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Full Length Article

CO_x-free hydrogen generation *via* decomposition of ammonia over copper and zinc-based catalysts

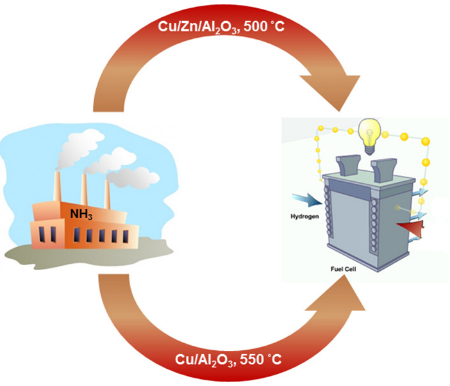
Venkata D.B.C. Dasireddy *, Blaž Likozar

Department of Catalysis and Chemical Reaction Engineering, National Institute of Chemistry Slovenia, Hajdrihova 19, 1001 Ljubljana, Slovenia

HIGHLIGHTS

- Ammonia decomposition over γ-Al_2O_3-supported Cu and Zn heterogeneous catalysts.
- Low-temperature production of pure hydrogen feedstock for fuel cells applications.
- Ultrasonic impregnation synthesis showed superior performance over wet impregnation.
- Hydrogen production rate of 36.2 mmol g^{-1} min^{-1} was achieved over the $Cu/Zn/Al_2O_3$.
- All catalysts showed excellent long-term run stability, especially above 400 °C.

GRAPHICAL ABSTRACT



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ABSTRACT

Production of hydrogen without any carbon dioxide or monoxide is of utmost importance for the chemical energy storage and conversion in a future low-carbon economy. Alumina-supported copper and $Cu/Zn/Al_2O_3$ catalysts were prepared by incipient wetness- and ultrasonic impregnation, while Zn/Al_2O_3 catalysts were also prepared to compare the effect of Zn. The characterisation of catalysts was carried out by N_2 physisorption, XRD, H_2-TPR, N_2O chemisorption, NH_3-TPD, CO_2-TPD, H_2-TPD, XPS and TEM. Catalysts prepared *via* ultrasonic impregnation showed a high metal dispersion and a small crystallite size, whereas Lewis acidic and basic sites were predominant on all catalysts, while the acid–base strength was strongly influenced by the presence of zinc in the case of $Cu/Zn/Al_2O_3$ catalysts. A high catalytic activity, reflected through the almost total conversion of ammonia at 600 °C with the H_2 production rate of 36.2 mmol g^{-1} min^{-1}, was achieved over $Cu/Zn/Al_2O_3$ catalyst, prepared by ultrasonic impregnation. The dispersion of metal and its acidic or basic nature played an important role, even more so than the presence of the two or three potentially synergistic metals on the surface of a catalyst. Under the applied reaction conditions, the catalysts showed an excellent stability for more than 100 h.

1. Introduction

With increasing global energy demands, paralleled by the irreversible decrease in fossil fuel reserves and the environmental deterioration, caused by fossil fuel combustion, alternative energy sources are urgently needed [1]. Hydrogen fuel may be thought of as one of such alternatives. Generally, hydrogen is produced from hydrocarbons by steam reforming, partial oxidation and autothermal reforming processes. However, due to a large amount of CO being produced simultaneously, its application in proton

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* Corresponding author.
E-mail address: dasireddy@ki.si (V.D.B.C. Dasireddy).

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exchange membrane fuel cells (PEMFC) is limited as their electrodes are poisoned by CO [2].

Recently, extensive efforts have been undertaken to explore CO_x-free alternatives for the production of hydrogen for fuel cell applications. On the other hand, the increasing problem of the atmospheric pollution by various nitrogen compounds (*i.e.* N_2O, NO, NO_2 and NH_3) has resulted in the stricter regulations of their emissions [3]. Thus, ammonia may be thought of as a hydrogen-carrying chemical vector; it is produced by the Haber–Bosch process, while many other industrial chemical procedures consume it as a reactant (*e.g.* urea manufacturing, hydro-denitrification process and DeNOx process).

Gaseous ammonia (NH_3) is the most abundant alkaline gas in the atmosphere. In addition, it is a major component of total reactive nitrogen. The largest source of NH_3 emissions is agriculture, including animal husbandry and NH_3-based fertilizer applications. In general, gaseous ammonia in mixtures can be recovered by a two-stage steam distillation process and liquid waste water-dissolved NH_3 can be abstracted using a low-cost source of magnesium ions [4]. Recent studies [5] have indicated that NH_3 emissions have been increasing over the last few decades on a global scale. The increase in NH_3 emissions negatively influences the environment and public health, as well as climate change. For these reasons, it is important to have a clear understanding of the sources, deposition and atmospheric behaviour of NH_3. On the other hand, with the extreme concerns over global warming and the depletion of fossil fuels, the development of sustainable, low-emission hydrogen technologies is the major challenge for stationary and on-board mobile applications. CO levels, however, have to be reduced to below 100 ppm or, preferably 10 ppm, for the use in fuel cells. Catalytic ammonia decomposition has been considered as one of potential hydrogen carriers to provide CO_x-free hydrogen for fuel cells due to a high energy density (3000 $W\ h\ kg^{-1}$) and hydrogen storage capacity (17.7%), as well as its basically low-CO_x production [6–8]. For the above reasons, we can consider NH_3 as a renewable fuel/chemical (storage) and a potential hydrogen source for fuel cells [5,9], as well as carbon capture and utilisation (CCU) (for example for urea).

The decomposition of ammonia is a mildly endothermic process yielding hydrogen and nitrogen. The process operated as such produces directly no CO or CO_2, but nitrogen as the only notable co-product. A considerable attention has been given to the steam reforming of methanol as a process for the generation of hydrogen as fuel cell feedstock [6]. However, a comparison of the economics for the hydrogen production (Electronic Supplementary information, Table S1) *via* the ammonia decomposition for alkaline fuel cells, as opposed to the production of hydrogen by the methanol reforming for acid fuel cells, has shown that ammonia decomposition is a more attractive process from the economic standpoint [8,10]. With these considerations, the decomposition of ammonia to hydrogen appears to be an excellent choice for the production of hydrogen for the former.

Currently, various metals and mixed metal oxides, containing Co, Fe, Ni, Pt, Rh and Ru have been tested for ammonia decomposition and Ru is regarded as the most active metal catalyst [11,12]. However, cracking ammonia to hydrogen over the Ru-based catalysts usually extensively begins only at the temperatures, as high as 450–550 °C, which makes the rate and extent of the ammonia decomposition in this process a bit less satisfactory for practical fuel cell applications. Nonetheless, even when taking this into account, a high cost of Ru limits its practical usage in fuel cells. Thus, there is a drive to seek inexpensive alternatives like transition metal oxides. Ganley et al. [13] investigated the activity of the ammonia decomposition over Ni/Al_2O_3 catalysts and found that the turnover frequency of the NH_3 conversion over the mentioned Ni catalyst is only 4.21 s^{-1}, reactions thus being much slower than over Ru catalysts. This is due to a very low dispersion of Ni, while on the other hand, also the intrinsic kinetics of Ni also exhibit a low activity when compared to ruthenium. Thus, one of the characteristics, which most notably influences ammonia decomposition rate, is the dispersion of the active metal on a catalyst. One of the limiting factors for the fuel cell application at high temperatures is that the metal catalysts for ammonia decomposition yield a significant amount of hydrazine [14]. Thus to obtain a higher conversion of NH_3 and to decrease the formation of hydrazine, it is important to find the alternative active catalysts for ammonia decomposition.

A more detailed examination of reaction data reveals the inadequacies of several catalytic pathway models; nonetheless, the ammonia decomposition into hydrogen has a simple mechanism that has been mapped out extensively by computations, and the reaction pathways have been proposed to proceed *via* the following steps:

$$NH_{3(g)} \leftrightarrow NH_{3(ads.)}$$

$$NH_{3(ads.)} \rightarrow NH_{2(ads.)} + H_{(ads.)}$$

$$NH_{2(ads.)} + H_{(ads.)} \rightarrow NH_{(ads.)} + 2H_{(ads.)}$$

$$NH_{(ads.)} + 2H_{(ads.)} \rightarrow N_{(ads.)} + 3H_{(ads.)}$$

$$2H_{(ads.)} \rightarrow H_{2(g)}$$

$$2N_{(ads.)} \rightarrow N_{2(g)}$$

These steps constitute the exact reverse of the ammonia formation from hydrogen and nitrogen, so it is reasonable to suppose that the catalysts, known to be particularly active for ammonia formation, would also be successful in ammonia decomposition. However, in particular iron shows a high activity for the formation, yet not for the decomposition. Thus, it is important to note that the mechanism-determining experiments were conducted in lab-scale conditions, very different from those that prevail in a typical ammonia synthesis reactor. In particular, lab-scale reactors ordinarily accommodate comparatively much lower pressures and higher temperatures. The rate-determining step may therefore change, and with it, an effective catalyst selection. In ammonia decomposition, nitrogen desorption is the rate-determining step. As reported in the literature [7–9], Co, Cr, Fe, Ni and Ru follow the predicted increase in the decomposition rate with the nitrogen desorption rate. However, Cu, Ir, Pd, Pt and Rh, follow the opposite trend, suggesting that the rate-determining step is changed, *i.e.* to the scission of the adsorbed $NH_{(ads.)}$. It has to be noted that the rate of N—H bond scission increases when the energy of nitrogen–surface bond is elevated, while the rate of $N_{(ads.)}$ desorption decreases with the mentioned energy rise. This occurs due to N–surface bond being formed during N—H scission, with this bond breaking upon $N_{(ads.)}$ desorption.

Supported copper catalysts have attracted a considerable attention because of their recent practical applications in promoting the steam reforming of methanol to produce hydrogen for fuel cell operation [15,16], the synthesis of methanol [17,18], and the selective catalytic reduction of nitrogen oxides by hydrocarbons in an oxygen-rich atmosphere [19]. The catalytic properties of active copper phase can be greatly influenced by the nature of the supporting oxide and the dispersion of active component [17,20,21]. For example, in methanol synthesis, it is suggested that the active component is not only Cu^+ but also Cu^0, and that the support plays a major role in controlling the Cu^+/Cu^0 ratio, which further influences catalytic activity [2,6,18]. It is well-known that the catalytic performance of the supported catalysts depends to a certain extent