



# Mild temperature palladium-catalyzed ammoxidation of ethanol to acetonitrile

Conor Hamill<sup>a</sup>, Hafedh Driss<sup>b</sup>, Alex Goguet<sup>a</sup>, Robbie Burch<sup>a</sup>, Lachezar Petrov<sup>b</sup>, Muhammad Daous<sup>b,\*</sup>, David Rooney<sup>a,\*\*</sup>

<sup>a</sup> School of Chemistry and Chemical Engineering, Queen's University Belfast, Belfast BT8 5AG, UK

<sup>b</sup> Chemical and Materials Engineering Department, King Abdulaziz University, Jeddah, P.O. Box 80035 Saudi Arabia

## ARTICLE INFO

### Article history:

Received 21 August 2015

Received in revised form

18 September 2015

Accepted 21 September 2015

Available online 25 September 2015

### Keywords:

Palladium

Bio-based chemicals

Renewable solvents

Product security

Sustainable chemistry

## ABSTRACT

The ammoxidation of ethanol is investigated as a renewable process for the production of acetonitrile from a bio-feedstock. Palladium catalysts are shown to be active and very selective (>99%) to this reaction at moderate to low temperatures (150–240 °C), with acetonitrile yields considered a function of Pd morphology. Further investigations reveal that the stability of these catalysts is influenced by an unselective product, and that any deactivation observed is reversible. Interpretation of this deactivation allows operating conditions to be defined for the stable, high yielding production of acetonitrile from ethanol.

© 2015 Published by Elsevier B.V.

## 1. Introduction

The development of sustainable industry requires a fundamental change in societal dependence on petroleum resources. The production of chemicals from 'carbon neutral' biomass offers improved supply securities and could significantly reduce industry's environmental impact [1]. Currently 95% of all organic chemicals are produced from fossil resources [2]. U.S. legislation is targeting a 25% replacement with biomass derived chemicals by 2025 [3], thus reinforcing the need for the development of sustainable processes to aid the realization of a bio-based chemical industry.

Acetonitrile is an important fine chemical which is widely used as a solvent in the agrochemical, pharmaceutical and petrochemical sectors. The pharmaceutical industry in particular accounts for over 70% of the total global demand [4]. Presently, acetonitrile is a co-product in the manufacture of acrylonitrile (SOHIO Process), whereby 40–60 kg of acetonitrile are produced for every tonne of acrylonitrile [5]. Consequently, output is heavily reliant on

propylene availability and acrylonitrile demand. Recently, Asahi Kasei announced the closure of a 150,000-ton/year acrylonitrile plant [6], citing increased propylene prices associated with shale gas production [7] and reduced acrylonitrile demands due to the slowdown in the Chinese economy. These markets trends are ominous for future acetonitrile reserves, and could prompt a situation similar to the observed crisis of 2008–2009 [8]. It is therefore imperative to develop a more secure supply of acetonitrile.

The ammoxidation of bio-ethanol affords a possible sustainable route for the production of acetonitrile. Bio-ethanol has the potential to become a renewable platform chemical due to its existing high volume production and the continued advancements in feedstock selection [9]. Ethanol ammoxidation was previously reported [10,11], however relatively high temperatures (>350 °C) were needed and the modest activity required high catalyst loading. More recently, Oishi et al. [12] have reported the ammoxidation of aromatic alcohols to nitriles. However, they note in their work, an inability to activate aliphatic alcohols. Nitrile synthesis from such alcohols has been reported previously [13]; however, the array of reagents required could be difficult and expensive to scale-up. The ammoxidation of ethane [8,14] and ethylene [15] have also been explored as alternative acetonitrile production routes. However, these suffer from high temperature demands and low product selectivity, (maximum yields of 26% reported at temperatures greater than 450 °C), and ultimately do not offer a solution to

\* Corresponding author. Fax: +966 26952257.

\*\* Corresponding author. Fax: +44 2890974687.

E-mail addresses: [mdaous@kau.edu.sa](mailto:mdaous@kau.edu.sa) (M. Daous), [d.rooney@qub.ac.uk](mailto:d.rooney@qub.ac.uk) (D. Rooney).

the overarching issue of product security, as they remain heavily dependent on petrochemical resources.

The production of acetonitrile from ethanol has also been explored via a reductive amination route [16–18], however, these again requires high temperatures ( $\approx 340^\circ\text{C}$ ) and display poor catalyst activity. The oxidative dehydrogenation of 'bio' ethylamine was proposed as a possible production route, reporting a selectivity of 80% under continuous conditions [19]. The economics of this proposed pathway are, however, doubtful, since mono-ethylamine is a more expensive chemical than acetonitrile [20]. The amination of glycerol to acetonitrile has also been examined [21], but the selectivity was less than 50%.

The application of noble metals for ammoxidation is limited [22,23], with the most widely applied ammoxidation catalysts comprising of supported oxides of vanadium and molybdenum [24]. However, the use of these sites for ethanol ammoxidation [10,25] have had limited success requiring high temperatures ( $>400^\circ\text{C}$ ) to display modest yields (60–80%). In the ammoxidation reaction partial oxidation species, in particular carbonyls, are widely acknowledged as crucial intermediates in facilitating nitrogen insertion [24,26]. In the present work supported palladium catalysts have been selected to investigate the ammoxidation of ethanol given the metal's ability to selectively oxidize alcohols to the corresponding aldehyde at low temperatures [27–29]. Herein we report on the moderate to low temperature production of acetonitrile via the ammoxidation of a renewable resource; ethanol, using highly selective palladium based catalysts under conditions yielding stable operation.

## 2. Experimental

### 2.1. Catalyst preparation

The supported Pd catalysts were typically prepared using a colloidal technique called sol immobilization [30,31]. In a standard preparation, an aqueous solution of  $\text{PdCl}_2$  (Sigma–Aldrich) was prepared. Polyvinyl alcohol (PVA) solution (1 wt%) was added to obtain a resulting ratio of  $\text{PVA}/\text{Pd}$  (wt/wt) = 1.2. A freshly prepared solution of  $\text{NaBH}_4$  (0.1 M,  $\text{NaBH}_4/\text{Pd}$  (mol/mol) = 5) was then added. After 30 min of sol generation, the colloid was immobilized by the support under vigorous stirring conditions. Note  $\text{TiO}_2$ -P25 (Degussa)  $\text{SiO}_2$  (BDH) and  $\text{ZrO}_2$  (Alfa–Aesar) supports were acidified to a pH of 1 using sulfuric acid prior to immobilization,  $\gamma\text{-Al}_2\text{O}_3$  (Grace) was untreated. After 2 h the slurry was filtered, the solid washed thoroughly with distilled water and dried at  $120^\circ\text{C}$  overnight. The same method was employed when preparing catalysts with different metal loadings.  $\text{Pd}/\text{TiO}_2$  was also synthesized via wet impregnation. A predetermined volume of  $\text{PdCl}_2$  solution was added to a specific quantity of  $\text{TiO}_2$ -P25. The mixture was stirred at  $50^\circ\text{C}$  until a paste like material was generated. This was then dried at  $120^\circ\text{C}$  for 4 h and calcined at  $500^\circ\text{C}$  for an additional 4 h. For details concerning characterization of these catalysts please see the supporting information.

### 2.2. Catalyst testing

Catalyst testing was performed in an isothermal fixed bed reactor (I.D 6 mm) placed in a ceramic tubular furnace controlled by a Eurotherm2604 PID controller. Typically a  $50\text{ s cm}^3\text{ min}^{-1}$  gas stream comprising of 525 ppm ethanol, 4200 ppm  $\text{NH}_3$ , 6825 ppm  $\text{O}_2$ , 1% Kr, balanced with Ar (unless otherwise stated), flowed through a 138 mg catalytic packed bed (particle size: 212–425  $\mu\text{m}$ ). The ethanol was fed via a calibrated temperature controlled saturator. The concentrations of ethanol and acetonitrile were analyzed using a PerkinElmer Clarus 500 GC, equipped with a flame ionized

detector (FID) and fitted with a 30 m Restek Stabilwax column. A Hidden HPR 20 mass spectrometer was operated in parallel to the GC to monitor the evolution of additional products. All GC data were recorded on a temperature ramp down. Each temperature interval was held for 40 min and an average analysis was recorded.

### 2.3. Catalyst characterization

The XPS measurements were carried out in an ultra-high vacuum multi-technique surface analysis system (SPECS GmbH, Germany) operating at a base pressure of  $10^{-10}$  m bar. A standard dual anode X-ray source SPECS XR-50 with  $\text{Al-K}\alpha$ , 1486.6 eV was used to irradiate the sample surface with 13.5 kV, 100 W X-ray power and a take-off-angle for electrons at  $90^\circ$  relative to sample surface plane. The high energy resolution or narrow scan spectra were recorded at room temperature with a  $180^\circ$  hemispherical energy analyzer model PHOIBOS-150 and a set of nine channel electron multipliers MCD-9. The analyzer was operated in Fixed Analyzer Transmission (FAT) and medium area lens modes at pass energy of 20 eV, step size of 0.1 eV and dwell time of 2.0 s. As is the standard practice in XPS studies, the adventitious hydrocarbon C1s line (285 eV) corresponding to CC bond has been used as the binding energy reference for charge correction.

The TEM analysis of the Pd catalysts was performed using a Tecnai G2 F20 Super Twin at 200 kV with a LaB6 emitter. The microscope was fully equipped for analytical work with an energy-dispersive X-ray (EDX) detector with a S-UTW window and a high angle annular dark-field (HAADF) detector for STEM imaging. Unless stated otherwise, the scanning transmission electron microscopy (STEM) imaging and all analytical work were performed with a probe size of 1 nm resulting in a beam current of about 0.5 nA. TEM images and selected area diffraction (SAD) patterns were collected on an Eagle 2K HR 200 kV CCD camera. The HAADF-STEM EDX and CCD line traces were collected fully automatically using the Tecnai G2 User Interface and processed with the Tecnai Imaging and Analysis (TIA) software Version 1.9.162.

The DRIFT spectra were recorded using a Bruker Equinox 55 spectrometer using an average of 128 scans and a resolution of  $4\text{ cm}^{-1}$ . The DRIFTS setup consisted of an in-situ high temperature diffuse reflectance IR cell (Spectra-Tech) fitted with ZnSe windows which was modified in house to behave as a plug flow reactor, the details of which have been previously reported [32,33]. The samples were pre-reduced for 1 h at  $100^\circ\text{C}$  in a pure  $\text{H}_2$  stream ( $40\text{ ml min}^{-1}$ ). The cell was then cooled to  $35^\circ\text{C}$ . A background spectra was collected after purging with Ar ( $40\text{ ml min}^{-1}$ ) for 30 min. A 1%CO/Ar stream ( $40\text{ ml min}^{-1}$ ) was subsequently passed through the cell for 30 min, with the resulting spectra recorded every minute. The gas flow was then switched back to Ar ( $40\text{ ml min}^{-1}$ ). The cell was evacuated for a further 30 min with spectra recorded every minute. During this step any weakly adsorbed CO species are removed, and only the features corresponding to strongly adsorbed CO molecules remain.

## 3. Results and discussion

Fig. 1a reports the ethanol ammoxidation activity obtained with the 0.3–10 wt%  $\text{Pd}/\text{TiO}_2$  (30–1000Pd) catalysts. Complete conversion of the alcohol was achieved from circa  $215^\circ\text{C}$  for the highest Pd loaded catalysts. It was observed that increasing the nominal loading of palladium from 0.3 wt% to 2 wt% (30–200Pd) has a minimal impact on this conversion. Further increases to 5 wt% (500Pd) and 10 wt% (1000Pd) yielded significant improvements in the rate of ethanol conversion. Note however, that there was no difference in the conversion profiles of the 500Pd and 1000Pd catalysts. Fig. 1b reports the acetonitrile selectivity of these materials as a

Download English Version:

<https://daneshyari.com/en/article/39066>

Download Persian Version:

<https://daneshyari.com/article/39066>

[Daneshyari.com](https://daneshyari.com)