Synthesis of a novel supported solid acid BF_3 catalyst

Karen Wilson and James H. Clark*

Green Chemistry Group, Department of Chemistry, University of York, Heslington, York, UK YO1 5DD. E-mail: jhc1@york.ac.uk

A novel and active form of supported boron trifluoride has been prepared and the active sites identified.

Tightening environmental legislation on the production of waste during homogeneously acid catalysed reactions has led to a demand for heterogenised systems that will aid recovery of the catalyst and minimise pollution. BF_3 is widely used as a Lewis acid catalyst in many organic reactions, including alkylation, acylation, polymerisation, isomerisation and addition reactions,[1] and may be used directly from the gas phase, or complexed with an organic or inorganic ligand (*e.g.* $BF_3{\cdot}OEt_2$ or $BF_3{\cdot}H_3PO_4$). Recovery of boron from the reaction however results in the formation of large amounts of waste, which on an industrial scale is environmentally unacceptable.

The use of a heterogeneous BF_3 system would offer ease of catalyst recovery and reuse, and minimise the production of waste currently formed during BF_3 recovery. However a suitable replacement supported system must also exhibit activities/selectivities comparable to the existing homogeneous route. To date previous attempts to produce oxide supported BF_3 has focused on the use of gaseous BF_3.[2–4] In this paper we report the synthesis, characterisation and reactive properties of a novel mesoporous SiO_2 supported solid acid catalyst prepared using liquid BF_3 precursors. The activity of the catalyst towards the alkylation of phenol with oct-1-ene to form octyl phenyl ether or octylphenol (important in the production of lubricants) was examined.

A range of SiO_2 supported BF_3 catalysts (4 mmol g^{-1} loading) were prepared from $BF_3(H_2O)_2$ (Aldrich 96%) and $BF_3{\cdot}OEt_2$ (Aldrich 99%) precursors. Mesoporous SiO_2 (K100-Merck) of surface area 310 m^2 g^{-1} was dried for 24 hours at 300 °C, then stirred under a N_2 atmosphere with a mixture of the precursor diluted in 100 ml of ethanol or toluene at 20 °C or reflux respectively. The catalyst slurry was stirred for 2 hours, then dried slowly on a rotary evaporator at 50 °C.

Characterisation of the acid sites present on the surface was performed by recording DRIFT spectra following titration of the supported BF_3 catalysts with pyridine as shown in Fig. 1. These show that all the catalysts exhibit both Lewis and Brønsted acidity, as indicated by the absorption bands at 1445 and 1461 cm^{-1}, (Lewis sites), and those at 1638 and 1539 cm^{-1} (Brønsted sites). The remaining bands at 1611 and 1489 cm^{-1} are assigned to pyridine bound at either Lewis or Brønsted sites. There is a striking difference in the nature of the acid sites depending on catalyst preparation, with the catalyst prepared from the $BF_3(H_2O)_2$ precursor in ethanol exhibiting the most intense Brønsted bands. Brønsted acidity in solid acid catalysts normally arises from polarised $^{\delta-}O{-}H^{\delta+}$ sites. The observation of strong Brønsted acidity following attachment of a Lewis acid centre to an oxide support has been reported in other systems,[4,5] and might be attributed to polarisation of surface hydroxyl groups *via* an inductive effect of the electronegative F atoms on BF_3. However what is remarkable in this instance is how the Brønsted acidity varies with catalyst preparation, with the catalysts prepared in ethanol exhibiting higher concentrations of Brønsted acid sites than those prepared in toluene.

The origin of the acid sites on the ethanol prepared $BF_3(H_2O)_2/SiO_2$ catalyst was investigated using thermogravimetric analysis coupled with evolved gas FTIR (TGIR), which allows molecules desorbing from the catalyst during thermal analysis to be identifed by their vibrational spectrum. Fig. 2 shows the thermal analysis results for supported $BF_3(H_2O)_2$ and $BF_3{\cdot}OEt_2$ catalysts which had been prepared in ethanol. Heating both catalysts above 100 °C results in significant weight loss and the observation of ethanol desorption in the IR. However the differential mass lost indicates that the ethanol desorption temperature from $BF_3(H_2O)_2/SiO_2$ is 10 °C higher than from $BF_3{\cdot}OEt_2/SiO_2$, and approximately twice the amount of ethanol is evolved. This corresponds to approximately 4 and 2.5 mmol g^{-1} of ethanol present on each catalyst respectively. The uptake of short chain alcohols has been used as an indication of the strength and concentration of Brønsted acid sites on zeolites.[6] These results therefore suggest that $BF_3(H_2O)_2/SiO_2$ possesses a higher coverage of stronger Brønsted acid sites compared to $BF_3{\cdot}OEt_2/SiO_2$.

Further heating beyond 400 °C results in an additional weight loss which is accompanied by the evolution of HF from the

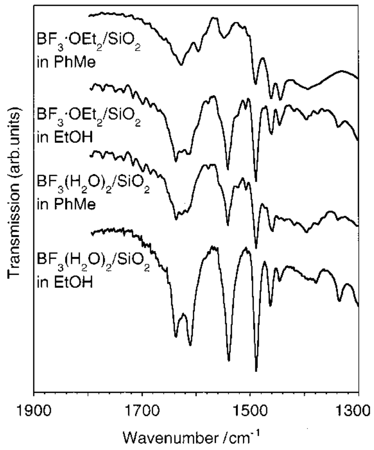


Fig. 1 DRIFTS following pyridine titration of 4 mmol g^{-1} BF_3/SiO_2 catalysts prepared using $BF_3(H_2O)_2$ and $BF_3{\cdot}OEt_2$ precursors in ethanol or toluene

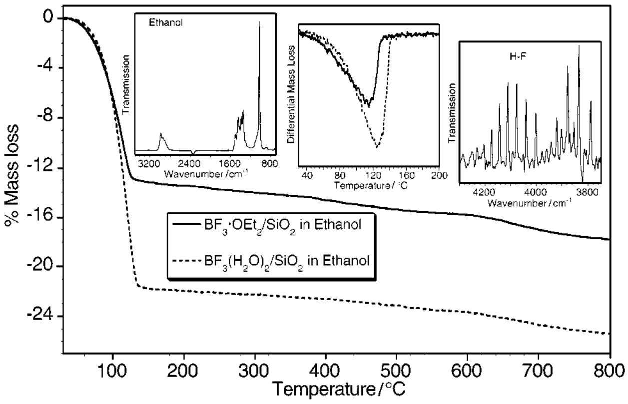


Fig. 2 TGIR comparing 4 mmol g^{-1} $BF_3(H_2O)_2/SiO_2$ and $BF_3{\cdot}OEt_2/SiO_2$. IR spectra recorded during decomposition reveal the evolution of ethanol and HF. The differential mass loss is also shown to indicate the peak ethanol desorption temperature.

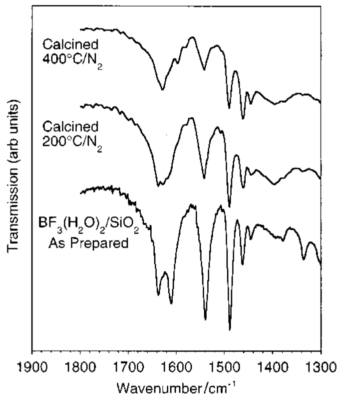


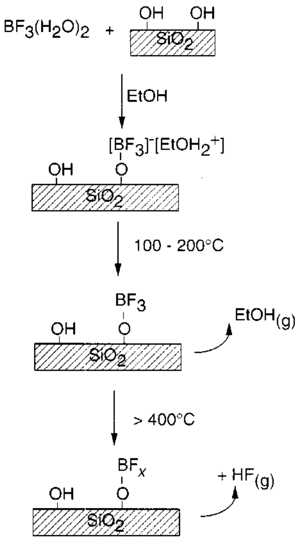
Fig. 3 DRIFTS following pyridine titration of 4 mmol g^{-1} $BF_3(H_2O)_2/SiO_2$ after calcination to 200 °C and 400 °C under N_2. All spectra were recorded at 20 °C.

catalyst. Corresponding DRIFTS/pyridine titrations of catalysts calcined to 200 and 400 °C under N_2, shown in Fig. 3, indicate that the Brønsted sites are gradually lost as the calcination temperature is increased.

While BF_3 alone is a Lewis acid, it is often used catalytically when bound to organic ligands to form strong proton donating complexes.[1] The evolution of ethanol at 120 °C coupled with the loss of Brønsted acidity indicates that Brønsted acid sites in the $BF_3(H_2O)_2/SiO_2$ catalyst may arise from the binding of ethanol to supported BF_3 centres resulting in the formation of a $[SiOBF_3]^-[EtOH_2]^+$ complex. Further evidence in support of this model comes from ^1H MAS NMR of the as prepared catalyst which show resonances at 1.343, 4.009 and 8.160 ppm which are consistent with CH_3, CH_2 and OH_2^+ of protonated ethanol respectively.[6] Previous studies have reported that ligand exchange between $BF_3\cdot OEt_2$ and ethanol results in the formation of $H^+[BF_3OEt]^-$ complexes.[7] However, to form the protonated ethanol complex proposed in this model interaction with a more protic BF_3 complex is required, *e.g.* $BF_3(H_2O)_2$, which can exist as $[H_3O]^+[BF_3OH]^-$.[1] The trend in Brønsted acidity observed between $BF_3\cdot OEt_2$ and $BF_3(H_2O)_2$ precursors can thus be understood in these terms.

Desorption of ethanol from the $BF_3(H_2O)_2/SiO_2$ catalyst following 200 °C calcination lowers the number of Brønsted sites titratable by pyridine (Fig. 3). We atttribute those remaining to the polarisation of surface hydroxyl groups on the support by the BF_x centres. By 400 °C dehydroxylation of the support further reduces the number of Brønsted sites leaving predominantly Lewis acid character, as evidenced by the DRIFTS bands at 1627 and 1462 cm^{-1} which are attributed to the BF_x sites. The evolution of HF above 400 °C observed by TGIR indicates that these BF_x groups start to decompose above this temperature, and by 600 °C no titratable acid sites remain indicating complete decomposition of the BF_x centres. Likewise BET measurements on calcined $BF_3(H_2O)_2/SiO_2$ catalysts reveal the surface area is maintained at 258 m^2 g^{-1} up to 200 °C, indicating that the BF_3 sites are stable to this temperature. An increase in surface area to 266 m^2 g^{-1} is observed on calcining to 400 °C, consistent with the decomposition of BF_3. It should be noted that due to outgassing procedures prior to BET measurements changes in surface area due to ethanol desorption cannot be observed. We believe that these spectroscopic results can be summarised by the model presented in Scheme 1.

The catalytic activity of these supported BF_3 samples was tested using the reaction of oct-1-ene with phenol (performed at 85 °C using 0.05 M of each reactant, in 100 ml of 1,2-dichloroethane with 1 g of supported BF_3 catalyst). Table 1 shows the phenol conversion and selectivities towards octyl phenyl ether obtained after 23 hours reaction time. It is clear that the activity of the $BF_3(H_2O)_2/SiO_2$ catalyst prepared in ethanol is superior to the other samples. The activity can thus be correlated with the number and strength of Brønsted acid sites identified on these catalysts using TGIR.



Scheme 1

Table 1 Phenol conversion and selectivities towards octyl phenyl ether after 23 h reaction for the different catalysts

Catalyst	Phenol conversion (%)	Ether selectivity (%)
$BF_3(H_2O)_2/SiO_2$ (EtOH)	30	61
$BF_3(H_2O)_2/SiO_2$ recycled	6	97
$BF_3(H_2O)_2/SiO_2$ ($PhCH_3$)	4	78
$BF_3\cdot OEt_2/SiO_2$ (EtOH)	3	85
$BF_3\cdot OEt_2/SiO_2$ ($PhCH_3$)	<1	92

Following reuse of $BF_3(H_2O)_2/SiO_2$ samples, a decrease in conversion and selectivity towards ring alkylation products is observed relative to the fresh catalyst. Preliminary characterisation of used catalyst, by DRIFTS and pyridine titration, indicates the nature of the acid sites remains essentially unchanged. The loss of activity on recycling the catalyst may result from organic residue deposited on the catalyst during reaction causing pore blocking and/or poisoning of active sites.

In conclusion, we have synthesised a novel form of supported boron trifluoride which is easy to prepare and handle, shows unusually high Brønsted acidity which can be controlled by activation temperature, and exhibits considerable catalytic activity.

We thank the EPSRC for funding the project, EPSRC/RAEng for a Clean Technology Fellowship (to J. H. C.), and colleagues at York and the University of Newcastle Chemical and Process Engineering Department for helpful discussions.

Notes and References

1 A. V. Topchiev, S. V. Zavgorodnii and Ya. M. Paushkin, *Boron fluoride and its compounds as catalysts in organic chemistry*, Pergamon Press, London, 1958.
2 C. Guo, S. Liao, Z. Qian and K. Tanabe, *Appl. Catal. A*, 1994, **107**, 239.
3 B. A. Morrow and A. Devi, *J. Chem. Soc., Faraday Trans.*, 1972, **68**, 403.
4 M. Marczewski, H. Marczewska and K. Witoslawski, *Bull. Soc. Chim. Fr.*, 1991, 366.
5 E. E. Getty and R. S. Drago, *Inorg. Chem.*, 1990, **29**, 1186.
6 A. Thursfield and M. W. Anderson, *J. Phys. Chem.*, 1996, **100**, 6698.
7 V. A. Tkach, V. A. Gruznykh, N. A. Murasheva, G. Myagmarsuren, T. V. Dmitrieva, G. V. Ratovskii, S. V. Zinchenko and F. K. Shmidt, *React. Kinet. Catal. Lett.*, 1991, **43**, 431.

Received in Cambridge, UK, 3rd August 1998; 8/06060F