Shielding protection by mesoporous catalysts for improving plasma-catalytic ammonia synthesis

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Abstract: Plasma catalysis is a promising technology for decentralized small-scale ammonia (NH₃) synthesis under mild conditions using renewable energy, and it shows great potential as an alternative to the conventional Haber-Bosch process. Here, we demonstrate that a rational design of supported Ni catalysts using mesoporous MCM-41 could enable efficient NH₃ production with >5% NH₃ yield under ambient conditions. A catalyst design strategy, named "shielding protection", has been proposed to enhance ammonia production efficiently.

Keywords: Non-thermal plasma (NTP); Plasma catalysis; Ammonia (NH₃) synthesis; Mesoporous catalysts; MCM-41.

1.Introduction

Ammonia (NH₃) is an important building block for fertilizers and many other chemicals. It is also a flexible long-term energy carrier and zero-carbon fuel. Nowadays, ammonia is mainly produced using the centralized Haber-Bosch (H-B) process at high temperatures (650-750 K) and pressures (50–200 bar), which is energy intensive and only economically feasible on a large scale. Hence, developing green and sustainable alternative technologies become more attractive for decentralized ammonia production under mild conditions. Non-thermal plasma (NTP) catalysis, is an attractive alternative technology for ammonia production at room temperature and ambient pressure. However, this emerging process still suffers from a low NH₃ yield due to limited knowledge in designing highly efficient catalysts and the in situ plasma-induced reverse reaction (i.e., NH₃ decomposition). In this work, we show that a bespoke design of supported Ni catalysts using mesoporous MCM-41 could enable efficient plasmacatalytic NH₃ production at 35 °C and 1 bar with >5% NH₃ yield at 60 kJ/L, which is among the best of the state-ofthe-art. Specifically, the Ni active sites were deliberately deposited on the external surface of MCM-41 to enhance plasma-catalyst interactions and hence improve NH₃ production. The desorbed NH₃ could then diffuse into the ordered mesopores of MCM-41 to be shielded from decomposition due to the absence of plasma in the mesopores, that is, shielding protection, thus driving the reaction forward effectively (Fig. 1). Comprehensive catalyst characterization and in situ characterization of plasma-catalyzed surfaces were carried out to elucidate the relevant mechanisms of this strategy, which can further shed light on the importance of a rational design of catalysts specifically for improving plasma-catalytic processes².



Fig. 1. Schematic diagram of plasma-enhanced ammonia synthesis over Ni-based mesoporous catalysts by shielding protection.

2. Materials and Methodology

The supported Ni catalysts on MCM-41 were prepared using the synthesis methods described previously³. Ni NPs (10 wt.% loadings) were deposited in different locations of MCM-41, including only in its mesopores, mainly on its outer surface, and across its framework, which is labelled Ni/MCM-in, Ni/MCM-out and Ni/MCM-both, as respectively. All the calcined catalytic samples were then sieved to 60-70 meshes, denoted as the as-prepared catalysts. For plasma-catalytic ammonia synthesis, the asprepared catalysts were reduced by Ar/H2 mixed gas (100 mL min-1; Ar/H₂ = 1:1) at 750 °C for 2 h before the plasma reaction (denoted as the reduced catalysts). The experiments were conducted in a coaxial DBD reactor with a special ground electrode. Water was circulated between two concentric quartz tubes using a circulation bath (Grant LT Ecocool 150) to maintain a reaction temperature of 35 °C during the experiments. The DBD reactor was connected to an AC high-voltage power supply with a peak voltage of up to 25 kV. The discharge power was controlled between 16-40 W, and the frequency was fixed at 9.2 kHz. To understand the mechanisms, an integrated DBD/gas cell was designed in-house for in situ FTIR (transmission mode) probing of plasma-assisted surface reactions in ammonia synthesis.

3. Results and Discussion

Compared to the plasma alone, packing the DBD reactor with SiO₂ or MCM-41 supports enhanced the ammonia synthesis rate (R_{NH3}), i.e., 575 µmol/g/h (plasma alone) vs. 1131 µmol/g/h (with SiO₂) and 1452 µmol/g/h (with MCM-41), as shown in Fig. 2a. The comparatively high R_{NH3} value of the plasma-MCM-41 system could be ascribed to the highly porous structure of MCM-41 compared to SiO₂. As expected, loading Ni onto either SiO₂ or MCM-41 enhanced the R_{NH3} significantly, proving the active role of metallic Ni in ammonia synthesis. Again, the Ni/MCM-41 catalysts were more active than Ni/SiO₂ with the following activity order: Ni/MCM-out > Ni/MCM-both > Ni/MCM-in > Ni/SiO₂. In particular, Ni/MCM-out exhibited a high NH₃ yield of about 3.7%, which was ~8 times higher than that of the plasma alone. A comparison of the ammonia concentration and energy yield for various metallic catalysts is given in Fig. 2b. Ruthenium (Ru), as the most studied metal in plasmacatalytic ammonia synthesis, shows a relatively higher energy yield but with a very low ammonia concentration (<1000 ppm), whereas other metals, such as Ni and Pd, could achieve a higher ammonia concentration with a lower energy yield (<1 gNH₃/kWh). As noble catalysts are relatively expensive, the plasma-catalytic system using Ni/MCM-out displays very promising performance (at a low flow rate of 40 mL/min) with a high NH₃ vield (5.3%)and concentration (27115 ppm) at an energy yield of 1.2 gNH₃/kWh. The energy yield of the Ni/MCM-out system could be improved to 3.9 gNH₃/kWh by increasing the flow rate to 1.2 L/min, but this operation compromises the ammonia concentration. To illustrate this enhancement of NH₃ yield using a mesoporous catalyst, we have developed a unique integrated plasma/FTIR cell for in situ probing of plasma-induced surface reactions over different Ni/MCM-41 catalysts, together with comprehensive catalyst characterisation and plasma diagnostics, to clearly demonstrate and elucidate this new strategy for enhanced plasma-catalytic ammonia synthesis at ambient conditions with solid and convincible evidence.





Fig. 1. (a) R_{NH3} and NH_3 yield of plasma alone and plasmacatalysis systems (with SiO₂, MCM-41 and catalysts based on them, SEI = 36 kJ/L, $Q_{gas} = 40$ mL/min, at 35 °C and 1 Bar. Each experiment lasted 3 h). (b) Reported energy yield *vs.* NH₃ concentration in the plasma catalytic NH₃ synthesis over different metallic catalysts using DBD.

4. Significance

For the first time, we have proposed and demonstrated a new strategy ("shielding protection") for the rational design of highly efficient catalysts – using the mesoporous structure of a catalyst to protect formed products (e.g., ammonia) due to the absence of plasma formed in mesopores while limiting reverse reactions (ammonia decomposition), thus significantly enhancing the plasmacatalytic ammonia synthesis under ambient conditions (single-pass ammonia yield >5%).

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6. References

[1] Y. Wang, M. Craven, X. Yu, J. Ding, P. Bryant, J. Huang, X. Tu, ACS Catal., 9, 10780-10793 (2019).

[2] Y. Wang, W. Yang, S. Xu, S. Zhao, G. Chen, A. Weidenkaff, C. Hardacre, X. Fan, J. Huang, X. Tu, J. Am. Chem. Soc., 144, 12020-12031 (2022).

[3] Z. Wang, Y. Jiang, R. Rachwalik, Z. Liu, J. Shi, M. Hunger, J. Huang, ChemCatChem, 5, 3889–3896 (2013).