



Nickel silicides prepared from organometallic polymer as efficient catalyst towards hydrogenation of phenylacetylene



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ABSTRACT

A single-phase Ni₂Si nanoparticle catalyst was prepared successfully by using temperature programmed pyrolysis method with polydimethylsilane-Ni(acac)₂ as precursor and was characterized by thermogravimetric analysis, X-ray diffraction, X-ray photoelectron emission microscopy, energy dispersive X-ray spectroscopy, and transmission electron microscopy. The pyrolysis temperature for generating pure Ni₂Si in H₂/Ar mixture is significantly lower than that for treatment in Ar. Ni₂Si nanoparticles would be reduced to Ni nanoparticles by H₂ with increasing pyrolysis temperature (>600 °C). The catalytic hydrogenation of phenylacetylene on Ni₂Si nanoparticles was investigated at 1.0 MPa hydrogen and 80 °C. The catalysts show suitable conversion of phenylacetylene and notable selectivity to styrene with 90%. In addition, catalytic performance on Ni₂Si prominently improves after removing the SiO₂ layer around Ni₂Si nanoparticles by alkali treatment.

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1. Introduction

Phenylacetylene (PA) removal is an important industrial process through semihydrogenation because PA is a poisonous impurity in styrene (ST) feed stocks, which results in deactivating polymerization catalyst and degrading the quality of polystyrene. Traditionally, a number of noble metals catalysts were used for selective hydrogenation, including supported Pd, Pt, Ru, and Rh, which have been developed and improved over the last few decades [1–6]. However, they are needed to be replaced by non-noble metal catalysts because of high cost and sensitivity of noble metals. Novel catalytic materials for PA semihydrogenation with high ST selectivity under mild conditions are highly desired.

Transition metal silicides with unique physical and chemical properties have shown high selectivity in some selective hydrogenation reactions [7–9]. As novel catalytic materials, transition metal silicides have been greatly concerned by researchers, due to their noble metal-like selectivity and excellent sulfur-tolerance compared with their metallic counterparts in hydrogenation reactions. Metal silicides are formed by silicon atom entering into metal lattice, which exhibit thermal, mechanical and chemical stability because of the unique geometrical and electronic structure [10–12].

Recently, a great number of methods were used to synthesize metal silicides. Tschan et al. [13] prepared the amorphous Pd₈₁Si₂₉ alloy by melt spinning method. CoSi nanoparticles supported on silica were synthesized by MOCVD of Co(SiCl₃)(CO)₄ [14]. Cheng et al. [15] prepared TaSi by implant the Ta ion into Si surface by high current. However, most metal silicides reported in the literature are multiphase. It's still a challenge to prepare single-phase transition metal silicides by general and controllable synthesis method, due to the complex phase behavior between metals and silicon and the complex stoichiometry and structure of their resulting compounds.

In recent years, transition metals are used to improve properties and yield of ceramics by direct pyrolysing mixture, in which transition metal or transition metal compounds are mixed with raw material, like polycarbosilane or polysilazane. Narisawa et al. [16] used metal chlorides to modify polymethylsilane precursor and got mixture of SiC, Si, and MSi_x. Ishikawa et al. [17] produced polyzirconocarbosilane using zirconium (IV) acetylacetonate and converted of the polymer into Si-Zr-C-O fiber with some impurity of SiC, ZrC, and ZrSi. To the best of our knowledge, few reports have been published on preparation of single-phase metal silicides as catalyst using above methods [18,19].

Herein, we report the single-phase Ni₂Si synthesized by temperature programmed pyrolysis method with polydimethylsilane-nickel acetylacetonate (PMS-Ni(acac)₂) as precursor. The as-prepared Ni₂Si catalysts were used in PA semihydrogenation reaction and show up high selectivity to ST.

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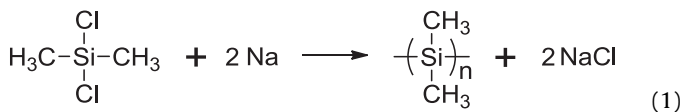
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2. Experimental

2.1. Polydimethylsilane synthesis

PMS was synthesized by sodium condensation method [20–22] using dimethyldichlorosilane ((CH₃)₂SiCl₂) as raw material. Firstly, about 7 g of sodium was added into 200 mL toluene, which was refluxed in Ar atmosphere at 110 °C for 1 h to get rid of the effect of H₂O and O₂. Then 20 mL of (CH₃)₂SiCl₂ was dropped slowly into toluene solution within 10 min. The sodium condensation reaction was carried out at 105–110 °C for 24 h as follows:



After reaction, water was dropped into solution slowly at room temperature with high-speed stirring in Ar atmosphere to remove by-products sodium and NaCl. (*This step must be very careful because of the severe reaction between water and sodium and the produced inflammable H₂.*) Then the supernatant purple liquid was dropped into 1000 mL methanol with stirring. The white powder PMS product was got by filtration and vacuum drying at 50 °C for 8 h.

2.2. Preparation and treatment of nickel silicides

The PMS and Ni(acac)₂ with the mass ratios of 3:2, 1:1, 2:3, and 1:4, respectively, were impregnated into 100 mL anhydrous tetrahydrofuran (THF) solvent. After being stirred for 24 h, solution was rotary evaporated and the as-prepared PMS-Ni(acac)₂ composites was vacuum dried at 50 °C for 8 h. 0.50 g PMS-Ni(acac)₂ composites with different mass ratios was temperature programmed pyrolysed in a quartz boat at Ar or H₂/Ar mixture atmosphere. Heating rate of the whole process was about 5 °C/min.

For etching the SiO₂ passivation layer, the as-prepared Ni₂Si nanoparticles were treated by 15 wt.% NaOH solution at 80 °C. The nickel silicide nanoparticles treated by alkali were used as catalysts in PA hydrogenation with the same reaction H₂ pressure and suitable reaction temperature.

2.3. Characterization

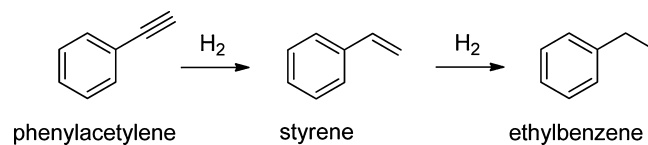
TG/DTG experiments were performed in Mettler Toledo TGA/SDTA851e thermo-gravimetry to understand decomposition process of samples. The samples were heated from room temperature to 900 °C at a rate of 10 °C/min in N₂.

X-ray diffraction (XRD) analysis of the samples was carried out using a Rigaku D/Max-2400 diffractometer with Cu Kα monochromatized radiation source, operated at 40 kV and 100 mA.

Surface compositions were investigated by X-ray photoelectron spectroscopy (XPS) employing an ESCALAB250 (Thermo VG, USA) spectrometer with Al Kα (1486.6 eV) radiation with a power of 150 W. Survey and individual high-resolution spectra were recorded with a pass energy of 50 eV. Ni 2p, Si 2p, and O 2s lines were monitored. All core-level spectra were referenced as the C 1s neutral carbon peak at 284.6 eV and were deconvoluted into Gaussian component peaks.

The morphologies of the as-prepared samples were studied by scanning electron microscopy (SEM, JEOL JSM-5600LV), operated at 15 kV. Elementary compositions were conducted with the EDX (energy-dispersive X-ray spectroscopy) detector as recorder.

The particle size and distribution of the samples were analyzed by transmission electron microscopy (TEM) (Philips CM200 FEG). Powder samples were ultrasonic treated in ethanol and dispersed on copper grids covered with a porous carbon film.



Scheme 1. Reaction network of phenylacetylene hydrogenation.

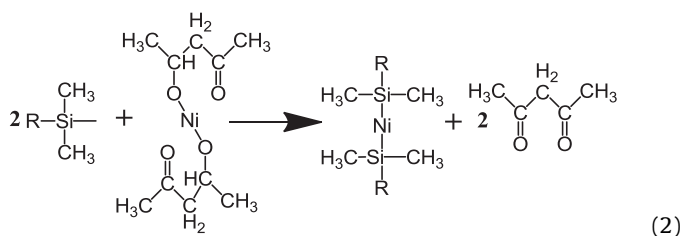
2.4. Hydrogenation of phenylacetylene

According to the procedure previously employed [23], PA hydrogenation (Scheme 1) were performed on nickel silicide catalysts in a 50 mL stainless steel autoclave under vigorous stirring. Before the reaction, catalysts were activated in an ultrapure hydrogen stream at 400 °C for 2 h and then cooled down to RT. The reaction was carried out at suitable temperature and 1 MPa H₂ with 0.10 g catalyst in 10 mL 1 M ethanol substrate solution. The products were analyzed by gas chromatography using a flame ionization detector with a SE-54/52 capillary column. A known amount of n-octane solution was used as an internal standard in this analysis.

3. Results and discussion

3.1. Preparation of nickel silicides

Fig. 1a shows TG/DTG curves of PMS prepared by sodium condensation method. There is only one main stage of mass loss from 300 °C to 400 °C as a result of PMS pyrolysis. Three differential thermogravimetric peaks at 100 °C, 250 °C and 430 °C in Fig. 1b. Three differential thermogravimetric peaks at 100 °C, 250 °C and 430 °C in Fig. 1b. The first peak at 100 °C was corresponding to the loss of H₂O and the rest two peaks with total weight loss (71%) is close to theoretical value of 70%, corresponding to the elimination of acetylacetonate. The weight loss between 370 and 460 °C can be attributed to the elimination of CO and CO₂, which came from the further decomposition of acetylacetonate. No further mass loss was detected above 500 °C, since the Ni(acac)₂·2H₂O has already been converted to metallic nickel. TG/DTG curves of PMS-Ni(acac)₂ composites in Fig. 1c show that ca. 16% mass loss from 50 °C to 150 °C was attributed to the loss of the solvent THF. The most mass loss of ca. 49% occurred between 200 °C and 400 °C due to the decomposition of PMS-Ni(acac)₂. And the main differential thermogravimetric peak occurred at 330 °C rather than 250 °C and 430 °C which were corresponding to thermogravimetric peaks of PMS and Ni(acac)₂. TG/DTG curves of PMS and Ni(acac)₂ which were mechanically mixed (Fig. 1d) was also measured to find out if there was a reaction between PMS and Ni(acac)₂ in THF. The first mass loss of 10% from 50 °C to 100 °C was due to the loss of water and solvent. Two stages of mass loss concentrating from 300 °C to 450 °C, and from 150 °C to 250 °C, were corresponding to pyrolysis of PMS and Ni(acac)₂, respectively. Compared Fig. 1d with c, it was proved that there was a reaction between PMS and Ni(acac)₂ when they were impregnated in THF. Zaheer et al. [19] reported that there was a cross-linking reaction between polysilazane and palladium compounds in THF. In addition, Ishikawa et al. [17] reported that polymethylsilane reacted with zirconium acetylacetonate. Therefore, the reaction between PMS and Ni(acac)₂ in THF is as follows:



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