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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 mol$_{H2}$ mol$_{Ru}^{-1}$ s^{-1} at 450 °C.

1. Introduction

Ammonia has been presented as an attractive alternative to hydrogen storage due its high hydrogen content both volumetrically and gravimetrically and a narrow flammable range.[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 ℃).[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 [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 [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.
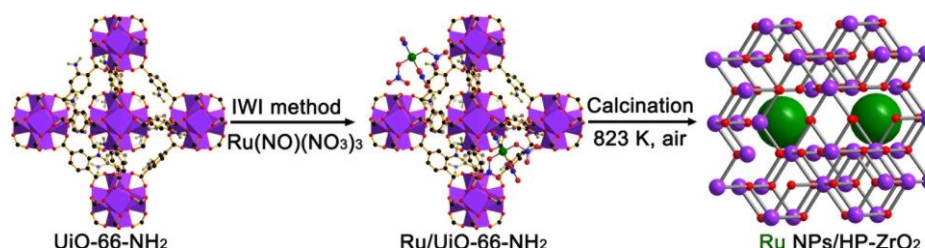
Scheme 1. Scheme for the preparation of Ru NPs/HP-ZrO$_2$ catalysts using incipient wetness impregnation (IWI) method.

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3. Results and discussion

Most of current studies have been devoted to the development of catalysts for ammonia decomposition at high temperatures (> 400 °C). 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 °C.[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-ZrO$_2$ (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 °C, 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 mol$_{H2}$ mol$_{Ru}^{-1}$ s^{-1}) and 5wt.% Ru NPs/HP-ZrO$_2$ catalysts (0.13 mol$_{H2}$ mol$_{Ru}^{-1}$ s^{-1}) are an order of magnitude higher than the 7wt.% Ru NPs/CNT catalyst (0.06 mol$_{H2}$ mol$_{Ru}^{-1}$ s^{-1}) and 3wt.% Ru/LSZ-DP catalyst (0.005 mol$_{H2}$ mol$_{Ru}^{-1}$ s^{-1}), respectively at the same reaction conditions. Similar values of activation energy in the Ru/CNT and Ru/HP-ZnO$_2$ catalysts suggests that encapsulation of the active sites in the latter case is compensated by enhanced diffusion of ammonia within the porous polar ZrO$_2$ (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.
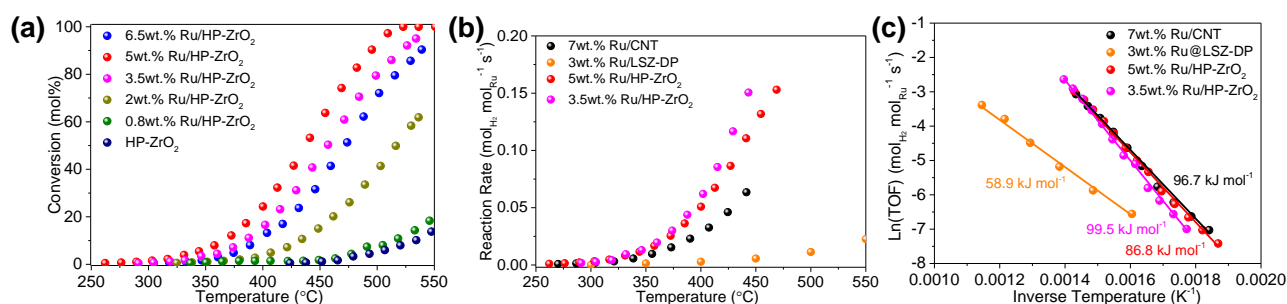
Figure 1. Ammonia decomposition conversion (a) and reaction rate (b) and Arrhenius plot (c) as a function of reaction temperature using a gas hourly space velocity (GHSV) of 6000 mL$_{NH_3}$ g$_{cat}^{-1}$ h^{-1}. The data of 7wt.%/CNT and 3wt% Ru/LSZ-DP are from our previous work with a GHSV of 5200 mL$_{NH_3}$ g$_{cat}^{-1}$ h^{-1} [4] and the literature with a GHSV of 4000 mL$_{NH_3}$ g$_{cat}^{-1}$ h^{-1},[6] respectively.

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-ZrO$_2$ shows a high ammonia conversion of 60% and reaction rate of 0.13 mol$_{H2}$ mol$_{Ru}^{-1}$ s^{-1} at 450 °C. Our study has suggested an alternative route to prepared noble metal catalysts supported by porous metal oxides *via* calcination of MOFs.

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