Ruthenium Catalysts Supported on MOFs derived Porous Zirconia for Hydrogen production via Ammonia Decomposition

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Highlights

- Metal-organic frameworks are presented as templates of highly porous metal oxide supports.
- MOFs loaded with ruthenium via incipient wetness impregnation (IWI) method can act as a well-defined precursor for preparing zirconia-supported Ru NPs catalysts.
- 5wt.% Ru NPs/HP-ZrO$_2$ shows a high ammonia conversion of 60% and reaction rate of 0.13 molH$_2$ mol$_{Ru^{-1}}$ s$^{-1}$ at 450 °C.

1. Introduction

Ammonia has been presented as an attractive alternative to hydrogen storage due to its high hydrogen content both volumetrically and gravimetrically and a narrow flammable range.\cite{1} According to recent reports of the US Department of Energy, its feasibility lies on the supply of hydrogen on demand at low temperatures (100-200 °C).\cite{1} During the last years, we have shown that ruthenium based catalysts supported on carbon nanotubes (CNT) are capable of decomposing ammonia at temperatures ~180°C \cite{2}. It is believed that this high activity is related to the ruthenium particle size (3 - 5 nm) where the concentration of B$_5$ active sites is maximized. However, further understanding of this size – activity relationship is needed for the design of the new generation of catalysts. Within this context, metal-organic frameworks (MOFs) consisting of metal clusters and organic ligands with atomic-level pores are presented as support precursors. Their high surface areas and small pore size (0.3 - 3 nm) and uncoordinated metal or nitrogen sites \cite{3} makes ideal support for the confinement of small (< 3 nm) particles. Upon calcination under inert gas or air conditions, the frameworks turn into metal catalysts supported by porous carbon or metal oxides. Herein, we utilize an amine functionalized MOF, UiO-66-NH$_2$, as porous zirconia precursor to prepare Ru NPs/ZrO$_2$ catalysts for ammonia decomposition reactions.

2. Methods

UiO-66(Zr)-NH$_2$ MOFs are impregnated with ruthenium(III) nitrosyl nitrate via the incipient wetness impregnation (IWI) method and stabilized by uncoordinated -NH$_2$ groups. After drying under vacuum at 80 °C, they are calcined at 550 °C for 5 hours leading to Ru NPs/HP-ZrO$_2$ (HP stands for highly porous) catalysts. Scheme 1 represents the stages in the catalyst preparation.

Scheme 1. Scheme for the preparation of Ru NPs/HP-ZrO$_2$ catalysts using incipient wetness impregnation (IWI) method.
3. Results and discussion

Most of current studies have been devoted to the development of catalysts for ammonia decomposition at high temperatures (> 400 ºC). Our previous studies have shown that ruthenium catalysts supported by carbon nanotubes (CNT) with cesium as a promoter are capable of decomposing ammonia at a low threshold temperature of 180 ºC.[4, 5] The specific activity of Ru NPs is closely related to their particle sizes and electronic modifications. Herein, we utilize an amine tethered MOF with molecular-level pore architecture (~1 nm) to confine ruthenium precursors and obtain Ru NPs/HP-ZrO2 (HP stands for highly porous) catalysts after calcination. From Figure 1a, with the increase of Ru loading from 0.8wt.% to 5wt.%, ammonia conversion increases from 25% to 60% at 450 ºC, but decreases to 32% at 6.5wt.% loading, likely due to approaching the encapsulation limit of Ru precursors inside the pores of MOFs. These values are higher than that of impregnated 3wt.% Ru/LSZ-DP (4%),[6] and 7wt.% Ru/CNT (50%).[4] It is worth noting that the molar reaction rates of both 3.5wt.% (0.16 molH2 molRu-1 s-1) and 5wt.% Ru NPs/HP-ZrO2 catalysts (0.13 molH2 molRu-1 s-1) are an order of magnitude higher than the 7wt.% Ru NPs/CNT catalyst (0.06 molH2 molRu-1 s-1) and 3wt.% Ru/LSZ-DP catalyst (0.005 molH2 molRu-1 s-1), respectively at the same reaction conditions. Similar values of activation energy in the Ru/CNT and Ru/HP-ZnO2 catalysts suggests that encapsulation of the active sites in the latter case is compensated by enhanced diffusion of ammonia within the porous zirconia (Figure 1c). These promising results suggest that MOF derived supports can provide vital understanding of the effect of particle size in a number of catalytic applications such as this, enabling fundamental understanding in catalysis design.

![Figure 1. Ammonia decomposition conversion (a) and reaction rate (b) and Arrhenius plot (c) as a function of reaction temperature using a gas hourly space velocity (GHSV) of 6000 mL NH3 gcat-1 h-1. The data of 7wt.% CNT and 3wt% Ru/LSZ-DP are from our previous work with a GHSV of 5200 mL NH3 gcat-1 h-1.[4] and the literature with a GHSV of 4000 mL NH3 gcat-1 h-1.[6] respectively.](image)

4. Conclusions

Our results have demonstrated that molecular-level organized metal-organic frameworks can act as an effective precursor for preparing metal nanoparticle catalysts supported on highly porous metal oxides. Among these catalysts, 5wt.% Ru NPs/HP-ZrO2 shows a high ammonia conversion of 60% and reaction rate of 0.13 molH2 molRu-1 s-1 at 450 ºC. Our study has suggested an alternative route to prepared noble metal catalysts supported by porous metal oxides via calcination of MOFs.

References


Keywords

Ammonia Decomposition; Hydrogen Storage, Ruthenium Catalysts; Porous Zirconia; Metal-Organic Framework