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Environmentally Benign Bi-functional Solid Acid and Base Catalysts

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ABSTRACT:

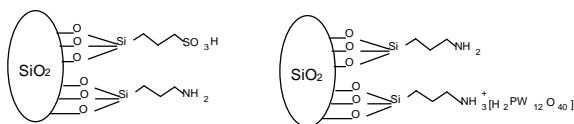
Solid bi-functional acid-base catalysts were prepared in two ways on an amorphous silica support: 1) by grafting mercaptopropyl units (followed by oxidation to propylsulfonic acid) and aminopropyl groups to the silica surface ($\text{NH}_2\text{-SiO}_2\text{-SO}_3\text{H}$), and 2) by grafting only aminopropyl groups and then partially neutralising with phosphotungstic acid, relying on the $\text{H}_2\text{PW}_{12}\text{O}_{40}^-$ ion for surface acidity ($\text{NH}_2\text{-SiO}_2\text{-NH}_3^+[\text{H}_2\text{PW}_{12}\text{O}_{40}^-]$, denoted as $\text{NH}_2\text{-SiO}_2\text{-PTA}$). Surface acidity and basicity were characterised by adsorption calorimetry, using SO_2 as a probe for surface basicity and NH_3 for surface acidity. Catalytic activities were compared in a two-stage cascade: an acid-catalysed deacetalisation followed directly by a base-catalysed Henry reaction. Overall, the $\text{NH}_2\text{-SiO}_2\text{-SO}_3\text{H}$ catalysts showed higher concentrations and strengths of both acid and base sites, and higher activities than $\text{NH}_2\text{-SiO}_2\text{-PTA}$. Both catalysts showed evidence of cooperative acid-base catalysis. Importantly, the bi-functional catalysts exhibited catalytic advantage over physical mixtures of singly functionalised catalysts.

1. INTRODUCTION

Many liquid phase processes in fine chemicals synthesis require acid or base catalysts. Conventionally, homogeneous acids and bases dissolved in the reaction mixtures are used. In most cases, replacing these with solid acids and bases brings substantial environmental benefit by reducing waste and simplifying product separation.¹⁻³ Almost inevitably, however, solid acids and bases are less active than their homogeneous counterparts. Despite this, one case where they might be able to offer particular advantage is where both acid and base catalysis is required, either in sequential steps or through a cooperative catalytic mechanism. For reactions of this type, a single, bi-functional acid-base solid catalyst can replace two liquid catalysts, and one reaction step can replace two, simplifying the process and reducing waste. Preparing materials of this type is difficult, not least because of mutual neutralisation, and the challenge remains to develop solid bi-functional acid-base catalysts with stabilities and activities of practical use.

Some metal oxides are amphoteric and exhibit bi-functional catalytic properties. The acidic and basic properties of zirconia can be tuned through doping and through controlling the crystalline phase of the oxide.⁴ An alternative approach is chemical grafting of acid and base groups to an inert support. Early examples used polymer supports.^{5,6} More recently rigid supports have been used, notably by Davis^{3,7}, by Shanks⁸ and by Gianotti and Diaz.⁹ Tethered aminoalkyl and aminoaryl groups have most commonly been used as the source of basicity. Acidity has been added in various ways. Sulfonic acid groups have been used, as well as carboxylic and phosphoric acid groups (there is an argument that weaker acids are more likely to remain protonated in the presence of amine).⁷ Sometimes the weakly acidic silanol groups on the support have been adequate.⁸ In our own earlier work, we tethered aminopropyl groups to SBA-15 silica and acidity was added by reacting phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) with a fraction of the amine groups on the surface, leaving $\text{H}_2\text{PW}_{12}\text{O}_{40}^-$ as the source of acidity, and unreacted amine groups to provide basicity.¹⁰ The work reported in this paper extends this to compare bi-functional acid/base catalysts prepared by this route (labelled $\text{NH}_2\text{-SiO}_2\text{-NH}_3^+[\text{H}_2\text{PW}_{12}\text{O}_{40}^-]$ or $\text{NH}_2\text{-SiO}_2\text{-PTA}$) with bi-functional catalysts prepared by supporting aminopropyl and propylsulfonic acid groups on the same support, tethered via alkoxysilanes (labelled $\text{NH}_2\text{-SiO}_2\text{-SO}_3\text{H}$; see Scheme 1).

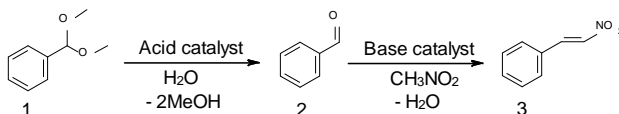
Scheme 1. $\text{NH}_2\text{-SiO}_2\text{-SO}_3\text{H}$ and $\text{NH}_2\text{-SiO}_2\text{-NH}_3^+[\text{H}_2\text{PW}_{12}\text{O}_{40}]^-$ bi-functional catalysts.



A difficulty associated with preparation of the aminopropyl/propylsulfonic acid bi-functional catalysts ($\text{NH}_2\text{-SiO}_2\text{-SO}_3\text{H}$) is that the acid group is grafted to the silica using (3-mercaptopropyl)trimethoxysilane (MPTMS) and an oxidation step is required to convert the thiol (-SH) to sulfonic acid (-SO₃H). The two main routes reported are based on hydrogen peroxide/sulfuric acid, and on nitric acid (as both oxidant and acidifier).^{11, 12} The method used must be chosen to effectively oxidise thiol¹² but with minimal reaction with the base groups. Nitric acid has been shown to be the more effective reagent under these conditions¹³ so nitric acid is used as the oxidant in the work reported here.

An amorphous silica gel has been used as the catalyst support, rather than the ordered SBA-15 silica used in our previous work. Silica gel does not exhibit the friability and low bulk density of SBA-15¹⁴⁻¹⁶ while the surface properties and stability are similar, and it can be functionalised in the same way. The silica gel used here has been chosen to have an average pore diameter similar to that of SBA-15. The tandem deacetalisation-Henry reaction shown in Scheme 2 has been used. The first step is the acid-catalysed deacetalisation of benzaldehyde dimethyl acetal in the presence of water to give benzaldehyde. The benzaldehyde then reacts with nitromethane under base catalysis to give nitrostyrene.

Scheme 2. Tandem deacetalisation-Henry reaction.



2. EXPERIMENTAL

2.1. Materials

Silica gel (particle size 40-63 μm ; average pore size 6 nm), (3-mercaptopropyl)trimethoxysilane (MPTMS), (3-aminopropyl)trimethoxysilane (APTMS), nitromethane, benzaldehyde dimethyl acetal, acetone, o-xylene, dichloromethane (DCM), ethanol (EtOH), and phosphotungstic acid were purchased from Aldrich. Benzaldehyde was purchased from Acros and nitric acid from Fischer. Unless noted otherwise, all chemicals were at least 99 % pure and used as received. Deionized water was used in all experiments. The silica gel was activated before use by refluxing 30 g in 150 ml HCl solution (37 %) for 4 h at 100 $^{\circ}\text{C}$, to remove any adsorbed metal ions and maximise the surface silanol concentration. It was washed thoroughly with hot water to remove all acid residues, and dried in still air at 120 $^{\circ}\text{C}$ for 12 h.¹⁷

2.2. Catalyst Synthesis

2.2.1. Supported Aminopropyl Catalysts ($\text{SiO}_2\text{-NH}_2$)

Activated silica gel (3.0 g) was suspended in 50 ml dry toluene, and 3 ml APTMS added. Using a slightly modified published procedure,¹⁸ the mixture was refluxed under dry nitrogen for 12 h at 80 $^{\circ}\text{C}$. The liquid was filtered, and the cake washed with 300 ml DCM and 200 ml EtOH, and then dried at 120 $^{\circ}\text{C}$ in still air for 12 h.

2.2.2. Supported Propylsulfonic Acid Catalysts ($\text{SiO}_2\text{-SO}_3\text{H}$)

Activated silica gel (3.0 g) was treated as above but with 3 ml MPTMS¹⁸ to form $\text{SiO}_2\text{-SH}$. To convert thiol groups to sulfonic acid groups, 0.5 g of $\text{SiO}_2\text{-SH}$ was suspended in 20 ml of 70% nitric acid solution (oxidant) at room temperature for 4 h.¹¹ The modified silica gel was filtered and washed with water until the pH of the washings was over 6, and allowed to dry overnight.

2.2.3. Supported Aminopropyl/Propylsulfonic Acid Bi-functional Catalysts ($\text{NH}_2\text{-SiO}_2\text{-SO}_3\text{H}$)

Activated silica gel (1.0 g) was suspended in 50 ml toluene at 80 $^{\circ}\text{C}$ followed by the addition of 1 ml of APTMS and 1 ml of MPTMS. The mixture was refluxed under nitrogen for 12 h at 80 $^{\circ}\text{C}$. The modified silica gel was filtered, washed with 300 ml dichloromethane and 200 ml ethanol and left to dry at room temperature, to yield $\text{NH}_2\text{-SiO}_2\text{-SH}$. This material (0.5 g) was then suspended in 20 ml of 70% nitric acid at room temperature for 4 h to convert thiol to sulfonic acid groups. The modified silica gel was rinsed with excess H_2O (4 x 500 ml) until the slurry reached a neutral pH. The solid was collected by filtration and allowed to dry overnight.

2.2.4. Supported Aminopropyl/Phosphotungstic Acid Bi-functional Catalysts (NH₂-SiO₂-PTA)

SiO₂-NH₂ (1.0 g), prepared as described above, was stirred with a methanolic solution of 0.05 mmol phosphotungstic acid per mmol of amine (amine content determined by nitrogen analysis) for 20 h. The solid was washed with warm water (60 °C) and dried to yield NH₂-SiO₂-PTA(0.05). Similar materials were prepared with 0.1, 0.5 and 0.9 mmol of phosphotungstic acid per mmol of amine and were labelled: NH₂-SiO₂-PTA(0.1), NH₂-SiO₂-PTA(0.5) and NH₂-SiO₂-PTA(0.9).

2.3. Catalyst Characterization

Nitrogen adsorption and desorption isotherms were measured at 77 K on a Micromeritics ASAP-2020 after evacuation at 423 K for 5 h. The surface areas and the average pore sizes were calculated from the adsorption isotherm using the BET method and the desorption isotherm using the BJH method respectively. Levels of functionalisation were initially assessed through nitrogen, sulfur and carbon elemental analysis (MEDAC Ltd). To obtain information on the local environment and the degree of condensation of the network, ³¹P and ¹³C cross-polarization (CP) magic angle spinning (MAS) NMR spectra were collected using a Varian VNMRS 400 spectrometer.

Catalyst basicity and acidity were quantified by SO₂ and NH₃ adsorption calorimetry, respectively. These experiments were performed using a system based on a flow-through Setaram 111 differential scanning calorimeter (DSC) and an automated gas flow and switching system, with a mass spectrometer (MS) detector for the downstream gas flow, described elsewhere.^{19, 20} In a typical adsorption experiment, the catalyst (30 mg) was activated at 120 °C under dry nitrogen flow at 10 ml min⁻¹. Following activation, and maintaining the sample at 120 °C, pulses of the probe gas (1% ammonia in nitrogen or 1% sulfur dioxide in nitrogen) at atmospheric pressure were injected at regular intervals into the carrier gas stream from a gas-sampling valve. The concentration of the probe gas downstream of the sample was monitored continuously. The amount of the probe gas irreversibly adsorbed from each pulse was determined by comparing the MS signal during each pulse with a signal recorded during a control experiment. The net heat released for each pulse was calculated from the DSC thermal curves. From this, the molar enthalpies of adsorption of sulfur dioxide or ammonia ($\Delta H^{\circ}_{\text{ads}}$) were obtained for the amount adsorbed from each

successive pulse. The $\Delta H_{\text{ads}}^{\circ}$ values are plotted against the amount of irreversibly adsorbed probe gas per gram of the catalyst, to give a profile that can be interpreted in terms of the abundance and strength distribution of active sites.

2.4. Catalytic Activity

Catalysts were activated before use at 120 °C for 2 h. Benzaldehyde dimethylacetal (0.15 ml, 1.0 mmol) and nitromethane (10 ml, 184.6 mmol) were added to a glass reactor. The mixture was heated to 90 °C under nitrogen and catalyst (0.05 g) and water (0.06 ml, 3.3 mmol) added. The stirrer speed was set to ensure that the reaction was not under diffusion control. Control experiments confirmed that the reaction did not proceed in the absence of catalyst. The reaction mixture was sampled regularly and analysed by gas chromatography (FID, 25 m BPI column). The gas chromatograph was calibrated for quantitative measurement of benzaldehyde dimethylacetal, benzaldehyde and nitrostyrene. In all cases, selectivity to the product benzaldehyde from the first reaction, and to the product nitrostyrene from the second reaction, was 100 %. See Supporting Information for details of product identification.

3. RESULTS AND DISCUSSION

Table 1 shows the elemental analysis data for the supported aminopropyl and aminopropyl/sulfonic acid catalysts, as molar concentrations (converted from reported weight percentages). The carbon data is useful in confirming that the functional groups are covalently bonded to the silica surface. The carbon to nitrogen (and/or sulfur) molar ratios of approximately three indicate that both the aminopropylsilane and the mercaptopropylsilane bind to the silica surface through three oxygen bridges (as shown in Scheme 1), and that there are no unreacted methoxy groups present.

Table 1. Elemental analytical data for supported aminopropyl and propylsulfonic acid catalysts.

Catalyst	C /mmol g ⁻¹	N /mmol g ⁻¹	S /mmol g ⁻¹	C /(N+S)
SiO ₂ -SO ₃ H	2.20	0.00	0.63	3.49
SiO ₂ -NH ₂	3.40	1.10	0.00	3.09
NH ₂ -SiO ₂ -SH	3.50	0.89	0.27	3.02
NH ₂ -SiO ₂ -SO ₃ H	3.40	0.86	0.26	3.04

The nitrogen and the sulfur contents can be taken as measures of the extent of functionalisation. The nitrogen levels are slightly lower in $\text{NH}_2\text{-SiO}_2\text{-SH}$ than $\text{SiO}_2\text{-NH}_2$, as might be expected. Nitrogen levels fall through the thiol oxidation step. It is possible that there is some leaching to the nitric acid (the oxidant) in this process. Sulfur concentrations are all lower than nitrogen. Thiol groups on MPTMS would be expected to interact more weakly with the mildly acidic hydroxyl groups on the silica surface than the amine groups on APTMS.²¹

Nitrogen adsorption–desorption isotherms are all of type IV (Supporting Information), indicating mesoporous structures.²² Table 2 shows surface area, pore volume and pore size data for the catalysts studied. With the introduction of organic functional groups the specific surface areas and pore volumes progressively decrease in similar ways for both $\text{NH}_2\text{-SiO}_2\text{-SO}_3\text{H}$ and $\text{NH}_2\text{-SiO}_2\text{-PTA}$ catalysts. This implies successful grafting of functional groups in the pores of the silica support and, in the case of $\text{NH}_2\text{-SiO}_2\text{-PTA}$ catalysts, reaction of amine groups with phosphotungstic acid in the pores as well as on external surfaces.

Table 2. Textural parameters for supported acid, supported base and supported bi-functional catalysts.

Catalyst	Surface area /m ² g ⁻¹	Pore volume /cm ³ g ⁻¹	Average pore diameter /nm
SiO ₂	452	0.75	5.1
SiO ₂ -SO ₃ H	418	0.57	4.4
SiO ₂ -NH ₂	351	0.52	4.3
NH ₂ -SiO ₂ -SO ₃ H	353	0.50	4.5
NH ₂ -SiO ₂ -PTA(0.05)	326	0.54	4.8
NH ₂ -SiO ₂ -PTA(0.1)	302	0.50	4.8
NH ₂ -SiO ₂ -PTA(0.5)	282	0.40	4.6
NH ₂ -SiO ₂ -PTA(0.9)	218	0.35	4.6

The extent of surface functionalisation can be estimated based on the known area on a silica surface (ca. 0.5 nm²) covered by one silane bound to silica by three oxygen bridges.^{23,24} For $\text{SiO}_2\text{-NH}_2$, an amine concentration of 1.10 mmol g⁻¹ (from elemental analysis) corresponds to a functionalised surface of 331 m² g⁻¹, which is about 75 % of the surface of the unreacted silica, suggesting this level of functionalisation with aminopropyl groups. A similar

calculation for SiO₂-SO₃H functionalised at 0.63 mmol g⁻¹ accounts for 190 m² g⁻¹, equivalent to about 45% functionalisation with propylsulfonic acid groups.

The ¹³C NMR spectra of the catalysts provide further evidence for the nature of the functional groups. The spectrum of SiO₂-NH₂ is shown in Figure 1a. Three peaks at 11, 22 and 43 ppm are assigned to the three carbon atoms on the aminopropyl group.²⁵ The absence of a signal at 51 ppm confirms that there are no free methoxy groups.²⁶ The spectrum for NH₂-SiO₂-SH in Figure 1b shows an additional peak for the mercaptopropyl carbons at 27ppm.²⁷ The expected peaks at 11 and 18 ppm are most probably present but hidden by the aminopropyl peaks. There is no peak at 51 ppm, again showing that there are no unreacted methoxy groups.

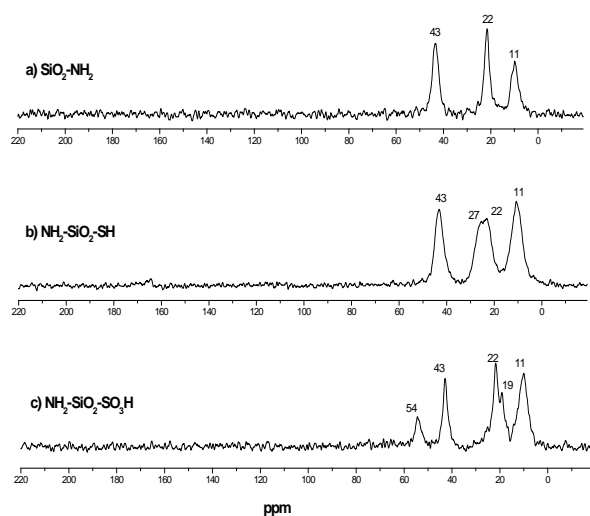


Figure 1. ¹³C CP MAS NMR spectra of silica catalysts bearing a) aminopropyl groups, b) aminopropyl and mercaptopropyl groups and c) aminopropyl and propylsulfonic acid groups.

For the bi-functional NH₂-SiO₂-SO₃H catalyst (Figure 1c), signals associated with aminopropyl groups are still present at 11, 22 and 43 ppm. The new peak at 54 ppm is due to the α-carbon atom on the propylsulfonic acid, with peaks at 19 ppm and 11 ppm expected for the β- and γ-carbons.²⁷ The absence of the CH₂-SH peak at 27 ppm is evidence for effective conversion of thiol to sulfonic acid²⁷, and the unchanged sequence of peaks for the aminopropyl group at 11, 22 and 43 ppm suggests that the amine group has been retained intact.

The spectra for $\text{NH}_2\text{-SiO}_2\text{-PTA}$ (0.9) similarly support the proposed structure of this bi-functional catalyst. The ^{13}C NMR spectrum (not shown) exhibits the characteristic signals for the aminopropyl group at 11, 22 and 43 ppm. The ^{31}P spectrum of $\text{NH}_2\text{-SiO}_2\text{-PTA}$ (0.9) (Supporting Information) shows a set of signals (three resolved but possibly more) at -11.7 to -13.7 ppm. This compares with the expected peak position for bulk, unsupported phosphotungstic acid (Keggin structure) at -15.3 ppm.^{28,29} In fact a small peak can be seen at this position. The signals at -11.7 to -13.7 ppm are characteristic of immobilised phosphotungstic acid, with shifts from -15.3 ppm caused by interaction with the silica support and by possible water loss from the Keggin ion structure as it is loaded on the surface.³⁰ The detection of several peaks in this range suggests multiple environments for phosphorus. This is not unusual when the normal symmetry of the bulk structure is disrupted.^{28,29}

Surface basicity was studied by calorimetric adsorption of SO_2 . Adsorption data are shown in Figure 2a as $-\Delta H_{\text{ads}}^\circ(\text{SO}_2)$ versus amount of SO_2 adsorbed for representative catalysts. These data can be broadly interpreted as basic site strength distribution profiles. The relative strengths of base sites are reflected in the values of $-\Delta H_{\text{ads}}^\circ(\text{SO}_2)$. It is generally assumed that significant basicity corresponds to values greater than 80 kJ mol^{-1} .³¹ The concentration of basic sites is related to the amount of SO_2 that adsorbs with enthalpy above this value. However, it is not possible to determine more than relative values for the concentrations of basic sites from this data because the $\text{RNH}_2:\text{SO}_2$ stoichiometry for tethered amine groups interacting with SO_2 is not known, although it is very likely greater than one.³² Stoichiometries of between 3:1 and 4:1 have been reported by others for SO_2 complex formation with amine-functionalised silica.³²

Figure 2a shows that the basicities of the two bi-functional catalysts, $\text{NH}_2\text{-SiO}_2\text{-SO}_3\text{H}$ and $\text{NH}_2\text{-SiO}_2\text{-PTA}(0.5)$, are between those of $\text{SiO}_2\text{-NH}_2$ and $\text{SiO}_2\text{-SO}_3\text{H}$. Significant basicity is retained in both bi-functional materials with $\text{NH}_2\text{-SiO}_2\text{-PTA}(0.5)$ showing slightly fewer and weaker base sites than $\text{NH}_2\text{-SiO}_2\text{-SO}_3\text{H}$, in line with other reports.³²

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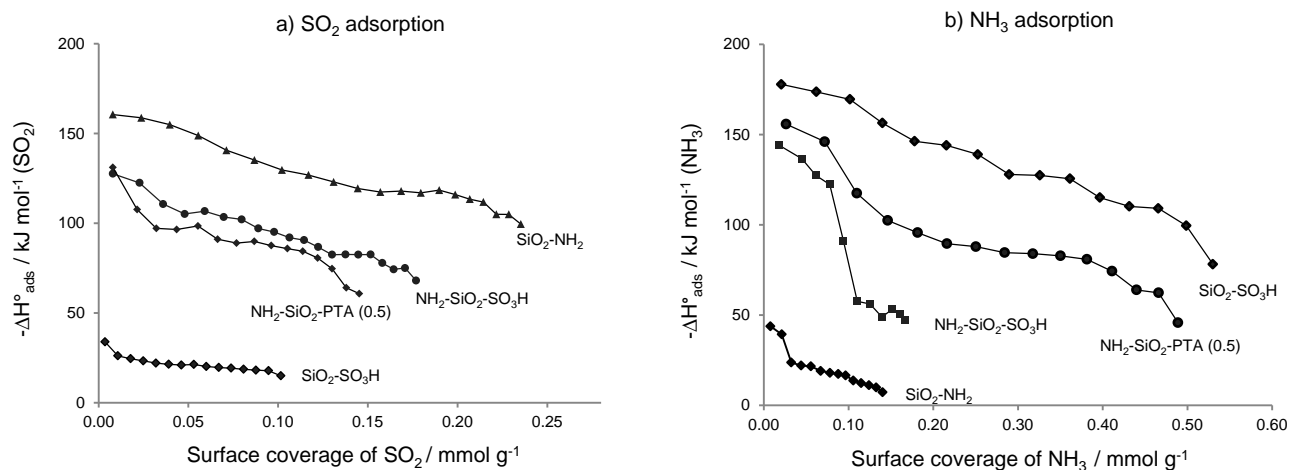


Figure 2. a) $\Delta H^{\circ}_{\text{ads}}(\text{SO}_2)$ vs. amount adsorbed at 120 °C and b) $\Delta H^{\circ}_{\text{ads}}(\text{NH}_3)$ vs. amount adsorbed at 120 °C, for supported catalysts.

Equivalent NH_3 calorimetric adsorption data for the supported sulfonic acid catalysts are shown in Figure 2b. In the same way as above, adsorption on significantly acidic sites is taken as that with enthalpy greater than 80 kJ mol^{-1} . With NH_3 it is generally assumed that adsorption on acid sites is stoichiometric (1:1) so acid site concentrations can in principle be determined from the amount of NH_3 that adsorbs with enthalpy greater than 80 kJ mol^{-1} . On this basis $\text{SiO}_2\text{-SO}_3\text{H}$ exhibits about 0.55 mmol g^{-1} acid sites and this compares with a sulfur content of 0.63 mmol g^{-1} . For the bi-functional catalysts, the acid site concentrations are much lower. In the case of $\text{NH}_2\text{-SiO}_2\text{-SO}_3\text{H}$ there are ca. 0.1 mmol g^{-1} detectable acid sites, based on Figure 2b, compared to 0.26 mmol g^{-1} sulfur, suggesting a degree of acid site loss, presumably by neutralisation. The acidity of $\text{NH}_2\text{-SiO}_2\text{-PTA}(0.5)$ reflects the phosphotungstic acid content and is significantly higher, in terms of both concentration and strength of acid sites, than for $\text{NH}_2\text{-SiO}_2\text{-SO}_3\text{H}$. However, in this case, the concentration of phosphotungstic acid added to the $\text{SiO}_2\text{-NH}_2$ was 0.55 mmol g^{-1} ($0.5 \times$ amine concentration based on elemental analysis) so a higher concentration of acid sites from the $\text{H}_2\text{PW}_{12}\text{O}_{40}^-$ ions on the neutralised amine sites than the $0.3\text{-}0.4 \text{ mmol g}^{-1}$ detected by ammonia adsorption from Figure 2b might have been expected. Despite the relatively low acid site concentration found in $\text{NH}_2\text{-SiO}_2\text{-PTA}(0.5)$, it is worth noting that the molar enthalpies of NH_3 adsorption are relatively high and similar to those measured typically for this heteropolyacid supported on silica in the absence of other surface functional groups.³⁴

The catalytic activity of $\text{NH}_2\text{-SiO}_2\text{-SO}_3\text{H}$ in the tandem deacetalisation-Henry reaction is shown as the conversion of benzaldehyde dimethyl acetal (1) to benzaldehyde (2) and on to nitrostyrene (3) in Figure 3. The first conversion from 1 to 2 is acid-catalysed, and conversion to 3 is base-catalysed. The basic sites appear to convert the benzaldehyde intermediate (2) almost immediately.

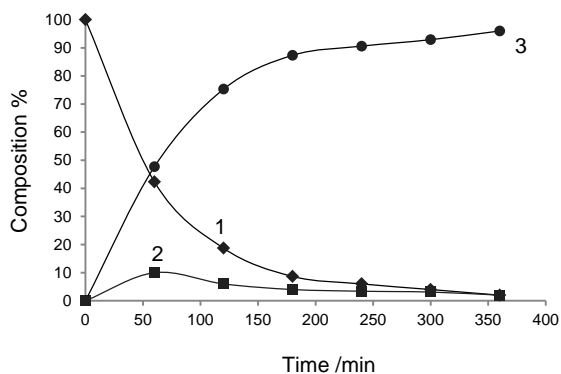


Figure 3. Composition of the reaction mixture vs. time for the reaction between benzaldehyde dimethyl acetal (1) and water to form benzaldehyde (2) and the subsequent reaction with nitromethane to form nitrostyrene (3), catalysed by $\text{NH}_2\text{-SiO}_2\text{-SO}_3\text{H}$ at 90 °C.

Also tested was a physical mixture of $\text{SiO}_2\text{-NH}_2$ and $\text{SiO}_2\text{-SO}_3\text{H}$ (50% w/w of each to give the same overall weight of catalysts: 0.05 g) and the data is shown in Figure 4. Based on calorimetric adsorption (SO_2 and NH_3) data, this mixture contains stronger and higher concentrations of both acid and base sites than the bi-functional $\text{NH}_2\text{-SiO}_2\text{-SO}_3\text{H}$ catalyst. It is therefore not surprising that the mixture shows much higher activity than the bi-functional catalysts in the first, acid-catalysed, reaction. But activity in the second, base-catalysed, step is comparatively low for the physical mixture. Comparing first order rate constants for the base-catalysed reaction, an approximate value for the bi-functional catalyst (Figure 3), assuming steady state in benzaldehyde, is $\geq 0.014 \text{ min}^{-1}$ (the first, acid-catalysed, reaction is rate determining). A value for the reaction catalysed by the physical mixture (Figure 4) is approximately 0.009 min^{-1} , calculated over the reaction period starting from 10 minutes. When these values are normalised for the concentrations of base active sites on the catalysts, the base-catalytic activity of the bi-functional $\text{NH}_2\text{-SiO}_2\text{-SO}_3\text{H}$ catalyst is at least twice that of $\text{NH}_2\text{-SiO}_2$. In other words, in this second step, the bi-

functional catalyst offers an advantage. It may be that amine groups adjacent to sulfonic acid groups can participate in an acid/base cooperative process, rapidly converting newly formed benzaldehyde to nitrostyrene, discussed further below.

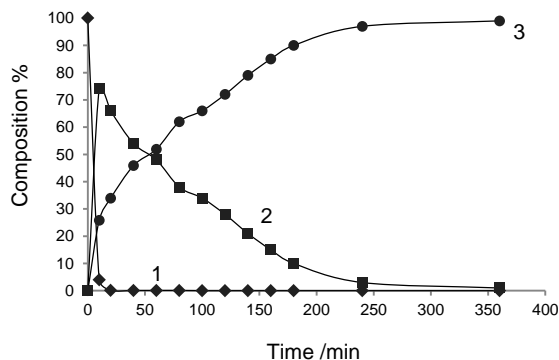


Figure 4. Composition of the reaction mixture vs. time for the reaction between benzaldehyde dimethyl acetal (1) and water to form benzaldehyde (2) and the subsequent reaction with nitromethane to form nitrostyrene (3), catalysed by the physical mixture of $\text{SiO}_2\text{-NH}_2$ and $\text{SiO}_2\text{-SO}_3\text{H}$ at 90°C .

The group of $\text{NH}_2\text{-SiO}_2\text{-PTA}$ catalysts with phosphotungstic acid: amine stoichiometric ratios of 0.9, 0.5, 0.1 and 0.05 were tested in the same two-step reaction and data appears in Figure 5. For the catalysts with nominal 0.9 and 0.5 phosphotungstic acid contents, the first step is faster than for $\text{NH}_2\text{-SiO}_2\text{-SO}_3\text{H}$, which is consistent with the relative acidities as measured by adsorption calorimetry. However, the rate of the second step, relying on residual amine groups, is very sensitive to the amount of acid used and is slower than for $\text{NH}_2\text{-SiO}_2\text{-SO}_3\text{H}$.

An additional observation here is that, for the catalysts with the two lower acid contents, $\text{NH}_2\text{-SiO}_2\text{-PTA}(0.1)$ and $\text{NH}_2\text{-SiO}_2\text{-PTA}(0.05)$, the acid-catalysed conversion of benzaldehyde dimethyl acetal stops after 61% and 20% conversion respectively. (The benzaldehyde that is produced is fairly quickly converted to nitrostyrene, as would be expected.) The acid sites in these catalysts are prone to poisoning, and the amount of phosphotungstic acid used in the synthesis of these materials seems to control the point at which reaction ceases. Preliminary tests in which the catalysts were washed with acetone after reaction showed that activity was recovered. Further tests in which nitrostyrene was added to the reaction mixtures beforehand resulted in complete loss in activity, suggesting that

nitrostyrene is responsible for the poisoning. Nitrostyrene evidently adsorbs on the catalyst surface, preventing the $\text{H}_2\text{PW}_{12}\text{O}_{40}^-$ ions acting as acid catalysts for the deacetalisation reaction of benzaldehyde dimethyl acetal.

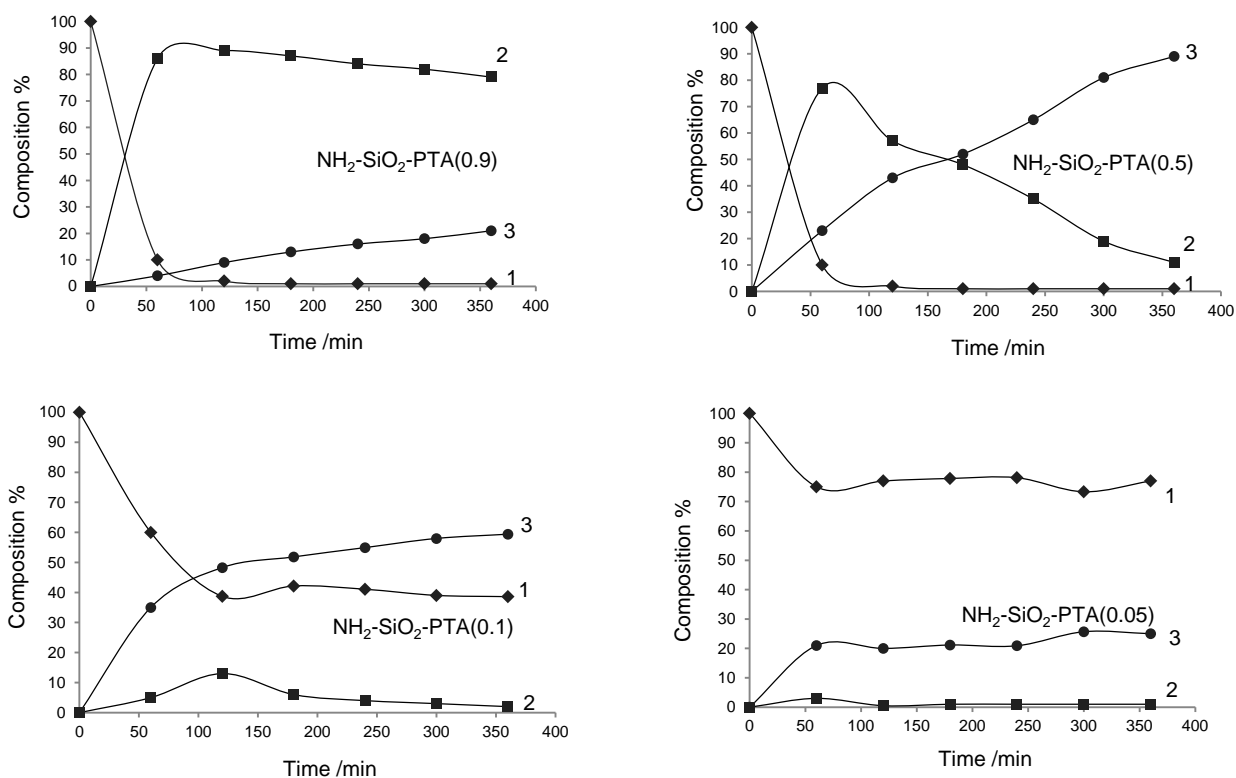


Figure 5. Composition of the reaction mixture vs. time for the reaction between benzaldehyde dimethyl acetal (1) and water to form benzaldehyde (2) and the subsequent reaction with nitromethane to form nitrostyrene (3), catalysed by $\text{NH}_2\text{-SiO}_2\text{-PTA}$ with acid/amine ratios of 0.9, 0.5, 0.1 and 0.05 at 90°C .

As stated above, a significant observation from Figures 3-5 is that the $\text{NH}_2\text{-SiO}_2\text{-SO}_3\text{H}$ bi-functional catalyst shows relatively high base-catalytic activity in the Henry reaction between benzaldehyde and nitromethane, higher even than the mono-functional $\text{SiO}_2\text{-NH}_2$ catalyst. This suggests that the mode of operation of $\text{NH}_2\text{-SiO}_2\text{-SO}_3\text{H}$ incorporates a degree of cooperative catalysis, such that the acid, as well as the base, catalytic centres are involved in the reaction. The mechanism for this reaction involves the base catalyst (tethered amine) abstracting a proton

from nitromethane to form CH_2NO_2^- , which then takes part in nucleophilic attack on the benzaldehyde carbonyl carbon. It seems quite possible that the role of the sulfonic acid site is to hydrogen bond to the carbonyl oxygen, activating the carbonyl carbon. Another possibility is that the sulfonic acid activates the carbonyl group as before, but then a surface amine attacks the carbonyl carbon forming an iminium ion, which in turn is attacked by the CH_2NO_2^- ion. Based on the lower base catalytic activity of $\text{NH}_2\text{-SiO}_2\text{-PTA}(0.5)$, which is directly comparable to $\text{NH}_2\text{-SiO}_2\text{-SO}_3\text{H}$ in terms of acid and base site concentrations, such a cooperative mechanism appears not to be possible where the acid site is an $\text{H}_2\text{PW}_{12}\text{O}_{40}^-$ ion.

A cooperative mechanism of this type requires the acid and base sites to be adjacent. One important feature of the bi-functional catalysts which is difficult to study is the extent to which the acid and the base groups are inter-dispersed on the surface, rather than existing in groups of sites of the same type. One test which was carried out to investigate this was based on the premise, mentioned above, that SO_2 requires several amine groups in close proximity in order to chemisorb on the surface. If this is the case, as it is thought to be,³² and certainly is for the somewhat similar adsorption of CO_2 on surface amines,^{33,35} then SO_2 should differentiate between well-dispersed and bunched amine groups. To test this, catalysts $\text{SiO}_2\text{-NH}_2$ and $\text{NH}_2\text{-SiO}_2\text{-SO}_3\text{H}$ were first saturated with SO_2 in a calorimetric adsorption experiment and then their catalytic activities in the Henry reaction between benzaldehyde and nitromethane were measured. The saturated $\text{SiO}_2\text{-NH}_2$ showed no activity, showing that SO_2 is indeed able to passivate amine groups. In contrast, the saturated $\text{NH}_2\text{-SiO}_2\text{-SO}_3\text{H}$ showed significant activity. This suggests that some amine groups on $\text{NH}_2\text{-SiO}_2\text{-SO}_3\text{H}$ are immune to reaction with SO_2 . This may be because those amine groups are well dispersed (amongst surface sulfonic acid groups) on the catalyst surface and are unable to act jointly to chelate SO_2 molecules. If so, then this could explain why this catalyst is able to participate in acid/base cooperative catalysis.

Another experiment carried out as part of this study is relevant. The catalyst $\text{NH}_2\text{-SiO}_2\text{-SO}_3\text{H}$ was prepared in a different way. The silica was first functionalised with propylamine groups using APTMS. When this step was complete it was functionalised with mercaptopropyl groups using MPTMS (which was then oxidised with nitric acid to sulfonic acid). This catalyst, prepared by this sequential functionalisation route showed a lower turnover frequency for base catalytic groups in the benzaldehyde conversion than $\text{NH}_2\text{-SiO}_2\text{-SO}_3\text{H}$ prepared as described

above (in which functionalisation was simultaneous). It seems highly likely that the simultaneous route would lead to a better dispersion of acid and base groups on the support surface than the sequential route, perhaps suggesting that effective dispersion leads to enhanced base catalytic activity.

It is not clear why the two functionalising molecules, APTMS and MPTMS, might tend to react in a dispersed, rather than a grouped, manner on the silica surface. A possibility is that acid-base interactions between the thiol and the amine groups might promote mixing, but it is difficult not to think that such interactions would lead to neutralisation, reducing, rather than enhancing, catalytic activity.

4. CONCLUSIONS

This work demonstrates that it is possible to functionalise a silica support with both acid and base precursor functional groups at reasonable levels. The two types of bi-functional catalysts studied here, $\text{NH}_2\text{-SiO}_2\text{-NH}_3^+[\text{H}_2\text{PW}_{12}\text{O}_{40}^-]$ and $\text{NH}_2\text{-SiO}_2\text{-SO}_3\text{H}$ (Scheme 1), show good activity for the tandem deacetalization–nitroaldol reaction. This shows that both the amine groups and the acid polyanions/sulfonic acid groups retain their activity after functionalisation. In general, however, the activity of the $\text{NH}_2\text{-SiO}_2\text{-SO}_3\text{H}$ catalyst is higher than that of the $\text{NH}_2\text{-SiO}_2\text{-NH}_3^+[\text{H}_2\text{PW}_{12}\text{O}_{40}^-]$ catalysts, and the latter are prone to poisoning when the acid contents are relatively low. It is notable that the catalyst $\text{NH}_2\text{-SiO}_2\text{-SO}_3\text{H}$, despite being prepared under conditions where internal neutralisation might seem likely, exhibits higher base catalytic activity than a physical mixture of singly functionalised catalysts. This indicates a degree of cooperative catalysis, such that the acid as well as the base catalytic centres are involved in the reaction. Adsorption calorimetric experiments with SO_2 indicate that acid and base groups are inter-dispersed on the surface, which is a pre-requisite for the cooperative mechanism.

SUPPORTING INFORMATION

The following is given: gas chromatograms for reactants and products in the tandem deacetalization-Henry reaction; the mass spectrum of the product (nitrostyrene); nitrogen adsorption-desorption isotherms at 77 K for catalysts; ^{31}P MAS-NMR spectra of silica catalyst bearing amine/phosphotungstic acid group. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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