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A new approach to synthesize supported ruthenium phosphides for hydrodesulfurization



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ABSTRACT

Supported noble metal ruthenium phosphides were synthesized by one-step H₂-thermal treatment method using triphenylphosphine (TPP) as phosphorus sources at low temperatures. Two phosphides RuP and Ru₂P can be prepared by this method via varying the molar ratio of metal salt and TPP. The asprepared phosphides were characterized by X-ray powder diffraction (XRD), low-temperature N₂ adsorption, CO chemisorption and transmission electronic microscopy (TEM). The supported ruthenium phosphides prepared by new method and conventional method together with contradistinctive metallic ruthenium were evaluated in hydrodesulfurization (HDS) of dibenzothiophene (DBT). The catalytic results showed that metal-rich Ru₂P was the better active phase for HDS than RuP and metal Ru. Besides this, ruthenium phosphide catalyst prepared by new method exhibited superior HDS activity to that prepared by conventional method.

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1. Introduction

Metal phosphides attract considerable attentions due to their unique chemical and physical properties. They can be used as catalytic, magnetic, electrode, and hard materials [1-6]. In particular, the VIII group phosphides (Ni₂P, Co₂P etc.) are widely studied for catalytic applications in hydrodesulfurization which is very important due to strict environmental legislations concerning the sulfur content in fuels [7]. Supported nickel phosphide catalysts have showed superior activity and stability to classical catalysts based on molybdenum sulfide [8–13]. Many methods are brought out for synthesizing the nickel phosphide. However, the synthesis and catalytic activity of noble metal phosphides are less reported than that of nickel phosphide [14–16]. Among the noble metal phosphides, ruthenium phosphide should be considered due to its low cost. Nowadays, several methods have been suggested to synthesize the supported ruthenium phosphide catalyst [17–21]. The conventional method to synthesize ruthenium phosphide is the reduction of ruthenium salt using phosphate as phosphor source, which is the also classic method to synthesize nickel

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phosphide and cobalt phosphide. However, this method has the disadvantage of requiring a high temperature, which leads to the aggregation of phosphides resulting in low activity of catalyst. So, it is necessary to synthesize ruthenium phosphide at a low temperature to get a highly active phase of catalyst. Recently, Guan et al. had prepared RuP and Ru₂P used ruthenium chloride and hypophosphite as precursors at the temperature of 673 K [22], but the obtained ruthenium phosphide needed post-treatment to remove salt impurity formed in the process of decomposition of hypophosphite.

We once prepared Ni₂P/SiO₂ catalyst using triphenylphosphine (TPP) as phosphorus source in a reducing atmosphere, and the catalyst exhibited high catalytic activity for high dispersion of active phase due to low synthesis temperature [23]. Since TPP is widely used as a ligand and forms complexes with noble metals [24,25], noble metal phosphides may be prepared through the above process. In this work, we tried to prepare SiO₂-supported ruthenium phosphide catalysts using ruthenium chloride and TPP as precursors in a flow of hydrogen, and both RuP/SiO₂ and Ru₂P/SiO₂ catalysts can be successfully synthesized. Unlike the method using hypophosphite as phosphorus source, this method does not need post-treatment. As-synthesized supported Ru₂P and RuP catalysts with 2.0 wt.% ruthenium loading exhibited higher catalytic activity in the HDS of DBT than supported RuP by conventional method as well as Ru catalyst with the same

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ruthenium loading. Besides this, metal-rich Ru_2P was proved to be a promising HDS active phase, and showed excellent HDS performance than RuP. This method offers another choice to synthesize high active noble metal phosphide catalysts at a low temperature.

2. Experimental section

2.1. Synthesis of supported ruthenium phosphides

2.1.1. Synthesis of RuP/SiO₂ and Ru₂P/SiO₂ by TPP method

All of the chemical reagents used are of analytical pure grade without further purification. SiO₂ supported ruthenium phosphides were prepared as followed. The silica support (BET surface area: 340 m²/g from Tianjin Chemical Institute) was dried at 393 K for 3 h and calcined at 773 K for 6 h before impregnation. The ruthenium-TPP solution was prepared by dissolving RuCl₃·3H₂O (2.556 g) with TPP (7.869 g) at the molar ratio of ruthenium to phosphorus of 1:3 in 100 ml ethanol and stirring at the temperature of 333K in a water bath for 2h (samples with different molar ratios of ruthenium to phosphorus were prepared by changing the amount of TPP). A certain amount of silica support was added to the solution and stirred for 6 h, followed by drying at 333 K overnight. The dry solid was subsequently treated in flowing hydrogen (60 ml/min) with increasing the temperature from room temperature to final temperature at a rate of 20 K/min and then kept at final temperature for 5 h. The synthetic temperature range was from 573 K to 823 K. The treated sample was cooled to RT in flowing H_2 and then passivated in a flow of $1 \text{ vol.} \% \text{ O}_2/\text{N}_2$. By controlling the final treated-temperature and adjusting the molar ratio of ruthenium to phosphorus, different type of ruthenium phosphides RuP and Ru₂P will be obtained.

2.1.2. Synthesis of RuP/SiO₂ using NH₄H₂PO₄ as phosphorus source by conventional method

For comparison, the ruthenium phosphide was also prepared by conventional method [8]. The solutions of ruthenium phosphate precursors were prepared by dissolving $RuCl_3 \cdot 3H_2O$ with $NH_4H_2PO_4$ (the molar ratio of Ru and P was 1:2) in distilled water, and the resulted solution was used to impregnate silica by the incipient wetness method. After the impregnation, the obtained sample was dried at 333 K overnight. Then the powder was reduced in H_2 flow of 60 ml/min with increasing the temperature from RT to 723 K at a rate of 4 K/min and from 723 to 873 K at a rate of 1 K/min. Finally, the temperature was kept at 873 K for 5 h. The resulted sample was cooled to RT in flowing H_2 , and then passivated in a flow of 1 vol.% O_2/N_2 .

2.1.3. Synthesis of supported metallic Ru

To prepare the supported Ru catalyst, $RuCl_3 \cdot 3H_2O$ was dissolved in distilled water to obtain incipient solution. Then the silica was added into the solution and stirred for 3 h. After the impregnation, the obtained sample was dried at 333 K overnight. The powder was reduced for 3 h at 673 K in a 30 ml/min H₂ flow.

2.2. Catalyst characterization

X-Ray diffraction (XRD) characterization was conducted using a Rigaku D/max-2500 powder X-ray diffractometer employing Cu Ka radiation (40 kV and 40 mA). Transmission electron microscopy (TEM) images were acquired using a TECNAI G2T20 high-resolution transmission electron microscope. The TEM samples were thoroughly ground and then suspended in ethanol using an ultrasonic bath. One drop of the suspension was placed on a carbon-coated copper grid that was placed on filter paper, and left in air to dry. Low temperature N_2 adsorption was employed to

measure the surface areas of samples using a Micromeritics ASAP 2010 instrument. The samples were degassed before analysis at 200 °C for 12 h under vacuum. Surface areas were computed based on the Brunauer–Emmett–Teller (BET) adsorption method. CO chemisorptions of the catalysts were performed using Micromeritics ChemSorb 2750 gas adsorption equipment. The sample was loaded into a quartz reactor and pretreated in a 10% H₂/Ar flow at 400 °C for 3 h. After cooling in He, pulses of 10% CO/He in a He carrier were injected at 25 °C.

2.3. HDS activity tests

The HDS reaction of dibenzothiophene (DBT 0.5 wt.% in decalin) was performed in a fixed-bed continuous-flow reactor. Prior to evaluation, 1.0 g (about 2 ml) catalyst (20–40 mesh) was reduced at 0.3 MPa pressure with H₂ (flow rate of 60 ml min⁻¹) at 673 K for 3 h. Catalytic activities were measured under a hydrogen pressure of 3.0 MPa. The weight hourly space velocity (WHSV) was 10 h⁻¹. The liquid samples were collected at 1 h interval after a stabilization period of 3 h and were analyzed by gas chromatography with an OV-101Capillary Column. The HDS properties of RuP and Ru₂P catalysts prepared by the TPP method, the RuP prepared by the conventional method of phosphate as phosphor source and metallic Ru with the same 2.0 wt.% metal loading were evaluated under the above reaction conditions.

3. Results and discussion

3.1. Synthesis of supported ruthenium phosphide by TPP method

3.1.1. The influence of temperature on ruthenium phosphide by TPP method

In order to illuminate the formation of ruthenium phosphide process clearly, higher loading ruthenium phosphide was prepared. Fig. 1 shows the XRD patterns of the SiO₂-supported ruthenium-TPP precursor with 23 wt.% Ru loading and Ru/P molar ratio of 1:3 treated at different temperatures in the hydrogen atmosphere for 5 h. After sample being treated at 573 K and 623 K, only a broad peak at 22.0° which is attributed to the amorphous phase of SiO₂ support is observed. When the temperature is



Fig. 1. The XRD patterns of the RuP/SiO₂ catalysts prepared by TPP methods at different temperature (a) 573 K, (b) 623 K, (c) 673 K, (d) 723 K and (e) 823 K.

increased to 673 K, three weak peaks appear at 2θ = 31.8, 44.2 and 46.0°, which are attributed to the RuP phase, indicating the formation of RuP. As the reaction temperature increases to 823 K, the intensity of these peaks increases which suggests the growing up of RuP crystalline size. Seven diffraction peaks locating at about 2θ = 29.1, 31.8, 32.5, 35.8, 44.2, 46.0, and 53.6° are observed at the treatment temperature of 823 K (Fig. 1e), which could be identified to the (002), (001), (110), (111), (112), (211) and (031) crystallographic planes of RuP, respectively. The XRD patterns for RuP are similar to that reported previously [26], while the synthetic temperature (673 K) was much lower in the current method.

3.2. The influence of molar ratio of ruthenium and phosphorus on ruthenium phosphide

Besides this, the Ru₂P can also be obtained by changing molar ratio of Ru/TPP from 1:3 to 1.5:1. The XRD patterns of samples with 23 wt.% Ru loading prepared at 723 K and different Ru/TPP molar ratios are shown in Fig. 2. When the molar ratio of Ru and P was below 1:1, the main peaks at 31.8°, 44.2° and 46.0° corresponding to RuP phase were observed. As the Ru/P ratio was changed to 2:1, the peaks at 38.1° and 47.1° attributed to Ru₂P phase appeared. However, the peak at 44.0° belonging to metal Ru existed. And when the molar ratio was 1.5:1, the peaks at 30.5°, 38.1°, 40.6°, 47.1° and 53.5° all corresponding to Ru₂P phase (JCPDS 65-2382) can be



Fig. 2. The XRD patterns of the ruthenium phosphides prepared by TPP methods from Ru/P molar ratio (a) 1:3, (b) 1:2, (c) 1:1, (d) 1.5:1, and (e) 2:1

presented. The average Ru_2P crystallite size of 13 nm for the Ru_2P/SiO_2 and RuP crystallite size of 10 nm for the RuP/SiO₂ were calculated by the Scherrer equation. It can also be seen from above results that the synthesis of RuP and Ru_2P can be controlled by simply adjusting Ru/P molar ratio. The phosphor content in the precursor before heat treatment was higher than that in the final product of RuP or Ru_2P , which can be explained by that the part of TPP will be evaporated at the temperature of 723 K higher than its boiling temperature (650 K).

For comparison, the SiO_2 supported RuP with 23 wt.% Ru loading was also prepared by conventional phosphate as phosphor source. The XRD patterns of samples reduced at different temperatures are shown in Fig. S1. It can be seen that the RuP can be synthesized by conventional method at 873 K for 6 h. This result was similar to the others reported [8].

For HDS reaction of DBT, the SiO₂ supported RuP with 2.0 wt.% ruthenium content was synthesized. The XRD patterns of phosphide catalysts prepared by TPP and conventional methods are shown in Fig. S2. Only the peak at 22.9° attributed to SiO₂ was observed due to the low loading or high dispersion of metal which is beyond the detection limit of XRD.

3.3. TEM images of samples

TEM investigation of 2.0 wt.% RuP/SiO₂ catalyst prepared by TPP method reveals that the particle size of RuP was about 2-5 nm and sphere-shaped RuP particles uniformly dispersed on the surface of SiO₂ (Fig. 3b). Meanwhile, the morphology of RuP/SiO₂ with same loading prepared by the conventional phosphate as phosphor source was also shown in Fig. 3a. It can be seen that the RuP obviously existed in the form of aggregation with a larger particle size of 5–15 nm. It suggests the effectiveness of the TPP method in increasing the dispersion of the active species. As shown in Fig. 3c, the particle size of Ru₂P prepared by TPP method was about 2-5 nm and sphere-shaped Ru₂P particles dispersed on the surface of SiO₂. Besides this, Ru_2P with the bigger particle size (~ 10 nm) coexisted. The particle size of RuP prepared by phosphate as phosphor source was bigger than that prepared by TPP method because that the higher temperature causes the sintering of the phosphide. It is also seen from the TEM investigation that the particle size of RuP and Ru₂P prepared by TPP method was similar.

3.4. Activity measurements

The activities of RuP/SiO₂ and Ru₂P/SiO₂ catalysts prepared by TPP, RuP/SiO₂ prepared by phosphate as phosphor source, together with Ru/SiO₂ catalyst were tested in the hydrodesulfurization (HDS) of DBT. The HDS activities of the four catalysts at different reaction temperatures were shown in Table 1. The conversions of DBT on these catalysts increased with increasing reaction temperature. And the supported noble metal phosphides of RuP and Ru₂P prepared by TPP method exhibited higher activity than Ru/SiO₂ catalyst. The HDS reaction network of DBT was shown in Scheme S1. The HDS products were analyzed and summarized in Table S1, and it can be seen that the selectivity of cyclohexylbenzene (hydrogenation product) over phosphides was higher than that over ruthenium catalyst which indicated the hydrogenation activity of ruthenium phosphides was higher than that of ruthenium. The result was consistent with that reported by Bowker et al. [21]. It is known that hydrogenation of DBT favored the HDS process. Compared with the RuP/SiO₂ catalyst prepared by phosphate as phosphor source, the RuP/SiO₂ prepared by TPP method presented much higher HDS activity in the test. In particular, the 37.6% initial activity of RuP/SiO₂ prepared by the TPP method is higher than that of RuP/SiO₂ prepared by conventional



Fig. 3. The TEM micrographs of 2.0 wt.% RuP supported on silica prepared (a) by the conventional method using NH₄H₂PO₄ as phosphor source, (b) by TPP method as well as (c) Ru₂P supported on silica prepared by TPP method.

Table 1
Conversion of DBT on SiO ₂ -supported ruthenium phosphide catalysts prepared by different methods

Catalysts	Ru content ^c	BET surface area (m²/g)	CO uptake (µmol/g)	Conversion of DBT (%) at different reaction temperatures			TOF (603 K)
	(wt.%)			583 K	603 K	623 K	$10^{-3} \mathrm{s}^{-1}$
RuP/SiO2 ^a	1.8	328	3.5	56.7	75.8	92.9	16.3
RuP/SiO2 ^b	1.8	301	3.2	34.5	42.9	55.3	10.1
Ru ₂ P/SiO ₂ ^a	1.7	310	3.6	89.4	97.4	100.0	20.5
Ru/SiO ₂	1.9	340	4.1	53.2	63.1	74.9	11.6

^a The catalyst prepared by TPP method.

^b The catalyst prepared by method of phosphate as phosphor source.

^c Analyzed by ICP-AES.

method and reached 92.9% at 623 K. The main reason for the difference of catalytic activity between the TPP method and the conventional method may be due to the higher preparation temperature of the latter. The particle size of active species was large because of the aggregation of phosphide on the carrier prepared by conventional method, hence affected the catalytic activity. The supported metal-rich phosphide Ru₂P prepared by TPP method exhibited the highest activity among all the tested catalysts, and its activity reached 89.4% at 583 K and ultimately reached 100% at 623 K. Although The Ru/SiO₂ catalyst had the highest amount of CO chemisorption, its turnover of frequency (TOF) was lower than Ru₂P and RuP prepared by TPP method. Among these catalysts, the Ru₂P was the most active phase due to its highest TOF value. The reaction time of HDS on Ru₂P/SiO₂ catalyst with 2.0 wt.% Ru loading was also prolonged to 42 h and the result was shown in Fig. 4. It can be seen that HDS conversion slightly decreased after 7 h and maintained at 80 %. The decline of activity may be due to the absorption of organic products.



Fig. 4. DBT HDS activity of the Ru_2P/SiO_2 catalyst prepared by the TPP method vs time at 593 K.

4. Conclusions

Our results demonstrate that SiO₂ supported RuP and Ru₂P catalysts can be easily prepared by hydrogen-thermal treatment of a complexe precursor. Compared with SiO₂ supported metallic Ru catalyst and RuP/SiO₂ catalyst prepared by phosphate as phosphor source, the as-prepared RuP/SiO₂ and Ru₂P/SiO₂ by TPP method shows excellent catalytic activity. Futher studies are focused on exploring this method for the synthesis of other noble metal phosphides (such as PtP₂, Rh₂P, Pd₅P₂, etc.).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j. materresbull.2015.10.021.

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