

Promoted Ru on high-surface area graphite for efficient miniaturized production of hydrogen from ammonia

Rasmus Zink Sørensen,^a Asbjørn Klerke,^a Ulrich Quaade,^b Søren Jensen,^c Ole Hansen,^c
and Claus Hviid Christensen^{a,*}

^aCenter for Sustainable and Green Chemistry (CSG), Department of Chemistry, Technical University of Denmark, 2800 Kgs Lyngby, Denmark

^bCenter for Individual Nanoparticle Functionality (CINF), Department of Physics, Technical University of Denmark, 2800 Kgs Lyngby, Denmark

^cMIC - Department of Micro and Nanotechnology, Technical University of Denmark, 2800 Kgs Lyngby, Denmark

Received 3 August 2006; accepted 10 August 2006

Promoted Ru/C catalysts for decomposition of ammonia are incorporated into micro-fabricated reactors for the first time. With the reported preparation technique, the performance is increased more than two orders of magnitude compared to previously known micro-fabricated reactors for ammonia decomposition. The catalytic activities for production of hydrogen from ammonia are determined for different promoters and promoter levels on graphite supported ruthenium catalysts. The reactivity trends of the Ru/C catalysts promoted with Cs and Ba are in excellent agreement with those known from earlier studies of both ammonia synthesis and decomposition, and it is shown how proper promotion can facilitate ammonia decomposition at temperatures below 500 K.

KEY WORDS: ammonia decomposition; hydrogen production; ruthenium catalyst; promotion; graphite support; micro-fabricated reactors.

1. Introduction

Ammonia has gained significant interest as a hydrogen source for fuel cells [1–4]. Stored safely, ammonia can become a favorable energy carrier [5, 6], but for use in low temperature fuel cells it must be catalytically decomposed to the elements before it can be utilized in the fuel cell.

One perceived area where fuel cells could make great impact is for miniaturized systems such as as “lab-on-a-chip”. Often, power supplies or batteries for small systems are very bulky compared to the system it supports. Thin fuel cells would be optimal for solving this problem, if the fuel could be delivered from an equally compact system.

Promoted Ru catalysts on porous graphitized carbon are generally recognized as the most active for decomposition of ammonia [7–10]. Due to the immense importance of industrial ammonia production for fertilizers, catalysts for the synthesis have been studied intensively over the last century [11, 12]. Decomposition of ammonia has mainly been studied to obtain detailed insight into the synthesis reaction, but in later years decomposition of ammonia has attracted attention as a possible route to hydrogen production. Of the elements, Ru is the most active catalyst for both processes at a wide range of conditions [13–17]. Interestingly, Ru is

more optimal under ammonia decomposition conditions than under industrially relevant ammonia synthesis conditions [18]. The highest activities are measured using graphite as the support [7–10], but unfortunately, graphite is not stable under ammonia synthesis conditions, as the high hydrogen pressure causes methanation of the graphite support [19, 20]. Graphite is far more stable under optimal decomposition conditions, which are at low pressures. This makes graphite supported Ru highly interesting for efficient decomposition of ammonia, and indeed several studies show such catalysts to exhibit superior activities [7–10].

So far, it has not been possible to integrate significant amounts of porous graphitized carbon supports in micro-fabricated reactors, and thus the best miniaturized systems used supports which are less optimal for ammonia decomposition [3, 21].

The most common approach to achieve a high surface area in micro-fabricated reactors is to manufacture the reactor itself to have a high surface area, e.g. by anodisation or by introduction of various structural components into the reactor chamber (walls, pillars etc.) [22]. Some groups have deposited support layers by filling the reaction chamber with a thin slurry followed by drying and sintering to produce a porous ceramic support [23, 24], while others used more advanced deposition methods such as chemical vapor deposition [25] or flame spray deposition [26]. Recently, a sol–gel method for filling up the entire reactor chamber with porous support was presented [27, 28], but unfortunately

*To whom correspondence should be addressed.
E-mail: chc@kemi.dtu.dk

this is not a feasible route for introducing graphite support into micro-fabricated reactors.

Here, a method for incorporation of a porous graphite support into micro-fabricated reactors is presented, and higher volumetric activities for ammonia decomposition than previously reported for similar micro-fabricated reactors are demonstrated. Furthermore, the micro-fabricated reactors are well suited for catalyst studies, since they can be kept isothermal under most reaction conditions and the gas flow stays laminar (plug flow behavior) over a large range of space velocities. This is used to investigate promotion of the Ru/C system with Cs and Ba, which are effective and carefully studied promoters for ammonia decomposition over Ru/C. The effects of driving the decomposition reaction close to equilibrium at relatively low temperatures are studied as well.

2. Experimental

The graphite support is prepared using an aqueous solution of commercial food grade sucrose (140 g/L) to fix finely ground Timrex HSAG300 high-surface area graphite in micro-fabricated silicon reactors of 3–4 μ L reactor volume. The reactors are produced using Deep Reactive Ion Etching as previously described [29, 30]. Reactors are produced with reaction chambers of 8 mm $\times$ 1.5 mm $\times$ 0.3 mm. To facilitate assembly of the setup, manifold connections are made through the silicon slab itself, the reactor slab being fixed against high temperature stable rubber o-rings on the gas handling system. The limited lateral heat conduction of the silicon slabs makes it possible to heat the catalyst-loaded reaction chamber while maintaining a low enough temperature of the o-rings to keep them from melting.

HSAG300 graphite is deposited in a number of steps: First, the micro-fabricated reaction chamber is filled with sucrose solution, which is then dried on a hot plate at 80 °C. Before the next step, sucrose deposited outside the reaction chamber is removed by polishing. The reaction chamber is then completely covered with finely ground HSAG300 and the open reactor is pyrolyzed at 250 °C for 1 h. This creates a highly porous carbon support, which binds sufficiently to the silicon to enable removal of excess carbon powder, and cleaning the surface of the silicon slab.

The ruthenium catalyst is deposited on the support by incipient wetness impregnation using a well defined total volume of Ru-nitrosyl nitrate (8.1 wt% Ru) dosed from a 10 μ L syringe. All samples are impregnated to contain 10 wt% Ru on the graphite support and dried at 80 °C.

Promotion is accomplished in the same way as the Ru impregnation. The precursors for Cs and Ba promotion are CsNO₃ and Ba(CH₃COO)₂, respectively. Both precursors are deposited as 0.5 M aqueous solutions, and the reactors are dried at 80 °C before the final cleaning of the silicon surface.

The micro-fabricated reactor is closed with a pyrex lid and sealed by anodic bonding. Bonding takes place at 320 °C with a voltage of 1 kV, and gives a completely gas-tight reactor. At the same time, the elevated temperature causes calcination of the catalyst. Thorough cleaning is very important for the success of the anodic bonding as individual atoms from one surface must migrate into the other during bonding. For this reason, anodic bonding is normally performed in clean-rooms only, but by taking care in the cleaning process bonding is possible in an ordinary lab even when the micro-fabricated reactor is loaded with the supported catalyst.

Surface area measurements of supports prepared by the described method show significant reduction in the surface area of the graphite support in the reactors compared to the starting material. BET areas are 322 m²/g before treatment with sucrose and 167 m²/g after the graphite is glued onto silicon with pyrolyzed sucrose. Most of this loss of surface area can be ascribed to mass increase due to the sucrose, which constitutes approximately 30–50% of the total mass. Still, the resulting surface area is comparable to what was reported for other supports in micro-fabricated reactors [26, 27].

All catalysts are tested in a specially build setup where the reactor is held in place and connected to the gas handling system by a clamp in one end, while the reaction chamber is heated by a silicon heating element placed over the chamber. The gas mixture is dosed to the reactor from a mass-flow controller, and the composition of the exit gas is measured by a microGC. Gasses are separated in two different columns: a plot U column designed for short hydrocarbons and volatile primary amines, and a molecular sieve column designed for noble gasses and gasses such as nitrogen, oxygen and hydrogen. The plot U column is used for detection of ammonia and is operated at 60 °C, while the molecular sieve column is used primarily for detection of hydrogen and nitrogen and is operated at 50 °C. Both columns are fitted with thermal conductivity detectors (TCD). The inlet gas consists of 20 mole% NH₃ and 5 mole% He in a carrier stream of Ar, where He acts as an internal standard in the microGC. Dilution of the NH₃ was chosen in order to avoid large changes in linear space velocity through the reactor at high conversions since this would influence the residence time in the reactor and thereby change the measured conversions.

3. Results and discussion

The use of micro-fabricated silicon reactors is limited by the number of porous support materials that it is possible to deposit into the reaction chamber. These supports are currently limited to Al₂O₃, MgAl₂O₄, and SiO₂ deposited using sol-gel synthesis and TiO₂ using flame spray deposition [23, 26–28]. So far, there have

been no reports on a method for deposition of porous carbon or graphite in micro-fabricated reactors. The only reported example of a carbon-based support material in a micro-fabricated reactor is by Schimpf *et al.* [31], who produced a carbon film in a micro-fabricated reactor by carbonization of a polymer solution. This gave a 0.27–6.22 μm thick layer of carbonized polymer on the reactor walls. No surface area was reported. Graphite-structured carbon materials are so far known to be the best supports for ammonia decomposition on ruthenium [7–10]. In ammonia synthesis, methanation of the carbon support is a challenge [20, 32]. However, the rate of methanation depends strongly on the hydrogen pressure which will always be much lower in a technical ammonia decomposition reactor than in a synthesis reactor. Rossetti *et al.* [33] found that the methanation rate is lowered significantly by graphitization of the carbon. Thus, HSAG is favorable as a support for Ru in ammonia decomposition.

Figure 1 shows a magnified view of a sealed micro-fabricated reactor prepared with graphite support using sucrose glue. The support is seen as a fairly evenly distributed porous black layer filling up about half the volume of the reaction chamber.

Compared to previous results using the same reactor type but with alumina support, graphite is clearly favorable. Figure 2 compares the previously reported data for Ba promoted Ru on Al_2O_3 with a similar catalyst on graphite support. The increase in activity is obvious, and corresponds well to what would be expected according to literature findings [34]. It is also seen that even without promotion, an otherwise similar

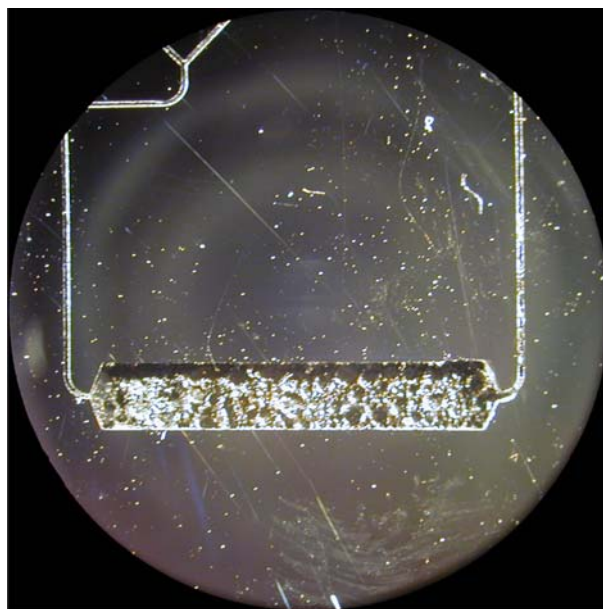


Figure 1. Micro-fabricated reactor prepared with graphite and sealed with a pyrex lid. The reactor chamber dimensions are 8 mm $\times$ 1.5 mm $\times$ 0.3 mm.

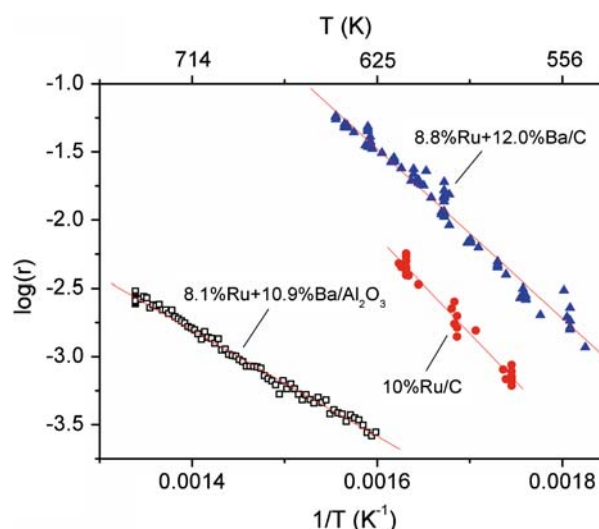


Figure 2. Activities of unpromoted and Ba promoted Ru/C catalysts compared to the Ru + Ba/ Al_2O_3 catalyst reported in [21]. r is in $\text{mol}_{\text{NH}_3}/\text{mol}_{\text{Ru}}/\text{s}$.

Ru catalyst on graphite is far more active than the promoted Ru on Al_2O_3 .

From literature [35–38], it would be expected, that promotion by Cs would give even higher activities than those obtained by Ba promoted Ru on graphite. Ba is thought to promote decomposition of ammonia by being present on the surface of Ru particles, where it acts as a structural promoter making more of the most active sites available for the rate-limiting N_2 dissociation [8], or as an electronic promoter [34, 39]. Additionally, TEM studies have shown Ba to be present as an oxide on the surface of small Ru crystals under low pressure ammonia synthesis conditions [40]. Furthermore, Ba stabilizes the active Ru particles and prevents agglomeration and sintering at temperatures above 500 $^\circ\text{C}$ [19]. Because the Ba species are present on the surface of the active ruthenium, the optimal amount of Ba promoter is relatively small, since it will cover active sites when the coverage increases. This has been observed experimentally [35, 37]. Similarly there have been speculations about the mechanism for promotion by Cs [38, 41, 42] and it has in some cases been found to give increased activity compared with Ba promoted catalysts.

Thus, Ru/C catalysts were prepared both with Cs added in approximately the same amount as that used for Ba promotion, and also with about three times as much Cs.

These catalysts showed significant differences in activity. As seen in figure 3, the low Cs promotion gives significantly lower activity than the corresponding Ba promotion. This corresponds well to what could be expected from the ammonia synthesis literature [38, 43], whereas the high Cs loading gives a dramatically higher activity than that achieved with the low Ba and Cs promoter loadings. Furthermore, the catalyst with high

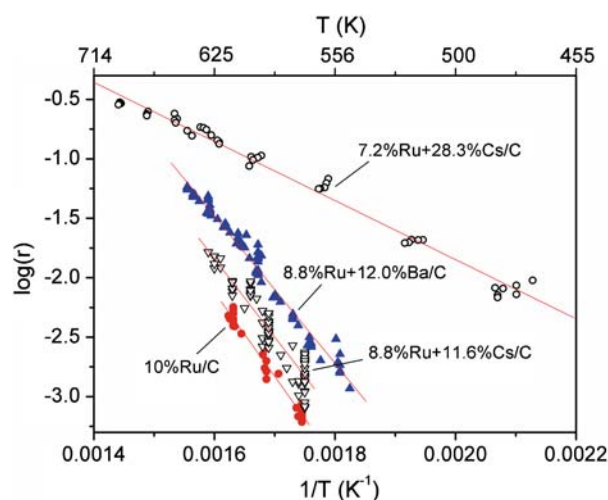


Figure 3. Activities of differently promoted Ru/C catalysts. The composition of each catalyst is given in the graph. r is in $\text{mol}_{\text{NH}_3}/\text{mol}_{\text{Ru}}/\text{s}$.

Cs loading gave lower apparent activation energy than the other catalysts. This change means, that the lower the temperature, the higher is the relative effect of promotion, and even at 473 K the activity is as high as that of the Ba promoted catalyst at 590 K. This is particularly interesting for miniaturization, as lower operating temperature reduces heat losses and thereby enables a lower overall fuel consumption. Unfortunately, the equilibrium is shifted towards NH_3 for low temperatures giving to low equilibrium conversions at temperatures below 500 K. However, with the reported Cs promoted catalyst a large fraction of the ammonia can be decomposed at relatively low temperature while most of the remaining ammonia can then be decomposed in an even smaller hot zone reactor. In this way the reactor volume kept at high temperature can be reduced, saving considerable amounts of energy, and thus the volume needed for fuel storage will be smaller.

The primary concern when designing a micro-fabricated reactor for hydrogen production by ammonia decomposition is to achieve high conversion with the smallest possible amount of catalyst. The data in figure 4 shows that the overall rate of decomposition decreases when the system is pushed towards higher conversions. This can be attributed to a negative reaction order in H_2 and to a closer approach to equilibrium. For ammonia decomposition, these effects are not easily separable, and most likely they are both responsible for the observed apparent activation energies in figures 2 and 3 as these are measured at a constant gas flow that makes rate and conversion correlate.

For development of a small portable power supply the decreasing rate close to equilibrium is an adverse effect as the ultimate goal is full equilibrium conversion using the minimal amount of catalyst. One way of getting closer to this goal is to remove hydrogen continually e.g. through a Pd membrane. This has been done in

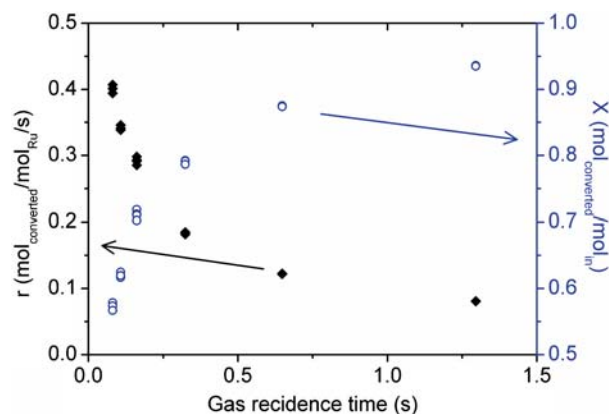


Figure 4. Comparison of rate and conversion as function of residence time at 694 K over a Ru + Cs/C catalyst with 7.2 wt% Ru and 28.3 wt% Cs.

larger systems but it demands a high pressure differential to get a useful flux through the membrane [44]. In micro-fabricated reactors, Ye *et al.* [45] have managed to integrate a 340 nm thin Pd film on a support of porous SiO_2 . This Pd membrane allows diffusion of hydrogen with a flux of $0.112 \text{ mol m}^{-2} \text{ h}^{-1}$ and high selectivity (H_2/N_2 ratio of 44). Removing hydrogen through such a membrane would make it possible to maintain a high rate up to higher conversions and also enhance the fuel cell activity by providing pure hydrogen for the fuel cell.

4. Conclusions

Graphite supported catalysts for decomposition of ammonia is incorporated in a micro-fabricated reactor for the first time. Since graphite carrier gives the most active ruthenium catalysts for this reaction, its incorporation in the micro-fabricated reactors enable a significant increase in the activity per reactor volume. This is important for miniaturizing ammonia decomposition systems for hydrogen production. At the same time, high Cs promoter loading is shown to facilitate high ammonia decomposition rates at temperatures below 500 K.

Acknowledgments

The Danish National Research Foundation is sponsoring the Center for Sustainable and Green Chemistry and the Center for Individual Nanoparticle Functionality, the project is also supported by The Danish Council for Strategic Research (Project no. 2104-05-0016)

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