



Short communication

Co-SBA-15 catalysts in the hydrolysis of NH_3BH_3 – Influences of Co precursors and catalyst pre-treatment

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ABSTRACT

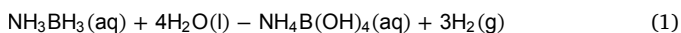
H_2 was released from ammonia borane (AB) through a hydrolysis reaction over several Co-SBA-15 catalysts. Each catalyst had an induction time prior to becoming active. The activation time related to the *in-situ* reduction of Co species to an active nano-particulate form and the length of this induction time varied as a function of the Co-precursor used. The rate of the hydrolysis reaction over the reduced and active catalysts depended on the precursor. While the induction time was not noted in subsequent reactions over the reduced catalysts, the reactivity differences remained. A rationale for the differences based on the preparation steps is suggested.

1. Introduction

A hydrogen fuel-cell powered transport fleet would have several important environmental advantages when compared to the internal combustion-powered vehicles currently used. Specifically, there would be a decrease in the emission of localised CO, particulate matter and NO_x and far improved fuel economy which would directly affect emissions of CO₂. Furthermore, as efforts to sustainably produce H_2 increase, greater impacts on CO₂ emission may be realised [1].

One of the technological limitations to the development of fuel cell powered vehicles relates to H_2 storage (with H_2 having a very low volumetric energy density (0.01 kJ L^{-1} at STP)) [2]. Options for the storage of H_2 include refrigeration and/or high-pressure systems, physisorption into various media and carbon nanostructures, and chemical storage in molecules such as methanol [3], ammonia [4] or higher hydrocarbons. In these cases, the fuels would be reformed to release H_2 on-board a vehicle.

The US Department of Energy has stipulated particular mass/volume requirements for the use of chemical H_2 storage materials [5]. With over 19% hydrogen by mass, ammonia-borane (AB), NH_3BH_3 , meets these requirements. For this reason, the removal of H_2 from AB (either through dehydrogenation or hydrolysis) has recently been extensively studied [6–8].



AB can release 3 equivalents of H_2 through reaction with water making it a suitable candidate for hydrogen storage. Aqueous AB solutions are relatively stable – and a catalyst is required to cause hydrolysis. Supported Pt catalysts are extremely active in the promotion of

this reaction [9], but for reasons of cost, and availability (Pt is classed as a critical element) [10,11], there has been a move to find replacement catalysts to promote the reaction. Of those studied, Co materials are promising [12–19]. Interestingly a recent publication has noted an effect of phosphide anions on the reactivity (and the induction time) of Co nanoparticles [20].

In general, it is known that these Co catalysts are relatively active following an induction time, and that the induction time is related to the reduction (by AB) of Co(II) ions to active Co metal, or Co–B alloy species and that the (*in situ* or *ex situ*) characterisation of this active phase is difficult, since the active material rapidly re-oxidises to an inactive material) once exposed to air [15]. Furthermore, the materials deactivate over time (it is thought due to deposition of borate salts onto the reduced active phase) [16].

In this contribution we have synthesised a number of Co-SBA-15 catalysts and evaluated their reactivity in the AB hydrolysis reaction both from their as prepared (oxidised) state and following induction (reduction) in AB mixtures. We have found that there is a memory effect in the catalyst's activity that relates to the counter ion used during the preparation. We have previously noted a similar counter ion effect in supported copper catalysts in the selective catalytic reduction of NO_x [21,22]. This effect relates to both the length of the induction time, and the rate of the catalysed reaction over the active catalysts.

2. Experimental

2.1. SBA-15 preparation

SBA-15 was prepared following the methods reported by Cai et al.

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[23]. In a typical preparation Pluronic P123 (8 g) was dissolved in a mixture of HCl (1.6 M, 300 mL). TEOS (17 g, 18.2 mL) was added and the mixture was stirred for 24 h at 40 °C, this mixture was then aged for 24 h at 80 °C. After filtration, washing and drying the material was calcined at 600 °C for 6 h.

This parent material was characterised using N₂ physisorption (using a Quantachrome 4200e instrument) and the data were treated to yield BET surface area (497 m² g⁻¹) and BJH pore size measurements (4.3 nm).

2.2. Cobalt catalyst preparation

SBA-15 supported cobalt catalysts were prepared (from chloride, nitrate, tetrafluoroborate, acetylacetonate and acetate precursors). All salts were > 99.9% purity and supplied by Sigma Aldrich. Each catalyst was prepared to contain a target loading of 2.00% Co. A solution of precursor Co²⁺ salt was prepared in 5 mL such that the solution contained 6 ng Co. this (red) solution was added to 300 mg of SBA-15 and the suspension sonicated for 3 min. Subsequently 1 mL of a solution of NaBH₄, (8 mg mL⁻¹) was added to the suspension. This addition caused a colour change from red to black as the Co²⁺ ions were reduced to Co⁰. The black suspension was allowed to settle for 2 h, filtered and washed with two 5 mL aliquots of distilled H₂O. During filtration the black powder oxidised over time to a white material. This material was stored in a glass vial prior to use.

2.3. Catalyst characterisation

Elemental analysis to determine eventual Co loading was carried out, following acid digestion, on a Varian SpectraAA 55B AA spectrometer. While the nominal Co loading was 2%, the actual loading on the materials varied between 0.7% (ex BF₄⁻ and Cl⁻), 0.71% (ex acetate), 0.81% (ex acac) and 1.57% (ex NO₃⁻). This suggests Co species remained in the suspension un-attached to the SiO₂ surface – and this was confirmed by UV visible analysis of the mother liquor.

Difference FTIR was carried out over each of the catalysts on a Vertex 70 FTIR spectrometer (using SBA-15 as the background) and UV - visible spectroscopy of the solid samples was carried out using a JASCO V-650 spectrometer equipped with a JASCO ISV-722 integrating sphere.

TEM was carried out on ex BF₄⁻ and ex NO₃⁻ catalysts both “as stored” (white and oxidised) and directly following treatment with a concentrated AB solution (black and reduced). The TEM was performed following deposition of a single drop of a suspension containing the catalyst in distilled water onto a copper TEM grid. The water was allowed to evaporate and TEM analysis was carried out using a Tecnai G2 TEM operating at 200 kV.

2.4. Hydrolysis experiments

During hydrolysis experiments an aliquot of catalyst (weighed such that it contained 2 mol% Co vs the eventual initial AB concentration) was suspended in a three-necked round bottom flask in 10 mL of distilled water. The flask was heated to 40 °C and connected to a volumetric apparatus and purged with N₂ for 10 mins prior to reaction. Following this, 1 mL of AB solution (10 mg mL⁻¹) was injected into the reaction vessel through a rubber septum and a stopwatch was started. Evolved H₂ was measured every 15 s until the reaction was completed. The reaction vessel was then purged once more with N₂ and additional solutions of AB could be added as required.

3. Results and discussion

Difference FTIR confirms the modification of the SBA-15 by deposition of the Co- containing species (see SI Fig. S11). A negative peak at 3750 cm⁻¹ relates to removal of silanols while all catalysts show

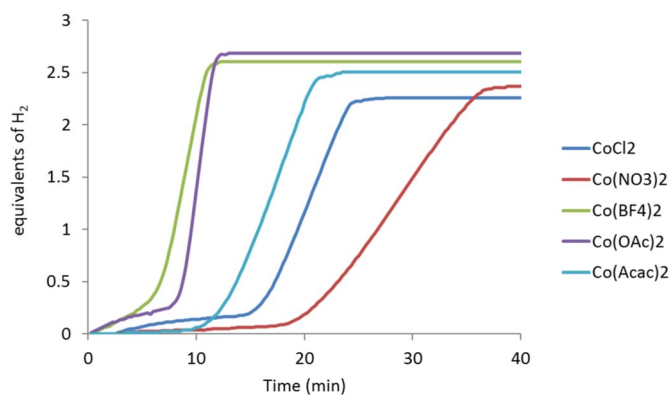


Fig. 1. H₂ evolution as a function of time over five “as-stored” Co SBA-15 catalysts (that differ as a function of the Co precursor) during the hydrolysis of NH₃BH₃.

Table 1

Showing the induction time for the first catalytic cycle (min) and the rate of H₂ evolution (mL min⁻¹) for the first, second and third catalytic cycles over the different Co-SBA-15 catalysts.

	Induction time/min	H ₂ evolution rate/mL min ⁻¹		
		Cycle 1	Cycle 2	Cycle 3
Ex-acetate	8.5	5.6 ± 0.1	2.9 ± 0.08	2.5 ± 0.09
Ex-BF ₄ ⁻	7.3	4.1 ± 0.1	2.8 ± 0.08	2.4 ± 0.1
Ex-acac	13.8	2.2 ± 0.2	1.4 ± 0.2	1.8 ± 0.1
Ex-Cl ⁻	17.8	2.0 ± 0.8	1.7 ± 0.2	1.5 ± 0.2
Ex-NO ₃ ⁻	23.3	1.1 ± 0.1	0.9 ± 0.09	0.8 ± 0.2

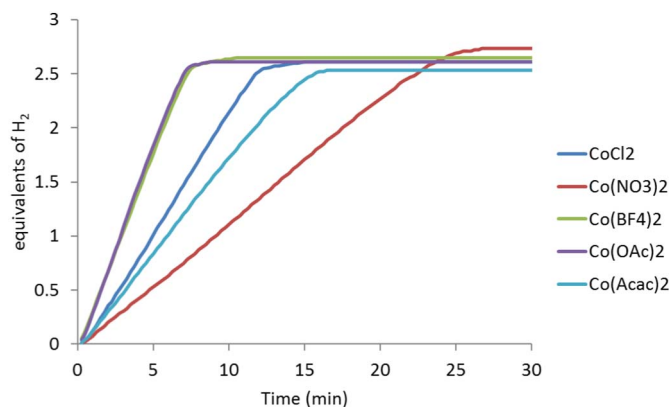


Fig. 2. H₂ evolution as a function of time over five Co SBA-15 catalysts (that differ as a function of the Co precursor) during a second cycle of hydrolysis of NH₃BH₃ (catalysts were activated during the first cycle).

peaks at 840, 960 and 1350 cm⁻¹ which relate to borate residue and peaks at 1650 and 3000–3500 cm⁻¹ relate to water and hydrogen bonded silanols respectively. Fig. S12 shows the UV-vis spectra of the as-stored catalysts with peaks at 530 nm relating to Co(II) species and peaks at 593 and 655 nm relating to Co(III) (interestingly – given the material's precursors were always Co(II) salts) [24,25]. The profile relating to the ex acac catalyst also shows a peak at 295 nm relating to the acac ligand (showing it had remained on the surface). Fig. S13 shows the UV Vis spectra of the catalysts following reduction by NaBH₄ (as they re-oxidise in air). These initially show a continuous absorption across the spectrum which decrease with time while features relating to Co(II) and Co(III) once again re-emerge (suggesting a reduction in NaBH₄ to Co(0) and a re-oxidation in air to Co(II) and Co(III) [15,16].

Fig. S14 shows a typical low angle PXRD profile of SBA-15 showing the characteristic reflections and Fig. S15 shows an XPS spectrum of a typical catalyst before and following reduction with NaBH₄.

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