Национальный исследовательский Томский государственный университет

# Новые катализаторы и каталитические процессы для решения задач экологически чистой и ресурсосберегающей энергетики

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# Influence of the amount of modified linker precursor to UiO-66-NH$_2$ synthesis

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Most of the valuable organic compounds are currently produced from depleting fossil fuels resources [1]. The application of biomass becomes promising due to the high sustainability of the feed as well as opportunity to synthesize a wide spectrum of compounds. Thus, biomass conversion is accompanied by the formation of valuable side products during the refining, such as 5-hydroxymethylfurfural (HMF) [2]. However, for realization of fully waste-free process potential, the use of catalytic systems is mandatory. For this, a large number of catalysts was investigated and synthesized, which can be divided into noble metal-containing and non-noble metal systems. These catalyst systems have their advantages and disadvantages, which helps to design an efficient catalyst for target reaction.

For supported metal catalysts, the choice of a support is key aspect of the design due to its acid-base or redox properties as well as possible metal-support interactions affecting the catalyst performance. Besides, the physical properties of support including specific surface area, the temperature of destruction etc. should also be considered [3].

Recently, the metal organic frameworks (MOFs) have attracted much interest in many applications due to their high porosity, diverse structures, and controllable chemical structures. Besides properties typical for highly porous structured materials such as the sieve effect, MOFs have several unique features. MOFs consist of metal ions or clusters and organic linkers. So, each of these parts brings new properties into MOF and their combining may lead to whole new properties of MOF.

The present work is devoted to the study of the physical and chemical properties of NH$_2$- modified UiO-66 used as support for Pd catalyst for HMF oxidation. Unmodified UiO-66 and fully or partially NH$_2$-modified UiO-66-NH$_2$ samples were synthesized by hydrothermal method using ZrO(NO$_3$)$_2$×H$_2$O as Zr-precursor and terephthalic acid and/or aminoterephthalic acid as linker. Hydrochloric acid and dimethylformamide (DMF) are used as modulator and solvent respectively. The samples prepared were studied by low temperature nitrogen sorption, XRD, and IR-spectroscopy.

According to XRD data, both unmodified and fully modified samples are characterized by the presence of crystalline phase with UiO-66 structure. The low temperature nitrogen sorption data indicates that the unmodified UiO-66 sample is characterized by a bimodal pore distribution with pores diameters around 0.6 nm and 0.9 nm and high specific surface area of 1100-1300 m$^2$/g, which well agrees with previous studies [4]. The modified UiO-66-NH$_2$ sample contains predominantly narrow pores with 0.5-0.6 nm diameter. The specific surface area of the UiO-66-NH$_2$ sample is ~700 m$^2$/g, which is significantly lower than for unmodified UiO-66 sample. These results can be attributed to additional crosslinking within pore volume via formation of -NH-C(=O)- bonds between linkers. To clarify this suggestion a series of partially modified UiO-66-NH$_2$ samples prepared using a mixture of modified and unmodified terephthalic acid with different molar ratios (0.25:0.75, 0.5:0.5, 0.75:0.25) was additionally studied.

The results on XRD, low temperature nitrogen sorption and IR-spectroscopy study of the partially modified UiO-66-NH$_2$ samples as well as catalytic properties of the supported Pd catalyst based on unmodified UiO-66 and modified UiO-66-NH$_2$ samples will be discussed.

**References**
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