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ARTICLE

Synthesis of Mixed Alcohols from CO Hydrogenation over Iron and Nickel Metal Phosphide Catalysts

SONG Xiangen[1,3], DING Yunjie[1,2,*], CHEN Weimiao[1], DONG Wenda[1,3], PEI Yanpeng[1,3], ZANG Juan[1,3], YAN Li[1], LÜ Yuan[1]

[1]Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Science, Dalian 116023, Liaoning, China
[2]State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China
[3]Graduate University of Chinese Academy of Sciences, Beijing 100049, China

Abstract: A series of silica supported iron and nickel metal phosphides with different molar ratios of P to metal were synthesized by the temperature programmed reduction method. Their catalytic performance for CO hydrogenation in a fixed bed reactor was tested with the conditions of 553 K, 5.0 MPa, and H_2:CO = 2 (molar ratio). With the FeP_x/SiO_2 catalysts (x denotes the molar ratio of P to metal), the product was a mixture of oxygenates containing methanol as the major component. With the NiP_x/SiO_2 samples, the liquid product was mainly methanol. The Fe_2P, Fe_3P, Ni, Ni_2P, Ni_3P, and $Ni_{12}P_5$ phases were stable during CO hydrogenation, while most of the metallic Fe phase transformed into iron carbide.

Key words: carbon monoxide hydrogenation; oxygenates; metal phosphides; silica; iron phosphide; nickel phosphide

Concerns about diminishing non-renewable petroleum resources, global climate change, and the energy crisis have increased interest in alternative fuel development, especially in biomass conversion. Biomass can be converted into bio-ethanol by an enzymatic process [1]. At present, ethanol is produced on the large scale primarily via the fermentation of sugars derived from corn or sugar cane, or via the hydration of petroleum-based ethylene. The ethylene hydration route suffers from the problem of rising crude oil prices and dependence on oil imports. The production of fuel-grade ethanol from fermentation is unattractive because of energy intensive distillation steps. Therefore, a more flexible approach using biomass and coal gas gasification to syngas (CO, CO_2, and H_2) followed by the catalytic conversion of the syngas to ethanol and other oxygenated products can be the route to solve the crisis in the near future [1].

Many catalysts reported for the conversion of syngas to oxygenated hydrocarbon products, such as Rh-based catalysts [2–4], alkali-doped Cu-based catalysts [5,6], modified Fischer-Tropsch (FT) synthesis catalysts [7–9], and Mo-based catalysts [10–12], are limited by poor selectivity. Rh-based catalysts have the highest ethanol selectivity among the catalysts investigated [2–4]. However, the issues of cost and supply mean that it would be difficult to commercialize for large scale processes. Therefore, there is significant interest in developing alternative catalysts for selective ethanol synthesis from syngas.

Recently, transition metal phosphides [13–18] were tested in a series of hydrogenation reactions. Supported phosphides can be easily prepared by the temperature-programmed reduction of phosphate precursors. Some researchers [13–18] have suggested that the phosphide catalysts possessed catalytic properties similar to precious metals, and they can also resist sulphur poisoning. The ligand effect and ensemble effect after the insertion of P atoms into the lattice of the metal can change the electronic properties and adsorption properties of the metal [13,14]. These characteristics could endowed the phosphides with the properties for a potential application in syngas conversion. Zaman et al. [19–21] reported syngas conversion over MoP/SiO_2 catalysts and showed that this type of catalyst gave

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*Corresponding author. Tel/Fax: +86-411-84379143; Email: dyj@dicp.ac.cn.

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reduced selectivities to hydrocarbons and increased selectivities to oxygenated products. Based on the catalytic results from Mo phosphides [19–21] for syngas conversion and iron group metal phosphides for hydrogenation, we have studied the catalytic properties of iron and nickel metal phosphides for syngas conversion. FeP_x/SiO_2 and NiP_x/SiO_2 catalysts with different molar ratios of P to metal were prepared and characterized using temperature-programmed reduction (TPR), X-ray diffraction (XRD), CO temperature-programmed desorption (CO-TPD), and chemisorptions techniques.

1 Experimental

1.1 Preparation of catalysts

The catalysts with different molar ratios of P to metal were prepared by a TPR method from supported phosphate precursors prepared by the incipient impregnation of the silica support. The silica support was calcined at 773 K for 3 h prior to use. To avoid the formation of an insoluble precipitate of the metal phosphate on mixing the aqueous solutions of metal nitrate and ammonium phosphate, a two-step impregnation was used to prepare the supported metal phosphate precursors. First, the silica support was impregnated with an aqueous solution of $(NH_4)_2HPO_4$. After drying at 393 K for 8 h, the support containing phosphorus was impregnated with the solution of metal nitrate. The impregnated supports were then dried at 393 K for 8 h and calcined at 773 K for 4 h. Second, the precursors were reduced to phosphides by heating from room temperature to 623 K at a ramping rate of 5 K/min and from 623 to 973 K at a ramping rate of 1 K/min. The samples were held at 973 K for 2 h in flowing H_2 with a flow rate of 350 ml/min per gram of precursor. The catalysts were cooled to room temperature in a H_2 flow and then passivated in a 1% O_2/Ar flow with a flow rate of 100 ml/min for 4 h. The catalysts with different molar ratios of P to metal were denoted as MP_x/SiO_2 (x = P/M molar ratio). The metal mass loading of all catalysts was 10% while the P loading varied.

1.2 Characterization of the catalysts

TPR experiments were performed on a Micromeritics Autochem 2910 apparatus. The metal phosphate precursor (80 mg) was calcined at 773 K for 4 h and then placed in a quartz reactor and reduced by a 10% H_2/Ar gas mixture at a flow rate of 50 ml/min. The temperature increased at 10 K/min to the final temperature and hydrogen consumption was recorded by a thermal conductivity detector (TCD). A mass spectrometer (QMS, Balzers OmniStar 300) was used to monitor desorbed species. MS signals at m/z = 2 (H_2), 18 (H_2O), and 34 (PH_3) were continuously recorded.

The CO uptake was measured using the same apparatus as used for H_2-TPR. The sample (100 mg) was loaded into the reactor and reduced in a H_2 flow with a flow rate of 60 ml/min at 773 K for 2 h. Then, the sample was flushed at 773 K with He at a flow rate of 80 ml/min for 2 h. Subsequently, the sample was cooled to 323 K. The gas (5% CO-He) was injected into a He carrier gas with a flow rate of 50 ml/min. CO uptake was measured using a TCD. CO pulses were repeatedly injected until the areas of consecutive effluent pulses were constant. The total CO uptake was then calculated. After CO adsorption, the sample was swept with a He flow (20 ml/min) until the TCD signal was stable. CO-TPD was performed in the He flow (20 ml/min) at a heating rate of 10 K/min with a quadrupole mass spectrometer (QMS, Balzers OmniStar 300) as detector to monitor the desorbed species. MS signals at m/z = 2 (H_2), 16 (CH_4), 18 (H_2O), 28 (CO), 44 (CO_2), and 12 (C) were continuously recorded.

The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area. Pore size distributions were determined from the desorption branch of the isotherms using the Barrett-Joyner-Halenda (BJH) method. Powder X-ray diffraction (XRD) measurements were recorded with a PANalytical X'Pert-Pro powder X-ray diffractometer using Cu K_α radiation (λ = 0.15418 nm), operated at 40 kV and 150 mA. Both the fresh and spent catalysts used in the XRD measurements were first passivated.

1.3 Activity studies

The catalyst was pre-treated in the fixed bed reactor as described in the TPR section. After cooling to 553 K in H_2 flow, the gas was switched to syngas (H_2:CO = 2) and the reaction was carried out at 553 K, 5.0 MPa, and GHSV = 5000 h^{-1}. Supported pure metal catalysts of iron and nickel were also tested for comparison. The volume of catalyst loaded was 1 ml. The reaction system consisted of a small fixed bed tubular reactor made of 316 L stainless steel with 300 mm length and 9.0 mm inner diameter with an external heating system. The catalyst particles (20–40 mesh) were placed on a packed bed of quartz sand inside the reactor and the space above the catalyst was also filled with quartz sand that acted as a pre-heater for the syngas. The effluent was passed through a condenser filled with cold and de-ionized water (283 K) to collect the liquid products. The outlet gases CO, H_2, CH_4, CO_2, and other C_1–C_5 hydrocarbons were analyzed online by an Agilent 3000A Micro GC with four packed columns (molecule sieve, PLOT Q, Al_2O_3, and OV-1) and TCD detectors. The liquid organic products and the aqueous products were analyzed offline on a Varian 3800 GC with an HP-FFAP capillary column and a FID detector after they were carefully separated. CO conversion and product selectivity were calculated by the equations of conversion = $(\sum(n_i \times M_i)/M_{CO}) \times 100\%$ and selectivity = $(n_i \times M_i/\sum(n_i \times M_i)) \times 100\%$, where n_i is the number of carbon atoms in product i, M_i is the total mole number of product i, and M_{CO} is the total mole number of carbon monoxide in the feed.