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Short communication

Novel route to control the size, distribution and location of Ni nanoparticles in mesoporous silica for steam reforming of propylene glycol in microchannel reactor

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ABSTRACT

Highly dispersed and size controlled Ni nanoparticles (NPs) in SBA-15 were synthesized by thermolysis of sucrose as a new delivery conveyor and sacrificial template. The Ni/SBA-15 catalysts were characterized systematically to elucidate their morphological structure and surface properties. It was found that the sucrose contributes majorly to control the size and higher distribution of Ni NPs by prevents their sintering into mesoporous nanochannels. The catalytic performance of Ni/SBA-15 catalysts was investigated by steam reforming of propylene glycol in microchannel reactor. As compared with conventional Ni-impregnated catalyst, the catalyst prepared with sucrose assisted route improves the coking and sintering resistance in steam reforming reaction of propylene glycol.

1. Introduction

Nickel based catalysts have been extensively applied for steam reforming reactions of alcohols such as methanol [1], ethanol [2], ethylene glycol [3], and glycerol [4] owing to their high stability, catalytic activity, and lower cost compared to noble metal catalysts. Unfortunately the nickel particles severely suffer from sintering and the surface of large nickel particles becomes more vulnerable to the carbon deposition, which blocks the active sites of nickel [5]. The carbon deposition affects the activity and stability of the catalyst and reduces the catalytic performance. However, the carbon deposition can be suppressed by preparing catalyst with controlled size and dispersion. Highly dispersed nickel nanoparticles (NPs) display attractive properties in relation with their size [6]. Size controlled Ni NPs can effectively enhance the coking and sintering resistance during high temperature reactions [7,8]. Therefore homogeneously dispersed and size controlled nickel based catalysts are highly desirable.

The activity and stability of nickel based catalyst can also be improved by carefully selecting the support materials because the dispersion and accessibility of the active particles within the support determine the activity of the catalyst [9]. Generally, a high surface area and large pore size of the support favors the higher loadings of Ni NPs. Hence, well-ordered mesoporous silica with uniform channels has been highlighted as an ideal support for uniform growth of nickel NPs [10]. However, mesoporous silica supported Ni catalyst is generally prepared by an incipient wetness route, which leads to poor filling of the Ni precursor into the mesoporous nanochannels and leaving behind the Ni on the external surface of silica. Nevertheless, the Ni precursors block the nanochannels with large particle size, which result in poor utilization of available space and reduce the activity. Therefore the poor filling of nickel particles into the confined space and/or blockage of nanochannels by large size particles cannot achieve simultaneous coke suppression and sintering resistance during high temperature catalytic reactions.

Herein, we report a new method to control the size, distribution and location of Ni NPs in the nanochannels of mesoporous silica by thermolysis of sucrose as new delivery conveyor. The sucrose-Ni^{2+} complex enters into the mesoporous nanochannels easily by capillary force, and the sucrose decomposes to carbon by heat treatment under an inert atmosphere. Sucrose, as sacrificial carbon template, contributes majorly for higher distribution of Ni NPs by preventing their sintering, and simultaneously hindering the migration of Ni NPs from the internal surface of mesoporous nanochannels to the external surface. The activity of catalysts thus obtained were investigated by steam reforming of propylene glycol using isothermal microchannel reactor, which is more appropriate for fast and highly exothermic or endothermic reactions [11–14].

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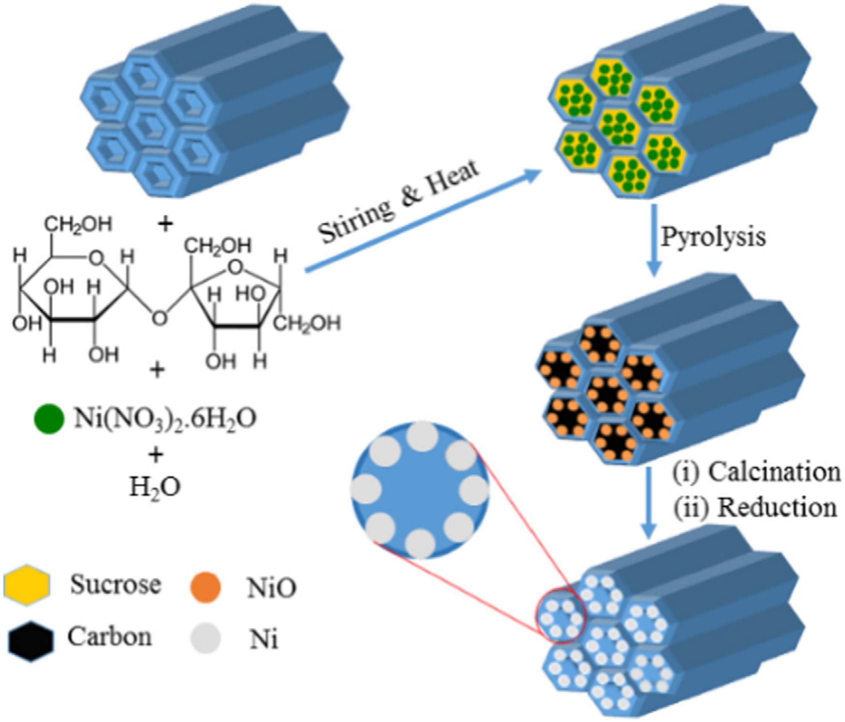

Fig. 1. Schematic illustration of the Ni/SBA-15-S catalyst.

2. Results and discussion

Fig. 1 shows a schematic illustration of the synthetic pathway to mesoporous silica SBA-15 confined Ni NPs catalyst. First, the Ni (10.8 wt%) precursor was delivered into the nanochannels of mesoporous SBA-15 using sucrose as a delivery conveyer. Then, the intermediate product was dried, and pyrolyzed in presence of N_2. Finally, highly dispersed and size controlled Ni NPs into nanochannels of mesoporous SBA-15 catalyst was obtained by removing the carbon template, which is confirmed by O_2-TPO and TGA (Fig. S1 and S2) by calcination in air and followed by reduction in H_2. The catalyst thus obtained was named as Ni/SBA-15-S. For comparison, the catalyst named as Ni/SBA-15 (10.8 wt% of Ni) was prepared without addition of sucrose and omitting the carbonization step.

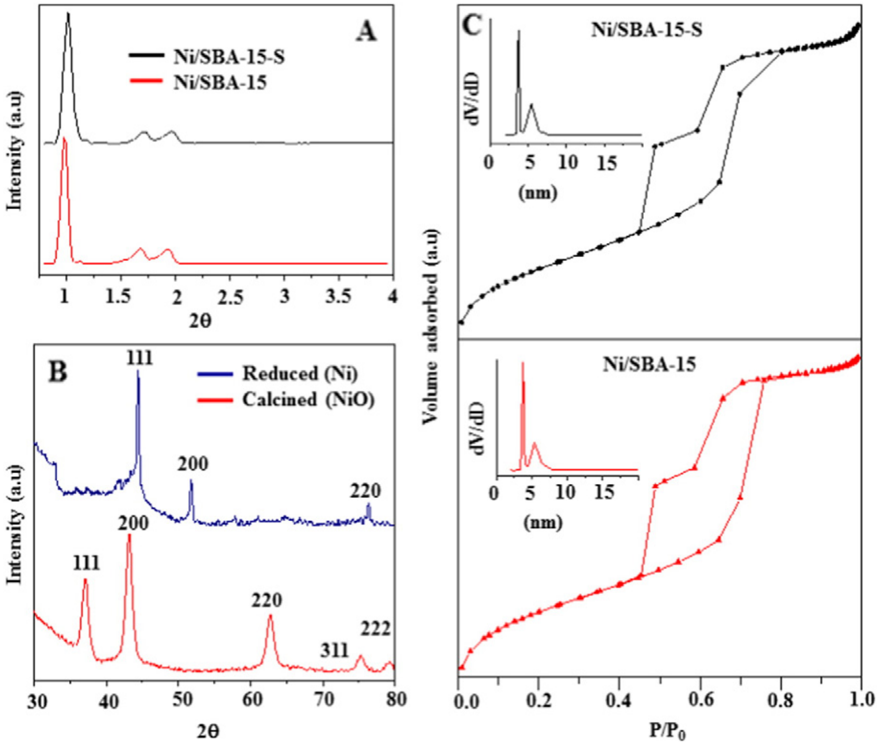

Fig. 2. Low-angle XRD of Ni/SBA-15-S and Ni/SBA-15 catalysts, wide-angle XRD of calcined and reduced Ni/SBA-15-S catalyst and nitrogen physisorption isotherms with pore size distribution of Ni/SBA-15-S and Ni/SBA-15 catalysts.