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Nitrogen transfer properties in tantalum nitride based materials

Said Laassiri[a], Constantinos D. Zeinalipour-Yazdi[b], C. Richard A. Catlow[b], Justin S.J. Hargreaves[a,*]

[a] WestCHEM, School of Chemistry, Joseph Black Building, University of Glasgow, Glasgow G12 8QQ, UK
[b] Kathleen Lonsdale Materials Chemistry, Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK

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ABSTRACT

$Ta_{3-x}M_xN_y$ (M = Re, Fe, Co; x = 0, 0.25, 0.5, 1) materials with different microstructural features (*e.g.* surface area) were successfully prepared using different synthesis techniques. The dependence of nitrogen transfer properties upon tantalum nitride microstructure and its chemical composition was evaluated using the ammonia synthesis with a H_2/Ar feedstream (a reaction involving lattice nitrogen transfer). It was shown that nitrogen reactivity for tantalum nitride is more dominated by lattice nitrogen stability rather than microstructural properties. In the case of non-doped tantalum nitride, only a limited improvement of reactivity with enhanced surface area was observed which demonstrates the limited impact of microstructure upon reactivity. However, the nature of the transition metal dopant as well as its content was observed to play a key role in the nitrogen transfer properties of tantalum nitride and to impact strongly upon its reactivity. In fact, doping tantalum nitride with low levels of Co resulted in enhanced reactivity at lower temperature.

1. Introduction

Nitrogen is of central importance in many industrial processes with nitrogen containing compounds being used in numerous commercial products including synthetic fertilizers, dyes, explosives, and resins [1]. Moreover, nitrogen is an essential component of proteins and thus is an important nutritional element [2]. Molecular nitrogen is relatively inert and the preparation of almost all nitrogen containing products requires the use of combined nitrogen such as HCN, HNO_3, $CO(NH_2)_2$, or simply NH_3 as an activated nitrogen building block. Behind this apparent diversity of precursor, NH_3 is used directly in the Andrussow Process to make HCN [3] and in the Ostwald Process to make HNO_3 [4] for example. However, in view of the energy intensive nature of industrial ammonia synthesis process, its large scale utilisation as a direct/indirect activated nitrogen building block incurs considerable economic and environmental costs [5]. The catalytic process of ammonia generation from dinitrogen and dihydrogen requires high pressure and moderate temperature operation to ensure acceptable industrial synthesis rates. The overall process consumes 1–2% of the world's annual energy production and requires significant quantities of natural gas for feedstock synthesis. Therefore, the necessity for developing new efficient routes for more direct nitrogen transfer/fixation reactions is an area of great interest which could have wide ranging impact.

Different approaches have been proposed for alternative pathways for nitrogen fixation including dinitrogen reduction to ammonia at ambient pressure using transition metal centres from nitrogenase in the liquid phase [6,7], electrochemical NH_3 generation [8–10] and dinitrogen photoreduction to ammonia [11–13]. However, numerous scientific challenges and technological issues need to be solved prior to practical use of these systems. In principle, the reactivity of lattice nitrogen of nitride materials towards dihydrogen to yield ammonia or towards more complex molecules (*e.g.* CH_4, MeOH) to yield nitrogen containing products constitutes a simple and novel pathway for developing a new generation of materials for nitrogen fixation reactions. Nitrogen mobility within binary and ternary nitride structures and their nitrogen transfer abilities have motivated several studies. For instance, Alexander et al. studied the ability of a number of binary nitrides to be reduced using dihydrogen to yield ammonia [14,15]. Ternary cobalt molybdenum nitride was also reported for his high nitrogen mobility and its ability to be reduced from Co_3Mo_3N to Co_6Mo_6N with H_2 to generate ammonia [16]. The hydrolysis of nitride materials has also been investigated as a means for solar ammonia production [17,18]. In this approach the ammonia synthesis reaction was separated into two different steps: (i) the metal nitride is obtained by dinitrogen reduction at high temperature and (ii) the metal nitride is subsequently hydrolysed to yield ammonia. Related to this concept Mg_3N_2 has been used as an *in-situ* source of ammonia in the

* Corresponding author.
E-mail address: Justin.Hargreaves@glasgow.ac.uk (J.S.J. Hargreaves).

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Table 1
Structural and textural properties of tantalum nitride related materials.

Samples	Nitridation conditions		S_{BET}[a]/m^2 g^{-1}	Phase composition/XRD	Nitrogen content[b]/wt.%
	Precursor	Ammonolysis			
C-Ta_3N_5	Crystalline Ta_2O_5	T = 900 °C for 9h	10	019–1291	11.28 (11.42)[c]
A-Ta_3N_5	Amorphous Ta_2O_5	T = 750 °C for 9h	50	019–1291	10.99
$Ta_{2.5}Re_{0.5}N_y$	Co-precipitate	T = 750 °C for 9h	10	019–1291	7.93
$Ta_{2.5}Fe_{0.5}N_y$	Co-precipitate	T = 750 °C for 9h	13	019–1291	5.54
$Ta_{2.75}Co_{0.25}N_y$	Co-precipitate	T = 750 °C for 9h	27	019–1291	5.12
$Ta_{2.5}Co_{0.5}N_y$	Co-precipitate	T = 750 °C for 9h	23	019–1291	8.54
$Ta_2Co_1N_y$	Co-precipitate	T = 750 °C for 9h	15	019–1291	6.11

[a] S_{BET} is the specific surface area evaluated using the BET model.
[b] nitrogen analysis undertaken using an Exeter Analytical CE-440 Elemental Analyser.
[c] Stoichiometric nitrogen content corresponding to phase pureTa_3N_5.

transformation of esters to primary amides in the presence of protic solvents [19,20]. In all these examples, nitride materials acted as a source of reactive nitrogen that can directly undergo reaction through mechanisms analogous to the Mars-van Krevelen (MvK) one, which is a current area of interest for both catalytic [21] and electrocatalytic [22] ammonia synthesis using nitride catalysts. If the regeneration of nitrogen depleted phases during reaction was realisable using dinitrogen directly, materials operating through processes akin to the MvK mechanism could be considered as means to by-pass the use of activated nitrogen building blocks such as ammonia itself in multistage processes. These routes would use the lattice nitrogen component as the source of pre-activated reactant.

In this context, tantalum nitride presents potential for developing very active nitrogen transfer materials. Ta_3N_5 is composed of irregular TaN_6 octahedra with both three and four coordinate nitrogen atoms and has the pseudobrookite (Fe_2TiO_5) structure [23,24]. The lattice nitrogen was found to be thermochemically labile and reactive to hydrogen to generate ammonia under reducing conditions [15]. Thus, Ta_3N_5 could be considered as reservoir of activated nitrogen species. In such a scheme, the reactivity might be controlled by lattice nitrogen mobility. Therefore, controlling the nitrogen mobility in tantalum nitride materials could be the key for developing highly active materials. In materials operating via mechanisms akin to MvK, lattice component mobility has been found to be dependent upon: (i) textural and structural properties [25], (ii) chemical composition [26] or a combination of both. In an analogous manner, the nitrogen transfer properties of Ta_3N_5 are expected to depend upon structural and textural properties i.e. surface area, and the reactivity of tantalum nitride "lattice N" under reaction conditions.

In this work we have explored the possibility to alter the reactivity of Ta_3N_5 by: (i) modification of the structural and textural properties of Ta_3N_5, (ii) alteration of the reactivity of tantalum nitride lattice nitrogen by doping with transition metals. For this, a series of $Ta_{3-x}M_xN_y$ (M = Re, Co, Fe) nitrides were prepared by high temperature ammonolysis of various precursors and their behaviour characterised.

2. Experimental section

2.1. Material synthesis

2.1.1. Preparation of Ta_3N_5 materials

Different approaches to the preparation of Ta_3N_5 have been adopted.

(I) Ammonolysis of crystalline tantalum oxide precursor: Ta_3N_5 was prepared by ammonolysis of crystalline Ta_2O_5 (Sigma Aldrich, 99%) under NH_3 (BOC, 99.98%) atmosphere at a flow rate of 60 ml min^{-1} at different nitridation temperatures as discussed later on. This material is labelled C-Ta_3N_5.

(II) Ammonolysis of amorphous tantalum oxide precursor: Ta_3N_5 was prepared by ammonolysis of an amorphous tantalum oxide precursor. Amorphous tantalum oxide was prepared by precipitation of $TaCl_5$, dissolved in ethanol, using ammonia as a precipitating agent [27]. Subsequently, the amorphous precursor was subjected to an ammonolysis step under NH_3 (BOC, 99.98%) gas at a flow rate of 60 ml min^{-1} at 750 °C (Table 1). The material is labelled A-Ta_3N_5.

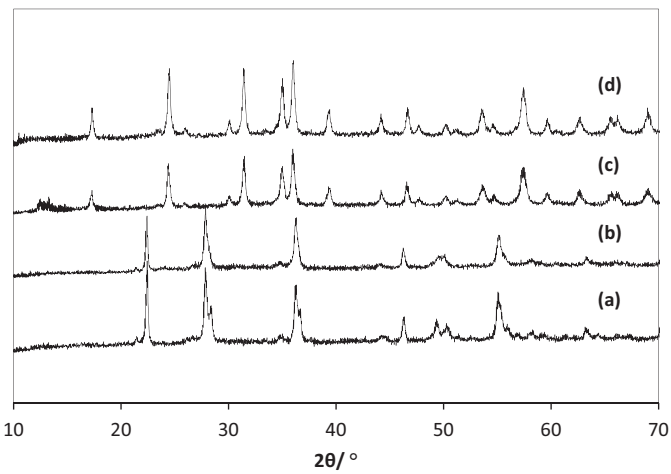

Fig. 1. X-ray diffraction patterns collected after the ammonolysis of crystalline Ta_2O_5. (a) Ta_2O_5, (b) ammonolysis T = 700 °C (c) ammonolysis T = 800 °C (d) ammonolysis T = 900 °C.

2.1.2. Preparation of doped $Ta_{3-x}M_xN_y$ (M = Re, Fe, Co and x = 0.5)

Doped tantalum materials were prepared by ammonolysis of co-precipitated $TaCl_5$ and transition metal precursors. In summary, appropriate amounts of $TaCl_5$ and metal precursors were dissolved in ethanol and then precipitated with a large excess of ammonia. The precipitate was collected by filtration, washed with ethanol and water several times and then after dried at 100 °C for 12 h. The as-prepared materials were then subjected to an ammonolysis step at 750 °C for 9 h.

2.2. Physical and textural characterization

2.2.1. Elemental analysis

Nitrogen analysis was undertaken using total combustion using an Exeter Analytical CE-440 Elemental Analyser.