and safer to handle. Unfortunately, solid acids such as clays and zeolites have significantly lower activities than homogeneous acids, although they can give greatly improved reaction selectivity. Thus, while the reaction of benzene with linear alkenes using $AlCl_3$ occurs rapidly at room temperature, the corresponding reactions with zeolites only occur under forcing conditions of temperature and pressure (3). Solid acids possessing strong acidic sites have been reported that exhibit activities comparable to that of $AlCl_3$ (4). However, their high susceptibility to water means that special handling conditions are required. There is a real need for a solid acid that offers the safety, stability, and recoverability advantages of zeolites while matching the activity of the best traditional acids.

In this paper we describe how the known solid acid, sulfated zirconia, exhibits a good combination of these properties in the alkylation of benzene with 1-dodecene. Sulfated zirconia (SZ) has attracted a lot of attention due to its high catalytic activity for the conversion of small hydrocarbons, especially *n*-butane isomerisation (5). However, its application in liquid phase organic reactions is less well known. SZ has been reported to possess high Lewis acid activity and this has encouraged some studies on its use in liquid phase Friedel–Crafts benzoylation reactions. However, these have only met with moderate success (6, 7).

Pyridine is a useful probe molecule for the determination of Lewis and Brønsted acid sites by FTIR spectroscopy (8). We have observed that sulfated zirconia (supplied by MEL chemicals and denoted SZ-I) calcined between 500–600°C with subsequent cooling in either a desiccator or under ambient conditions, exhibited only Brønsted acidity. Even predrying at 300°C in an IR cell failed to produce significant Lewis activity in the material. These results can be compared with those obtained by Davies *et al.* (13). They observed that SZ calcined at 650°C exhibited significant Lewis acidity. However, in their analysis the SZ was reactivated at 400–600°C prior to pyridine adsorption. In our studies pyridine was adsorbed in the absence of any thermal treatment after calcination. Thus, the observation that the catalyst possesses only Brønsted acid sites appears to be a result of adsorption of atmospheric water at the Lewis acid centres. Therefore, under reasonable handling and pretreatment conditions for a liquid phase, batch type

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application, activated SZ can be considered as being essentially a Brønsted acid. This can be expected to have a significant effect on its performance as a solid acid catalyst. Thus, in Friedel–Crafts acylations using acid chlorides, SZ might not be expected to be very effective. This seems to be the case. In a model reaction, benzene (0.5 mol) was reacted with benzoyl chloride (0.05 mol) at 85°C using SZ (10 g, calcined at 550°C). The rate of reaction was slow with complete conversion after 48 h. However, with the more reactive anisole, complete reaction can be achieved after 1 h at 140°C. The SZ is reusable and we were able to reach turnover numbers of >20 without significant loss in activity. This activity and stability compares quite well with, for example, clay-based catalysts but the activity is well below that of a soluble acid such as $AlCl_3$. However, it should be noted $AlCl_3$ is not recoverable and usually requires a stoichiometric amount for sufficient reaction to occur. Friedel–Crafts alkylations using alkenes should, however, be more amenable to Brønsted acid catalysis and this is borne out by our results. Most of our studies have used 1-dodecene as the alkylating agent as the desired product monododecylbenzene is the precursor to linear alkylbenzene sulphonate which is the most widely used surfactant in the detergent industry (3, 10, 11).

The alkylation reaction was carried out as follows. 1-Dodecene (0.025 mol) was added gradually over 40 min to benzene (0.25 mol) and SZ-I (1 g calcined at 500°C, dried in a desiccator, and then oven dried immediately before use at 300°C) at 35°C. This resulted in complete conversion of the alkene (after the final addition of the alkene) and the formation of 93% monododecylbenzene, 43% of which is the (preferred) 2-isomer (10). Only zeolites have been shown to give higher selectivities but at the cost of very low activity (even at >100°C reaction is incomplete after 10 h) (3). The calcination temperature is critical. Activity drops precipitously at calcination temperatures below 450°C and above 550°C (e.g., only 42% conversion after 40 min using SZ calcined at 580°C). It is known that at temperatures that are too low active sites are not formed (5). As the calcination temperature increases, the surface area and the sulfate loading, critical for acidity, decreases (Fig. 1) giving a narrow window of optimum activity. These results can be compared to work by Yadav *et al.* on the alkylation of *p*-cresol with isobutylene. Sulfated zirconia, calcined at 650°C for 3 h, exhibited good activity towards both mono- and dialkylation (14). However, no optimisation of the calcination temperature was discussed. Therefore, it should be noted that the effect of calcination temperature on the activity of SZ should be considered together with the reaction being undertaken. For the reaction discussed here, involving the formation of large bulky molecules, a large surface area and mesoporous pore structure (discussed later) are favourable.

The catalyst was found to be completely deactivated after the first use. Thermal analysis of the deactivated catalyst shows a significant new weight loss at ca. 500°C; this is in addition to a lower temperature weight loss which can be attributed to adsorbed product (Fig. 2). The higher temperature weight loss is possibly due to alkene oligomers which will block smaller pores and the accompanying exotherm is a result of their deoligomerisation. For comparison, we investigated two other sulfated zirconias (supplied by MEL chemicals). The first, SZ-II, possessed an almost identical pore structure to the initial catalyst, SZ-I (N_2 adsorption isotherm indicates both catalysts possess a mixture of micro- and mesopores; SSA = 130 m^2/g, pore volume = 0.1 cm^3/g). However, SZ-II possesses a lower sulfate loading than that of SZ-I (sulfate loadings, prior to calcination, are 6% and 10% respectively). The second catalyst, SZ-III, exhibited a significantly greater mesoporous structure (SSA = 162 m^2/g, pore volume = 0.22 cm^3/g) but possessed a sulfate loading similar to that of the initial SZ-I (sulfate loadings, after calcination, are 6% and 6.5% for SZ-I and SZ-III respectively). It was observed that the two microporous catalysts were deactivated after the initial reaction, with SZ-II exhibiting lower activity (only complete conversion after 120 min). However, SZ-III was found to be reusable, although activity was reduced on reuse (complete conversion obtained after 90 min compared to complete conversion after 40 min for the initial reaction).

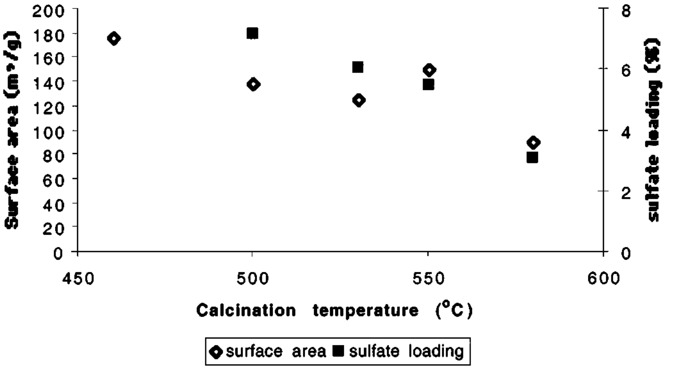

FIG. 1. Effect of calcination temperature on sulfate loading and surface area (SZ-I).

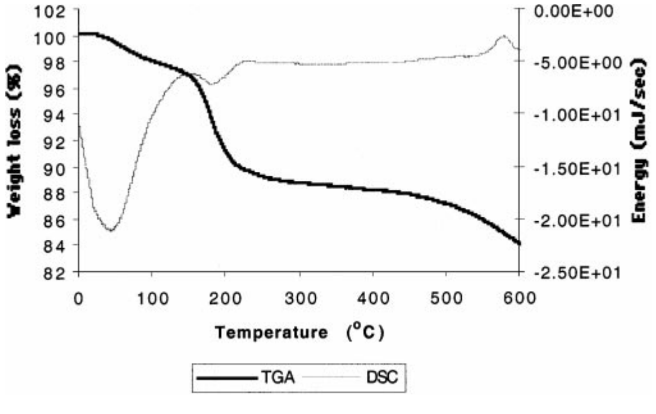

FIG. 2. Thermal analysis of the deactivated SZ-I.

These results suggest that the loss in catalyst activity is due, in part, to blockage of the pores with oligomerised dodecene. Thus, the increased mesoporosity of SZ-III results in this effect being reduced; hence, the catalyst is reusable. Thermal analysis of SZ-III after the initial reaction shows only a small weight loss of 1–2% at 500°C. The same catalyst after the second use exhibits a much greater weight loss at this temperature (∼5%) comparable to the weight loss observed for SZ-I after the initial reaction (Fig. 2). This seems to suggest that there is a build-up of oligomerised 1-dodecene on successive use and reuse. Loss of acid sites from the catalyst surface does not seem to be the cause of deactivation. Sulfate analysis of the catalyst before and after the reaction show almost identical sulfate loadings (6.5% and 6.3% respectively). However, it should be noted that reduction of the sulfate groups as a possible mode of catalyst deactivation has not been ruled out. This has been suggested as a mechanism for SZ deactivation in *n*-butane isomerisations (12). In recent years several workers have prepared mesoporous zirconias using anionic and cationic surfactants as structure-directing templates (analogous to MCM-41 materials) (15–17). These zirconias possess high surface areas (∼500 m^2/g) and narrow pore size distributions in the mesoporous range. Thus, zirconias prepared by this methodology, once sulfated, may offer significant advantages in terms of activity and reuse over other sulfated zirconias. However, Morterra *et al.* (18) have observed that SZ, active in *n*-alkane isomerisations, could only be prepared from sulfation of either the amorphous hydroxide or the oxide when in the tetragonal crystal phase (SZ was inactive if prepared from the monoclinic phase). Hence, the templated zirconia would have to be in the tetragonal phase to obtain an active catalyst.

We have found that the deactivated SZ can be partially regenerated by solvent extraction to remove most of the “heavy” products. Thus, the used SZ was refluxed in diethyl ether for 15 min, resulting in almost complete removal of the products from the catalyst surface (as determined by thermal analysis). Further refluxing in deionised water (for 15 min), followed by thermal treatment at 300°C for 4 h, resulted in the SZ converting 50% 1-dodecene after 40 min. In addition, the solvent-extracted SZ could be completely regenerated by calcining at 550°C for 3 h. Optimisation of this process is currently being investigated.

We have found that SZ-I can be stored under ambient conditions with deactivation only occurring after prolonged periods (approximately 14 days). In addition, the deactivation is reversible, with the catalyst activity completely restored by thermal treatment (300°C in air for 2 h). Initial deactivation can be overcome by storing the catalyst under anhydrous conditions. A sample of the same catalyst stored in a desiccator for 14 days resulted in only partial deactivation (65% conversion of 1-dodecene under standard reaction conditions). Deactivation was further reduced when the catalyst was stored under partial vacuum (>80% conversion of 1-dodecene). Similar results were also obtained for both SZ-II and SZ-III.

The reaction seems to be general to alkenes. C6–C16 alkenes give almost identical rates of conversion and selectivities to the corresponding monoalkylbenzenes (Table 1). The combination of activity comparable to the most active Lewis acids, good selectivity, and the stability and handling advantages of zeolites is unique and makes sulfated zirconia a very attractive catalyst for the alkylation of benzene.

TABLE 1

Alkylation of Benzene Catalysed by Optimally Activated Sulfated Zirconia (SZ-I)[a]

	Composition of product mixture (%)[b]		
Alkene	Alkene	Monalkylate	Dialkylate
1-Hexene	<0.5	91	8
1-Octene	0	94	6
1-Dodecene	<0.5	93	6
1-Hexadecene	2.5	94	0[c]

[a] Reactions were carried out as described in the text.
[b] By GC (corrected).
[c] 3% of other products.

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