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Ammonia decomposition over cobalt/carbon catalysts—Effect of carbon support and electron donating promoter on activity

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ABSTRACT

This paper sets the new design parameters for the development of low temperature ammonia decomposition catalysts based on readily available cobalt as an alternative to scarce but highly active ruthenium-based catalysts. By using a variety of carbon materials as catalytic supports, we systematically demonstrate that microporous supports capable of stabilising small cobalt crystallites (~2 nm) lead to high catalytic activities compared to bigger nanoparticles. Additionally, the degree of graphitisation of the carbon support has a detrimental effect on the activity of the cobalt (0) active sites, likely due to their potential as an electron donator. Consequently, the addition of electron donating promoters such as cesium substantially decreases the activity of the cobalt catalysts. This relationship deviates from the trends observed for ruthenium-based catalysts with an optimum 3–5 nm size where an increase of the graphitisation degree of the support and the addition of electron donating promoters increases the ammonia decomposition activity.

1. Introduction

Hydrogen is commonly presented as a promising alternative to fossil fuels in what is called the *hydrogen economy*. At the moment, there are few prototypes in the market for the use of hydrogen as road transportation fuel for proton exchange membrane fuel cells (PEM-FC) [1,2]. Although its widespread implementation would facilitate the reduction of emissions at the point of use, with associated beneficial environmental impacts, there are current concerns about the safe transportation and storage of hydrogen [3,4] due to its high flammability. This has triggered the scientific community to develop novel hydrogen storage technologies, mainly based on porous materials [3,5]. However, none of them currently fulfil the 9 wt.% gravimetric hydrogen storage target established by the US Department of Energy in 2015 [6].

Within this context, ammonia is presented as an attractive carbon-free energy vector molecule with a hydrogen content of 17.3 wt.%, higher than liquid hydrogen on both a volumetric and gravimetric basis [7]. Additionally, ammonia has a relatively narrow combustion range of 16–25% in air, compared with 4–75% for H_2 [8]. However, the feasibility of ammonia as an energy vector relies on the ability to decompose it to release hydrogen (Reaction (1)) at a temperature similar to the operation of the PEM fuel cell (below 150–180 °C).

$$2NH_3(g) \leftrightarrows 3H_2(g) + N_2(g) \quad (1)$$

Under these relatively low temperature conditions, the decomposition of ammonia reaction is kinetically limited by the recombinative desorption of nitrogen adatoms from the metal sites [9]. Previous studies have demonstrated a volcano-type relationship between the ammonia decomposition rate of different metals as a function of their nitrogen binding energy, where the optimum nitrogen binding energy falls in the range of 544–586 kJ/mol, which corresponds to ruthenium [9]. Indeed, the most active and extensively studied catalysts reported in the literature for the decomposition of ammonia are based on ruthenium [10,11]. The activity of ruthenium-based catalysts, especially at low temperatures, can be further enhanced by the use of electron donating promoters such as alkali metals [12] and highly conductive supports such as graphitised carbon nanotubes [13]. Despite this, the cost and scarcity of ruthenium have, in the last few years, generated a renewed interest in the development of ammonia decomposition catalysts based on alternative, readily available non-noble metal catalysts including iron [14,15], cobalt [11,16,17] and nickel [18,19]. Amongst these, the nitrogen biding energy of cobalt is the closest one to the optimum value range. Indeed, Co/CNT catalyst prepared by incipient wetness impregnation shows superior

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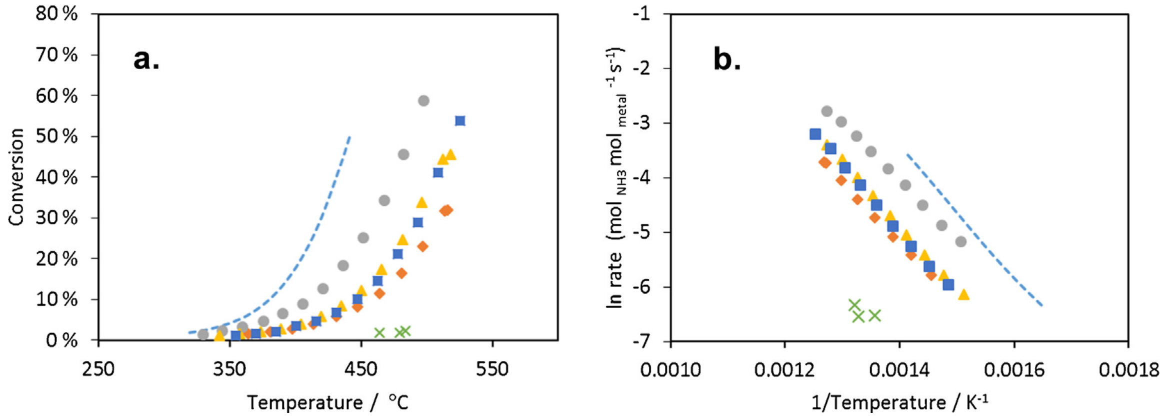

Fig. 1. (a) Ammonia decomposition conversion as a function of reaction temperature of 7 wt.% cobalt/carbon catalysts. (b) Arrhenius' plot (●) Ax-21, (♦) CNTs, (▲) MSC-30, (■) MESO-C and (x) Activated charcoal. The dashed line represents the activity for 7 wt.% Ru/CNTs as reference catalyst. All catalysts were pre-reduced in-situ at 400 °C.

activity to that of Ni/CNT and Fe/CNT [20]. A recent kinetic study by Lendzion-Bielun et al. [21] showed a lower ammonia decomposition activation energy on cobalt than on iron-based catalysts. Previous studies suggest that the catalytic activity of cobalt-based catalysts can be related to *i.* the level of dispersion and crystallite size [22] and *ii.* the cobalt-support interaction [17]. However, a recent review of the decomposition of ammonia decomposition using non-noble metals [23] reveals the lack of systematic investigation on the development of these catalysts and the need of fundamental understanding of the effects of catalyst parameters on the resulting activity. By using a range of carbon supports with different physical and chemical properties, this paper reveals the effect of metal dispersion, metal particle size, support porosity and the electronic modification of the active sites of cobalt/carbon catalysts on the decomposition of ammonia catalytic activity, providing guidelines for future catalyst development in the field.

2. Experimental procedure

Catalysts were prepared by incipient wetness impregnation using $Co(NO_3)_2 \cdot 6H_2O$ as metal precursor on various carbon supports, including multi-walled carbon nanotubes (CNT), activated charcoal and MESO-C (from Sigma Aldrich) and Ax-21 and MSC-30 (from Kansai Coke and Chemicals ltd). Acetone was used as metal solvent in preference of water as the lower surface tension of acetone allows for greater pore filling of the support [24]. The different supports were dried in a vacuum oven at 80 °C overnight prior determination of their respective wetness volume by adding acetone dropwise until wetness saturation is reached. The wetness impregnation volumes were estimated as 10.1, 1.9, 1.7, 3.0 and 2.8 mL g^{-1} for CNT, activated charcoal, MESO-C, AX-21 and MSC-30 respectively. $CsOH \cdot xH_2O$ and $Ru(NO)(NO_3)_3$ were used as cesium and ruthenium precursors in the promoted and reference catalysts respectively. The required amount of metal precursor was dissolved in the respective wetness volume and the different supports were impregnated dropwise. In the case of promoted catalysts, cesium was impregnated sequentially after drying the catalysts after cobalt impregnation. After synthesis, the catalysts were dried for 3 h at 80 °C under vacuum to remove the solvent. Catalysts were reduced under pure hydrogen flow for three hours at 400 °C.

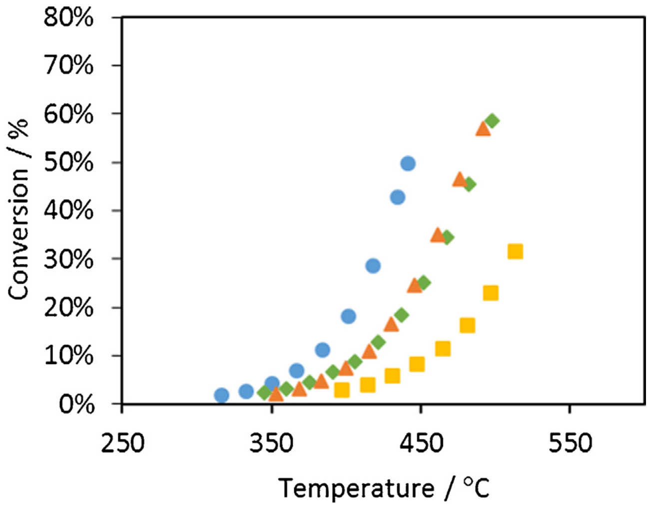

Fig. 2. Ammonia decomposition conversion as a function of reaction temperature of ● 7 wt.% Ru/CNT, ▲ 7 wt.%Ru/Ax-21, ♦ 7 wt.% Co/Ax-21 and ■ 7 wt.% Co/CNT.

Nitrogen adsorption analyses were carried out at −196 °C using a Micromeritics ASAP 2020 instrument. The surface area was calculated using the Brunauer, Emmett and Teller (BET) method. A JEOL TEM −2100 200 kV ultra-high resolution transmission electron microscope was used for imaging of the samples. Samples were prepared by dispersing the samples in ethanol (0.5 mg mL^{-1}). A drop of the dispersion was added to a Lacey carbon-coated copper mesh grid and dried under vacuum. Temperature programme reduction (TPR) experiments were carried out in a Micromeritics Autochem II instrument. The samples were degassed at 400 °C under flowing argon for 20 min prior to TPR analysis up to 1000 °C using a temperature ramp rate of 10 °C min^{-1} under 30 mL min^{-1} flow of 5% H_2/Ar. Raman analyses were carried out using a Renishaw inVia Raman microscope using a 532 nm green Renishaw Diode Laser.

Ammonia decomposition reactions were carried out in a continuous differential packed bed flow reactor situated inside a Carbolite tubular oven equipped with a PID control with a gas hourly space velocity of 5200 mL$_{NH3}$ g$_{cat}$$^{-1}$ h^{-1} using 25 mg of catalyst diluted in a 4 cm^3 silicon carbide bed. The inlet flow of the reactor was controlled with mass flow controllers. All the pipes were heated to 60 °C to avoid any ammonia condensation and consequent corrosion. During each catalytic study, the reaction temperature was ramped from around 200–550 °C at 2.5 °C min^{-1}. The reaction temperature was measured using a thermocouple situated over the catalytic bed to avoid any temperature lag. The outlet flow of the reactor at different reaction temperatures was analysed on-line using a gas chromatograph fitted with a Hayesep Q column and a thermal conductivity detector. The mass balance closure precision was within a ± 7% error.