



Hydrodechlorination of trichloroethylene over MoP/ γ -Al₂O₃ catalyst with high surface area



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ABSTRACT

Alumina-supported molybdenum phosphide (MoP/ γ -Al₂O₃) with high surface area was successfully synthesized by combining sol-gel and temperature-programmed reduction (SG-TPR) method and was firstly used to study the hydrodechlorination (HDC) of trichloroethylene (TCE). The properties of the catalysts were evaluated by several different characterization techniques, such as Brunauer-Emmett-Teller (BET) surface area, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and transmission electron microscopy (TEM). The results prove that a well-dispersed and high BET surface area catalyst can be obtained by SG-TPR method, which shows higher catalytic activity than those prepared by impregnation and mechanical mixing method for the HDC of TCE.

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1. Introduction

Trichloroethylene (TCE) is one of the halogenated organic compounds that can be easily found in the emission from chemical processing, ground water, and soils due to its extensive uses in industries [1–3]. It has been pointed out that TCE is a volatile organic compound with potent carcinogenicity and resistant to natural degradation leading to long-term environmental and health risks [4]. Also, the emission of TCE into the environment is now strictly regulated [5]. As a result, there is substantial interest in the development of efficient, economic methods for remediating ground water, and soils contaminated with TCE.

It has been recognized that the traditional remediation technologies, such as incineration and solidification, are not entirely satisfactory, because they require high capital, operation cost, and extremely long-time [5,6]. In addition, they can lead to the formation of carcinogenic byproducts [6]. Compared with the conventional methods, the catalytic hydrodechlorination (HDC) for treating TCE is a viable and nondestructive low-energy alternative, which transforms the chlorinated waste streams into nontoxic, easily degradable, or useful raw materials [7]. Therefore, as a safe method, the catalytic HDC of TCE has attracted more and more attention.

Over the past years, studies on HDC of TCE compounds have been carried out mainly using supported metal, notably Pt, Pd [4,8–10]. Although they exhibit good catalytic activities, they are expensive and easily deactivated due to HCl poisoning, metal sintering or carbon deposition, which limits their application in industry [11]. Recently, transition metal phosphides have been reported as a new class of high activity hydroprocessing catalysts that have substantial promise as next-generation catalysts [12]. The group of Nozaki first reported the catalytic activity of phosphides in 1980 [13]. In 1998, Oyama group found that MoP could be easily synthesized by temperature-programmed reduction (TPR) of a metal phosphate precursor [14], transition metal phosphides began to be widely used in catalytic reaction. Especially, they exhibited excellent reactivity in hydrodenitrogenation (HDN) [15] and hydrodesulfurization (HDS) [16]. Considering the similarity of HDN, HDS, and HDC, we synthesized the MoP catalysts used for HDC of TCE. However, the low BET surface area limits the performance of the catalysts [16]. In this paper, well-dispersed MoP/ γ -Al₂O₃ with high surface area was prepared by SG-TPR method for the first time, and the application of the catalyst in the HDC decomposition of TCE was compared with those prepared by impregnation and mechanical mixing methods.

2. Experimental

2.1. Preparations

In this paper, *s*-MoP/ γ -Al₂O₃ represents the catalyst prepared by sol-gel method. *i*-MoP/ γ -Al₂O₃ represents the catalyst prepared

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by impregnation method. *m*-MoP/ γ -Al₂O₃ represents the catalyst prepared by mechanical mixture method. The detailed preparation methods are as follows:

For *s*-MoP/ γ -Al₂O₃ catalyst, firstly, a mixture of 1.25 g (NH₄)₆Mo₇O₂₄·4H₂O (AR, Hefei Kehua Fine Chemical Research Institute) and 0.94 g (NH₄)₂HPO₄ (AR, Xilong Chemical Co., LTD., China) was dissolved in 15 mL deionized water and stirred for 3 h under 80 °C. Secondly, a solution was made by mixing AlCl₃·6H₂O (24.43 g, 0.1 mol) (AR, Sinopharm Chemical Reagent limited corporation), 24 mL water with 56 mL ethanol, and heated to 80 °C, while stirred for 0.5 h. After that, the mixture prepared in the first step was poured into the solution. Then, propylene oxide, as gelation inducing agent, was added to the solution, cooled in ice water bath. Gel formation typically occurred within 40 min at the temperature of 30 °C. The gel parts were then soaked in a bath of absolute ethanol for 24 h to exchange the water and reaction byproducts from the pores of the material. After the dryness at 120 °C, the sample was calcined in air at 500 °C for 5 h, pressed, and sieved to particles between 420 and 840 μ m in diameter for use.

The particles obtained above were reduced by heating from room temperature to 300 °C at a rate of 10 °C/min, then from 300 to 650 °C at a rate of 1 °C/min, and kept at 650 °C for 2 h in flowing H₂ (50 mL/min), followed by cooling to room temperature.

Bulk MoP, *i*-MoP/ γ -Al₂O₃, *m*-MoP/ γ -Al₂O₃, and Mo/ γ -Al₂O₃ catalysts were prepared as the procedure reported references [14] and [17].

Bulk MoP catalyst was prepared as the procedure: a mixture of 4.0 g ammonium heptamolybdate (NH₄)₆Mo₇O₂₄·4H₂O and 3.0 g diammonium hydrogen phosphate (NH₄)₂HPO₄ was dissolved in 30 mL deionized water. A white solid obtained following evaporation of the water. Then the sample was calcined in air at 773 K for 5 h to give a dark blue solid, subsequently pressed, broken, and sieved to particles between 420 and 840 μ m in diameter for use (mesh size 20–40). And then the sample was reduced by H₂ as the same as the preparation method of *s*-MoP/ γ -Al₂O₃ catalyst. *i*-MoP/ γ -Al₂O₃ catalyst was prepared as the procedure: a commercial aluminum oxide was used as the support. Impregnating solutions were prepared by dissolving 2.45 g (NH₄)₆Mo₇O₂₄·4H₂O and 1.83 g (NH₄)₂HPO₄ in approximately 60 mL water. Then 10 g Aluminum oxide was added to it. The mixture was stirred 12 h at the room temperature. After evaporation of the water at 80 °C, the following operation was the same as the preparation method of unsupported MoP. Mo/ γ -Al₂O₃ catalyst was prepared as the same method as *i*-MoP/ γ -Al₂O₃ catalysts except for the absence of P.

MoP loadings for all the MoP/ γ -Al₂O₃ catalysts in this paper equal to 15 wt%.

2.2. Characterizations

BET surface areas were determined from the nitrogen adsorption-desorption curves by the conventional multipoint technique with a Belsorp Mini 2. XRD patterns of the samples were acquired on a Bruker D8 Discover X-ray diffractometer using Cu K α radiation and a nickel filter ($\lambda = 1.5406 \text{ \AA}$) at a respective voltage

of 40 kV and current of 40 mA. TEM was carried out on a FEI-G20-2010 electron microscope operated at an acceleration voltage of 200 kV. XPS measurements were carried out using a Thermo Scientific K-Alpha instrument. Binding energies were corrected for sample charging using the C (1s) peak at 284.6 eV for adventitious carbon as a reference.

2.3. Catalysts activity measurement

Trichloroethylene HDC reactions were carried out using a continuous fixed-bed quartz reactor (id. = 10 mm) at 400–600 °C and atmospheric pressure. A total of 8 mL catalyst was put in the middle of the quartz reactor. The hydrogen flow rate was 100 mL/min. Using a bubbler for TCE supply, the amount of evaporated TCE corresponds to the weight loss of the bubbler. The flow ratio of H₂ to TCE was adjusted approximately 14:1. The produced HCl was trapped in a water bubbler and the amount of formed HCl can be determined very accurately by NaOH titration with a pH-indicator (e.g. phenolphthalein). So the decomposition rate of C–Cl bonds, which reflects the catalyst activity, can be calculated as the following formula:

$$RC - Cl \text{ bonds decomposition} = \frac{n(HCl)}{3n(C_2HCl_3)} \times 100\%$$

3. Results and discussion

The BET surface area, pore volume, and average pore diameter for the *s*-MoP/ γ -Al₂O₃, *i*-MoP/ γ -Al₂O₃, *m*-MoP/ γ -Al₂O₃, bulk MoP catalysts, and γ -Al₂O₃ support are listed in Table 1. The low BET surface area of the bulk MoP (<10 m²/g) limits the application of MoP as catalyst. Cheng et al. [18,19] synthesized bulk MoP and 8 wt% MoP/Al₂O₃ with high surface area by combining citric acid and temperature-programmed reduction (CA-TPR) method. However, in this communication, we successfully improved the MoP/ γ -Al₂O₃ catalyst surface area to 417.8 m²/g by SG-TPR method for the first time. As presented in Table 1, *s*-MoP/ γ -Al₂O₃ catalyst has a much higher BET surface area than *i*-MoP/ γ -Al₂O₃ (104.6 m²/g), *m*-MoP/ γ -Al₂O₃ (111.2 m²/g) and bulk MoP (7.2 m²/g).

Fig. 1 shows the XRD patterns for *s*-MoP/ γ -Al₂O₃, *i*-MoP/ γ -Al₂O₃, *m*-MoP/ γ -Al₂O₃ catalysts as well as for the γ -Al₂O₃ support and the bulk MoP. The XRD pattern of bulk MoP shows peaks at 27.91°, 32.08°, 43.07°, 57.14°, 64.75°, 67.49°, and 74.19°, which can be attributed to the (001), (100), (101), (110), (111), (102), and (201) crystal planes of the MoP phase [20]. The XRD patterns for the *m*-MoP/ γ -Al₂O₃ catalyst shows the same peaks as those observed for bulk MoP, confirming that the MoP crystallites are present on the γ -Al₂O₃ support. In addition, the *i*-MoP/ γ -Al₂O₃ catalyst exhibits one weak peak at 74.19° for (201) crystal planes of the MoP phase except the characteristic peaks of γ -Al₂O₃ support. Zaman [21] once discovered that it was difficult to identify a MoP phase on silica supported catalysts prepared by impregnation method at loadings below 15 wt% and the MoP/SiO₂ catalyst only showed weak characteristic peaks of MoP at 15 wt% loading. Based on this research

Table 1
Physicochemical properties of the studied catalysts.

Sample	BET (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)	Ref
MoP	7.2	0.05	26.6	
γ -Al ₂ O ₃	133.3	1.10	33.1	
<i>m</i> -MoP/ γ -Al ₂ O ₃	111.2	0.67	24.2	
<i>i</i> -MoP/ γ -Al ₂ O ₃	104.6	0.41	15.6	
<i>s</i> -MoP/ γ -Al ₂ O ₃	417.8	1.34	12.8	
MoP	8.2	–	–	[18]
MoP(CA-TPR)	122	–	–	[18]
8wt%MoP/Al ₂ O ₃ (CA-TPR)	161.9	–	–	[19]

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