Effect of preparation method on Ni_2P/SiO_2 catalytic activity for $NaBH_4$ methanolysis and phenol hydrodeoxygenation

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ABSTRACT

A comparative study has been performed on Ni_2P/SiO_2 catalysts prepared by: (i) conventional temperature-programmed reduction (TPR) of calcined precursors following wet impregnation of the support, (ii) TPR of a sol−gel prepared NiO/SiO_2 precursor impregnated with $NH_4H_2PO_4$ and (iii) a solution-phase reaction in the presence of the SiO_2 support using $Ni(acac)_2$ and trioctylphosphine. Catalyst characterization shows that the Ni_2P prepared by the solution-phase method has a uniform particle size (7.5 ± 0.8 nm) and H species can easily transfer from the nickel sites to the SiO_2 support on this catalyst. These properties result in a high $NaBH_4$ methanolysis to hydrogen activity. In contrast, the sol−gel prepared Ni_2P/SiO_2 has a relatively high catalytic activity for phenol hydrodeoxygenation due to a higher concentration of $Ni^{\delta+}$ species that act as Lewis acid sites and metal sites, and a higher Ni_2P crystallinity.

Introduction

Hydrogen is a clean, renewable energy carrier that can address increasing concerns related to the depletion of fossil fuels and their environmental impact. The safety and efficiency of hydrogen storage and supply plays a critical role in the practical application of hydrogen as an energy carrier [1].

Among the methods of hydrogen supply, $NaBH_4$ reaction with methanol to yield hydrogen (Eq. (1)), with high volumetric and gravimetric hydrogen capacity, has been extensively studied because the reaction activation is lower than that of $NaBH_4$ hydrolysis and the system can be operated at a rather low temperature (<0 °C) benefiting from the low freezing point of methanol [2−4]. Up to now, catalysts studied for $NaBH_4$

methanolysis include Ru/Al$_2$O$_3$, Fe−B nanoparticles, Co/TiO$_2$ and Co/Al$_2$O$_3$.

$$NaBH_4 + 4CH_3OH \rightarrow 4H_2\uparrow + NaB(OCH_3)_4 \qquad (1)$$
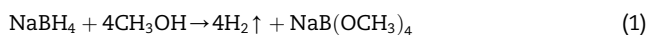
Transition metal phosphides are a class of catalysts that have shown potential in hydrotreating reactions such as hydrodeoxygenation (HDO) [5], hydrodesulphurization (HDS) [6] and hydrodenitrogenation (HDN) [7]. These catalysts have also recently been shown to catalyze higher alcohol synthesis from synthesis gas [8—10] and the hydrogen evolution reaction [11]. In hydrotreating, including HDO, Ni$_2$P has been identified as having the highest activity among the metal phosphides due to appropriate electronic and acid properties [6,12,13]. However, the preparation of uniform nanoparticles of Ni$_2$P remains a challenge [14].

The conventional preparation method of Ni$_2$P is temperature-programmed reduction (TPR) of metal phosphate precursors. However, high reduction temperature (up to 1000 K) leads to agglomeration or sintering of the Ni$_2$P particles and minimal control of Ni$_2$P particle size [15]. To address this issue, solution-based strategies have been developed that involve the reaction of metal salts with phosphines to yield almost monodispersed nanoparticles. Muthuswamy et al. [16] studied the effects of the reductant oleylamine and the phosphorus source on the morphology of Ni$_2$P and Savithra et al. [17] reported on the HDS performance of supported Ni$_2$P prepared by solution-phase reaction. They found that Ni$_2$P nanoparticles prepared by solution-phase reaction have a weak interaction with the amorphous silica support, resulting in sintering under conditions required to achieve HDS catalysis and, consequently, these catalysts have a low HDS activity. In a second approach, Chen et al. [18] prepared NiO nanoparticles supported on SiO$_2$ by a sol−gel method and following impregnation with NH$_4$H$_2$PO$_4$ and TPR. They synthesized highly dispersed Ni$_2$P (4.2 nm) that was stable and highly active for hydrodechlorination of chlorobenzene.

In the present study, Ni$_2$P nanoparticles supported on SiO$_2$ were synthesized using three methods: (i) conventional temperature-programmed reduction (TPR) of calcined precursors following wet impregnation of the support, (ii) TPR of a sol−gel prepared NiO/SiO$_2$ precursor impregnated with NH$_4$H$_2$PO$_4$ and (iii) a solution-phase reaction in the presence of the SiO$_2$ support using Ni(acac)$_2$ and trioctylphosphine following the method of Muthuswamy et al. [16]. The as-prepared samples from the three different methods were characterized to identify differences in their physicochemical properties and their catalytic performance was measured for both NaBH$_4$ methanolysis and phenol HDO. To the best of the authors' knowledge, NaBH$_4$ methanolysis using Ni$_2$P catalysts is reported herein for the first time.

Experimental

Catalyst synthesis

The solution-phase synthesis of the supported Ni$_2$P catalyst was performed by a one-pot strategy under N$_2$ atmosphere (99.99%). In a typical preparation, Ni(acac)$_2$ (526 mg, 95%) and oleylamine (2.0 mL, 80−90%) were added to a 50-mL three-necked flask equipped with a thermometer and a Graham condenser. The mixture was stirred moderately and heated to 393 K at a heating rate of 20 K min^{-1} using a heating mantle. Trioctylphosphine (TOP; 3.6 mL, 97%) and SiO$_2$ (Sigma−Aldrich, 285 m^2 g^{-1}, 800 mg) were added to the flask successively and the mixture was continuously stirred at 393 K for 30 min, and then heated to 613 K (with a heating rate of 20 K min^{-1}) and held at this temperature for 2 h. After naturally cooling to room temperature, the obtained dark mixture was washed with a solution of hexane and ethanol (v:v = 1:1), followed by centrifugation at 10, 000 rpm for 3 min. The washing process was repeated three times. The final powder was then washed with ethanol, passivated and dried at 308 K in an O$_2$/N$_2$ mixture (1.5 vol.% of O$_2$) for 3 h. The catalyst obtained was named Ni$_2$P-TOP.

For comparison, a SiO$_2$-supported Ni$_2$P catalyst was prepared by the conventional TPR method. The synthesis process was similar to that described by Sawhill et al. [19] for Ni$_2$P/SiO$_2$ catalysts. The catalyst precursor was prepared by an incipient wetness impregnation of the same SiO$_2$ support used above, with ammonium dihydrogen phosphate (NH$_4$H$_2$PO$_4$) and nickel nitrate hexahydrate (Ni(NO$_3$)$_2$·6H$_2$O) solution. The impregnated SiO$_2$ precursor was dried at 393 K and calcined at 823 K (with a heating rate of 5 K min^{-1}) for 4 h. Subsequently, the calcined precursor was reduced in a flow of H$_2$, while heating from room temperature to 523 K at a heating rate of 10 K min^{-1} followed by heating from 523 K to 923 K at 1 K min^{-1} and holding for 3 h. The reduced catalyst was passivated at 308 K in O$_2$/N$_2$ mixture (1.5 vol.% of O$_2$) for 3 h, and was denoted as Ni$_2$P-TPR.

A modified TPR method was also adopted to synthesize SiO$_2$-supported Ni$_2$P catalyst according to Chen's work [18]. NiO/SiO$_2$ was prepared by a sol−gel method and calcined to obtain a high dispersion of nickel. Then the NiO/SiO$_2$ was wet impregnated with ammonium dihydrogen phosphate (NH$_4$H$_2$PO$_4$) solution, followed by temperature-programmed reduction and passivation following the same procedure described above for the Ni$_2$P-TPR preparation. The catalyst obtained was named Ni$_2$P-sol−gel.

The nominal Ni metal loading of all the three catalysts prepared was 15 wt.%. For the Ni$_2$P-TOP preparation, an organic layer originating from oleylamine and TOP [11,20], is invariably present on the surface of Ni$_2$P-TOP, despite several washing steps with hexane and ethanol. The organic layer on the surface of the Ni$_2$P-TOP can be removed after thermal treatment in Ar flow at 723 K. Thus, Ni$_2$P-TOP treated in argon atmosphere (99.999%) at 723 K (with a heating rate of 2 K min^{-1}) for 30 min is denoted as Ni$_2$P-TOP(Ar). Since the passivation layer on the sample surface may have an influence on the catalytic performance, the catalysts were pretreated before catalytic reaction in a H$_2$/N$_2$ mixture (10 vol.% of H$_2$) at 723 K (with a heating rate of 2 K min^{-1}) for 30 min and are denoted as Ni$_2$P-TOP(H$_2$), Ni$_2$P-TPR(H$_2$), Ni$_2$P-sol−gel(H$_2$), respectively.

Catalyst characterization

The BET surface area, pore volume, and mesopore size distribution of the samples were determined from N$_2$ adsorption/