



Wells–Dawson type $\text{Cs}_{5.5}\text{H}_{0.5}\text{P}_2\text{W}_{18}\text{O}_{62}$ based $\text{Co}/\text{Al}_2\text{O}_3$ as bifunctional catalysts for direct production of clean-gasoline fuel through Fischer–Tropsch synthesis



Chunling Wang^a, Xianni Bu^b, Jingwei Ma^c, Cheng Liu^a, Kuochih Chou^a, Xunli Wang^d, Qian Li^{a,e,*}

^a State Key Laboratory of Advanced Special Steel & Shanghai Key Laboratory of Advanced Ferrometallurgy & School of Materials Science and Engineering, Shanghai University, Shanghai 200072, PR China

^b CAS Key Laboratory of Low-Carbon Conversion Science and Engineering, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201210, PR China

^c College of Material Science and Engineering, Donghua University, Shanghai 201600, PR China

^d Department of Physics & Materials Science, City University of Hong Kong, 83 Tat Chee Avenue, Kowloon, Hong Kong, China

^e Institute of Genomic Material, Shanghai University, Shanghai 200444, PR China

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ABSTRACT

Polyoxometalates (POMs) possess unique strong Brønsted acidity. However, little attentions were paid to the effect of POMs with respect to the hydrocracking. Herein we show that Wells–Dawson type POMs $\text{Cs}_{5.5}\text{H}_{0.5}\text{P}_2\text{W}_{18}\text{O}_{62}$ (CsDP) combined with conventional Fischer–Tropsch catalyst $\text{Co}/\text{Al}_2\text{O}_3$ forming a highly efficient bifunctional catalyst for the direct production of clean gasoline from syngas. The Brønsted acidity of the CsDP results in hydrocracking of the heavier hydrocarbons formed on $\text{Co}/\text{Al}_2\text{O}_3$. The selectivity for the gasoline product could reach 48.8%, which has increased by 129% than that of conventional FTS catalyst. Furthermore, the catalytic performance of Wells–Dawson type POMs $\text{Cs}_{5.5}\text{H}_{0.5}\text{P}_2\text{W}_{18}\text{O}_{62}$ and Keggin type POMs $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ based catalyst is compared. The former exhibits higher CO conversion and C_5 – C_{12} selectivity than those of the Keggin type of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$.

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1. Introduction

Fischer–Tropsch synthesis which converts non-petroleum carbon resources such as shale gas, coal, and biomass based syngas to clean fuels and valuable chemicals over iron, cobalt, ruthenium based catalysts regains global interest because of the urgent need of optimum using the natural resources and reducing atmosphere pollution [1]. In FTS, Co-based FTS catalyst has attracted ever growing attentions because they have relatively high hydrocarbon productivity, less expensive expenditure and commercial availability. Over conventional Co-based FTS catalysts, the normal aliphatic hydrocarbon distribution generally followed the unselective Anderson–Schulz–Flory (ASF) distribution, which indicated that the FTS hydrocarbon $\text{C}_n\text{H}_{2n+2}$ number range from 1 to over 100 including the products of fuel gas, gasoline distillate, diesel distil-

late, and solid waxes [2]. Improving catalytic selectivity of certain range of hydrocarbon product is one of the most attractive and difficult challenges. Many efforts have been made to tune the selectivity of FTS reaction by exploring various acid catalyst supports or catalysts to acquire synthetic gasoline from syngas directly. Studies of Tsubaki and co-workers showed that the acidic zeolite combined with FTS catalyst forming core–shell structure catalyst not only hydrocracked the FTS products but also isomerized the products [3–5]. Wang and co-workers found that mesoporous zeolite as catalyst support lead to high gasoline or diesel selectivity [6,7]. We have recently demonstrated that the Keggin type of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ based catalyst made a significant improvement of gasoline product through FTS process, which showed that the POMs played an important role in hydrocracking of heavier hydrocarbon products at their acid sites [8].

Polyoxometalates (POMs) are well defined metal-oxygen clusters with vary structures composed of highly oxidized early transition metals (W^{VI} , Mo^{VI} , V^{V} , Nb^{V} , Ta^{V}) [9]. As a typical class of solid-acid and oxidation catalyst materials, the acidities (Brønsted acid [10] and Lewis acid [11]) and redox properties of POMs could

* Corresponding author at: State Key Laboratory of Advanced Special Steel & Shanghai Key Laboratory of Advanced Ferrometallurgy & School of Materials Science and Engineering, Shanghai University, Shanghai 200072, PR China
E-mail address: shuliqian@shu.edu.cn (Q. Li).

be accurately controlled by tuning their constituent elements, type of structures, and number of charges rationally [12]. For catalysis, it has been found that POMs possess activities in many catalysis systems such as hydrogenation of alkenes [13], oxidation of light alkanes [14], aerobic oxidation of formaldehyde [15], and so on. To the best of our knowledge, very little research involving POMs have been reported directly related Fischer–Tropsch synthesis (FTS) reactions so far, although the acidity of POMs could efficiently hydrocrack the heavier FTS hydrocarbon products [16].

As we all know, the catalytic properties of Keggin type POMs have been well investigated because of their excellent super acidity, simple synthesis procedure and good thermal stability. Variations in the structure could modify the acidic properties of POMs and thereby affect their catalytic performance. According to the electrostatic theory, Wells–Dawson type $H_6P_2W_{18}O_{62}$ would be expected to have stronger Brønsted acidity than the Keggin type $H_3PW_{12}O_{40}$. In the present work, we synthesized Wells–Dawson type POMs $Cs_{5.5}H_{0.5}P_2W_{18}O_{62}$ (CsDP) catalyst, and further investigate the catalytic performance of CsDP based FTS catalyst Co/Al_2O_3 for the production of gasoline through FTS reaction. The proper acidity of Wells–Dawson type POMs $Cs_{5.5}H_{0.5}P_2W_{18}O_{62}$ over conventional FTS catalyst leads to a significant improvement of the C_5 – C_{12} selectivity during the FTS process. The catalytic performance of the Dawson type catalyst CsDP-Co and Keggin type POMs $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (CsKP-Co) is also compared in this paper.

2. Experimental

2.1. Catalyst preparation

All chemicals used for synthesis were of analytic reagent grade and used without further purification.

2.1.1. Synthesis of POMs catalyst

Wells–Dawson type tungstophosphoric acid $H_6P_2W_{18}O_{62}$ (HDP) were synthesized according to the modified method of literatures [17–19] and characterized by IR spectra. $Na_2WO_4 \cdot 2H_2O$ (15 g) was dissolved in hot water (35 ml), and then 12.5 ml of an aqueous solution of H_3PO_4 (85%) was added with vigorous stirring. The solution was heated to boiling and the resulting yellow solution was refluxed for twenty-four hours. Then the solution was cooled to 0 °C and the precipitate was separated by the filtration. The precipitate was dissolved in a small amount of water and re-crystallized at room temperature. It was extracted with diethyl ether. Yellow powder product was obtained by re-crystallization from water. Elemental analysis of the POMs, Calcd (%): P 1.39, W 74.66; Anal found (%): P 1.34, W 74.77. FT-IR data: (KBr pellet): $\nu = 1091.3(s), 963.1(s), 916.1(s), \text{ and } 788.3 \text{ cm}^{-1}(s)$.

Wells–Dawson type $Cs_{5.5}H_{0.5}P_2W_{18}O_{62} \cdot xH_2O$ (CsDP) was synthesized according to the modified procedure described in the literature method [20]. An appropriate amount of $CsNO_3$, $H_6P_2W_{18}O_{62}$ with molar ratios of 5.5:1 was ground with ball milling for two hours followed by washing with water for twenty times to remove the NO_3^- ions. Then drying the sample and the solid powder was calcined at 300 °C in flowing air for two hours. Elemental analysis for $Cs_{5.5}H_{0.5}P_2W_{18}O_{62} \cdot xH_2O$, Calcd (%): Cs 13.86, P 1.17, W 62.73; Anal found (%): Cs 13.85, P 1.16, W 62.71. FT-IR data: (KBr pellet): $\nu = 1091.6(s), 959.5(s), 915.5(s), \text{ and } 786.2 \text{ cm}^{-1}(s)$.

2.1.2. Synthesis of conventional FTS catalyst

The Al_2O_3 (SCCA-5/200 γ -alumina $S_{BET} = 118 \text{ m}^2 \text{ g}^{-1}$, pore diameter of 12.1 nm, and total pore volume of $0.41 \text{ cm}^3 \text{ g}^{-1}$) support was provided by SASOL company. Co/Al_2O_3 catalyst was obtained using incipient wetness impregnation of cobalt nitrate hexahydrate $Co(NO_3)_2 \cdot 6H_2O$ solutions in water. Then the catalyst precursor was

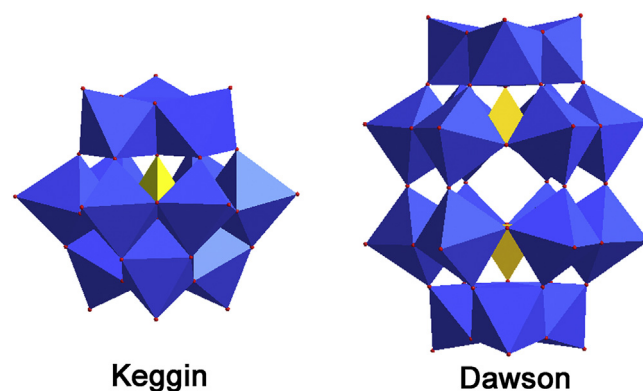


Fig. 1. The polyanion structures of Keggin type catalyst CsKP (left) and Wells–Dawson type catalyst CsDP (right) with the represented by polyhedra. Color codes: W blue, P yellow, O red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

evaporated for 3 h, dried at 100 °C for 10 h, and calcined in air at 350 °C for 3 h. The cobalt loadings in the samples were 10 wt%.

2.1.3. Synthesis of bifunctional FTS catalyst

The bifunctional catalyst CsDP-Co was prepared by mechanically mixing CsDP catalyst and FTS catalyst Co/Al_2O_3 . The content of CsDP in the CsDP-Co catalysts was 5 wt%, 10 wt%, 20 wt% and 50 wt%.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) measurements were performed with a Rigaku Ultima IV powder X-ray diffractometer using $Cu \text{ K}\alpha$ radiation with a wavelength of 1.54056 Å at 40 kV and 40 mA. Reduction mechanism and reduction extent of bifunctional catalyst were assessed by H_2 -TPR (Micromeritics Auto Chem II 2920). The catalytic products were analyzed by a GC (Shimadzu GC 2014) with dual detectors (TCD and FID) and different columns. Elemental chemical analysis was performed using inductively coupled plasma (ICP) measurements with a Varian 710-ES Inductively Coupled Plasma Atomic Emission Spectrometer to determine the bulk composition in each sample. The thermal decomposition of the catalyst precursors was studied by a thermogravimetric (TG) method using an SDTQ600 thermal analyzer. Measurements were performed in the temperature range of 40–600 °C with a linear temperature program ($10 \text{ }^\circ\text{C min}^{-1}$) in continuous flow of air (30 ml min^{-1}).

2.3. Catalytic tests

The Fischer–Tropsch synthesis was carried out in a stainless steel fixed bed reactor (i.d. 12 mm, length 600 mm). A quantity of 1.0 g bifunctional catalyst (60–80 mesh) diluted with silica sand (60–80 mesh) was loaded into the isothermal region of the reactor tube for all reaction tests. Prior to each test, the catalyst was reduced *in situ* under flowing H_2 (100 ml min^{-1}) at 400 °C for two hours at 2.0 MPa. After reduction, the temperature of the reactor was lowered to 200 °C under flow of H_2 , and a flow of a mixture of H_2 , CO and N_2 (N_2 as internal standard for chromatography, H_2 :CO volume ratio of 2:1) was established through the reactor. The temperature was raised up to 250 °C at a rate of $1 \text{ }^\circ\text{C min}^{-1}$. The temperature in the catalytic bed was controlled by two thermocouples connected to independent PID controllers. The finally reaction conditions were 2.0 MPa, GHSV = 6000 h^{-1} , and the reaction temperature was 250 °C.

The tail gas was analyzed by gas chromatography using a TDX-01 column ($2.0 \text{ m} \times 3.00 \text{ mm}$) with TCD and FID detectors. The liquid

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