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Short communication

Effect of plating conditions for electroless Ni deposition on catalytic properties of K_2MoO_4/Ni-SiO_2 catalyst

Yingjuan Hao[a,*], Yiquan Yang[b], Weiping Fang[b]

[a] College of Sciences, Hebei University of Science and Technology, Shijiazhuang 050018, PR China
[b] Department of Chemistry, College of Chemistry and Chemical Engineering, and National Engineering Laboratory for Green Chemical Productions of Alcohols, Ethers and Esters, Xiamen University, Xiamen 361005, PR China

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ABSTRACT

A series of K_2MoO_4/Ni-SiO_2 catalysts with Ni-SiO_2 as support for methanethiol synthesis from H_2S-rich synthesis gas were prepared and characterized by BET, ESR, XPS and HRTEM techniques. The optimum electroless plating condition was explored for the preparation of Ni-SiO_2 support. Physicochemical characterization results show that the Ni-SiO_2 support prepared under the alkaline condition and relatively high plating temperature makes molybdenum species dispersing more uniformly, leading to an appropriate K/Mo atomic ratio on its surface owing to the advantage of surface morphology. The sulfurized catalyst was found to have a suitable pore diameter distribution and a suitable molar ratio of S_2^{2-}/S^{2-} (close to 1) on the surface of the catalyst, which were confirmed to be in favor of the improvement of the catalytic performance of the catalyst.

1. Introduction

As an important chemical intermediate applicable to the production of a variety of agricultural chemicals, in particular, methionine, a feed additive for poultry [1], methanethiol is usually synthesized by the reaction of methanol and hydrogen sulfide [2–5]. Because methanol can be synthesized from carbon oxides and hydrogen, the methanethoil synthesis from carbon oxides, hydrogen and hydrogen sulfide over supported catalysts has been widely investigated since 1970s [1,6–14]. Olin et al. have brought forward that methanethiol can be synthesized from H_2S-containing synthesis gas in the presence of a saturated amine such as cycloaliphatic amine or saturated heterocyclic amine over the hydrodesulfurization catalyst [6]. Buchholz et al. [1] have reported that the conversion of carbon monoxide over the nickel-based catalyst promoted by cesium could achieve 53% under the reaction conditions of 4.82 MPa, 572 K, $CO/H_2S/H_2 = 1/6/2$ (molar ratio) and the space velocity of CO being at 120 h^{-1}. Subsequently, methanethiol could be synthesized from the mixture gas of carbon oxides and hydrogen sulfide using the sulfided VB metal catalysts supported on TiO_2 or Al_2O_3, respectively [7,9]. However, in these studies, the yield of methanethiol was low though it was synthesized under a stringent reaction condition, such as high reaction pressure, low space velocity or high concentration of H_2S in feed gas. In our previous studies on the synthesis of mixing alcohols from synthesis gas over the Mo–S–K/SiO_2 catalyst, it was found that when the concentration of H_2S in synthesis gas was over 1.6%, mixed low-carbon alcohols disappeared and the methanethiol selectivity exceeded 90% [11]. Afterwards, the K_2MoO_4/SiO_2 catalysts for the methanethiol synthesis from H_2S-rich synthesis gas were developed and the catalytic performance of the catalysts was found to be significantly enhanced by Co- or Ni-doping [12–14].

It is well known that the catalytic properties of the catalysts depend not only on their composition, but also on the preparation and pretreatment conditions of the catalysts [15]. Chemical deposits, as a class of novel electrochemical materials, are mostly used as decorative and functional coatings in electronics, machinery, automobile, and materials [16,17]. For example, electroless plating (EP) nickel (or copper) has been attempted in decoration on carbon nanotubes [17] and graphite [18]. Nowadays, EP technique has been widely applied to catalysis fields. Fukuhara et al. have investigated the CO shift performance over a copper-based catalyst prepared by EP method [19]. Song et al. [20] have studied that the nickel phosphide catalysts synthesized by the silver-induced EP method show high catalytic activity for the hydrodesulfurization of dibenzothiophene. They have brought to light that the active phase can be well dispersed on the surface of the Ni_2P/SiO_2–Al_2O_3 support. Li et al. have reported that mesoporous Ni nanowires can be synthesized by Ni electrolessly plating on the functionalized SBA-15 support, and exhibit higher activity than Raney Ni in

* Corresponding author. Tel.: +86 311 81669971; fax: +86 311 81668512.
E-mail address: yingjuanhao@126.com (Y. Hao).

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Table 1
Electroless plating conditions.

Chemical composition	Ni–P system	Ni–B system
Ni precursor	$NiSO_4{\cdot}6H_2O$ (AR), $NiCl_2{\cdot}6H_2O$ (AR), $Ni(CH_3COO)_2{\cdot}4H_2O$ (AR)	$Ni(CH_3COO)_2{\cdot}4H_2O$ (AR)
Reducing agent	$NaH_2PO_2{\cdot}H_2O$ (CP)	$NaBH_4$ (CP)
Complexing agent	$Na_3C_3H_6O_7$ (AR)	$C_2H_8N_2$ (AR)
Stabilizing agent	$(NH4)_2SO_4$ (AR)	HBO_3 (CP)
pH Value	5.4–10.2 ($NH_3{\cdot}H_2O$)	14 (NaOH)
Plating temperature	318–363 K	363 K

AR, analytical reagent; CP, chemical pure reagent.

liquid-phase p-chloronitrobenzene hydrogenation for their high surface area and highly ordered arrangements [21]. According to our previous reports [14,22], a small amount of nickel deposited on SiO_2 support by EP was verified to have a significant promoting effect on the catalytic performance of K_2MoO_4/SiO_2 catalysts for methanethiol synthesis from H_2S-rich synthesis gas.

In this work, a series of K_2MoO_4/Ni-SiO_2 catalysts with Ni-SiO_2 support for methanethiol synthesis from H_2S-rich synthesis gas were prepared and investigated. The optimum EP condition for preparing Ni-SiO_2 supports was investigated. Brunauer–Emmett–Teller (BET) surface area, electron spin spectroscopy (ESR), X-Ray photoelectron spectroscopy (XPS) and high resolution transmission electron microscopy (HRTEM) techniques were used to characterize the K–Mo-based catalysts and the supports Ni-SiO_2. The surface morphologies of both the support and the catalysts prepared were connected with the catalytic performances of the catalysts.

2. Experimental

2.1. Materials

SiO_2 with specific surface area of 270 m^2/g was purchased from Qingdao Marine Chemical Factory. Other chemical reagents used in this experiment (seen in Table 1) were purchased from China National Pharmaceutical Group Corp. All chemical reagents were used as received without further purification.

2.2. Preparation of Ni-SiO_2 [14]

A calculated amount of commercial SiO_2 was washed with distilled water, and then dried, followed by immersing the washed SiO_2 in a mixing solution of H_2SO_4 (4.5 mol/L) plus H_2O_2 (0.88 mol/L) (1:1 by volume) for 5 min under agitating. The cleaned SiO_2 obtained was then immersed in a $PdCl_2$/HCl (0.1 g/L) solution for 10 min for activation, followed by washing with distilled water again. Finally, the activated SiO_2 was put into a plating solution to be electrolessly plated. After 30 min plating, the Ni-modified support obtained was dried at 383 K for 10 h and denoted as Ni-SiO_2. A series of Ni-SiO_2 supports were prepared under different plating conditions, including changing Ni precursor, reducing agent types, plating temperatures and the pH values of the plating solution in turn. The EP conditions are listed in Table 1.

2.3. Preparation of KMo/Ni-SiO_2

The KMo/Ni-SiO_2 (12/100) catalyst contained 12% MoO_3 and 7.9% K_2O by weight was prepared by incipient wetness impregnation. A calculated amount of Ni-SiO_2 was soaked in a mixing aqueous solution of ammonium heptamolybdate, potassium hydroxide and citric acid. The pH value of the impregnation solution was adjusted to 9 using $NH_3{\cdot}H_2O$. After an overnight impregnating at room temperature, the resulted sample was dried at 383 K for 8 h to generate a catalyst, which was denoted as KMo/Ni-SiO_2. With the same chemical composition in the solution, supports A, B, C were prepared under the conditions of the pH value of 5.4 and the plating temperature of 360 K, the pH value of 9.0 and the plating temperature of 318 K, the pH value of 9.0 and the plating temperature of 363 K, respectively. Their corresponding catalysts were denoted as catalyst-A, catalyst-B and catalyst-C, respectively.

2.4. Activity testing

The catalyst was evaluated in a stainless steel tubular reactor filled with 0.5 mL of the dried catalyst under the reaction conditions of 0.2 MPa, 573 K, feed gas composition $CO:H_2:H_2S = 1:1:2$ (by volume) and GHSV = 2000 h^{-1}. Hydrocarbon, sulfur-containing products, CO and CO_2 were analyzed by on-line GC equipped with flame ionization detector (GDX-103 column, 1.5 m × ϕ8 mm), flame photometric detector (HP-Plot/Q capillary column, 30 m × 0.54 mm × 40 μm) and thermal conductivity detector (carbon molecular sieve column, 1.5 m × ϕ8 mm), respectively. The activity data were obtained when the steady state had reached.

2.5. Characterization techniques

BET characterizations of different supports and catalysts were performed on auto physical chemistry adsorption test apparatus Micromeritics Tristar 3000. Prior to the analysis, the supports and catalysts were out-gassed in vacuum. The pore diameter and pore size distribution were calculated from the adsorption and desorption isotherms by Barrett–Joyner–Halenda (BJH) method. ESR characterization was conducted on a Bruker EMX-10/12 EPR spectrometer at room temperature. α-diphenyl β-picrylhydrazyl was used for the calibration of *g* value. The sample tube was filled with 2.3 mg of the sulfide sample. XPS characterization was recorded on a PHI Quantum 2000X spectrometer operating with Al Ka radiation source. The binding energy in the narrow spectra was calibrated against the adventitious carbon C_1s (Eb = 284.7 eV) peak. The HRTEM images of the samples were obtained using a Phillips Analytical FEI Tecnai 30 electron microscope operating at 300 kV. The samples were ground to fine powder, which was mixed with ethanol to make a suspension. A drop of the suspension was placed on a copper grid, subsequently dried at room temperature for measurement.

3. Results and discussion

3.1. Performances of the catalysts as a function of the pH value of plating bath and the plating temperature

The catalytic performances of the catalysts for methanethiol synthesis from H_2S-rich synthesis gas as a function of the pH value of the plating bath and plating temperature, under which the Ni-SiO_2 supports were prepared, are presented in Fig. 1. Fig. 1(a) shows that the conversion of CO (X_{CO}) and selectivity to methanethiol (S_{CH3SH}) over the KMo/Ni-SiO_2 catalysts increased with increasing the pH value from 5.4 to 9.0 and then slightly decreased by switching the pH value from 9.0 to 10.2. When the pH value was adjusted to 9, both the X_{CO} and S_{CH3SH} reached their maxima of