

CHAPTER VI
MICROWAVE HEATING SYNTHESIS OF FLOWER-LIKE SAPO USING
ATRANE PRECURSORS AND ITS ACTIVITY FOR THE PREFERENTIAL
OXIDATION OF CO OVER Pt/FLOWER-LIKE SAPO

6.1 Abstract

A flower-like silicoaluminophosphate (SAPO), 6–8 μm in size and consisting of six petals, has been synthesized by microwave technique using alumatrane and silatrane precursors. Trialkanoamines molecules generated during hydrolysis of alumatrane and silatrane acted as structure-directing agents to synthesize the flower-like SAPO. The addition of tetrapropylammonium bromide (TPABr) resulted in a multilaminate flower with multilayered petals. The samples were characterized using X-ray diffraction (XRD), scanning electron microscope (SEM), and transmission electron microscope (TEM). The influences of pH, aging time, and heating time were investigated. Pt metal impregnated on flower-like SAPO prepared for studying its catalytic activity for the preferential oxidation (PROX) of CO reaction showed 100 % CO conversion.

6.2 Introduction

Aluminophosphates (AlPO_4) were firstly discovered by Wilson *et al.* [1]. The incorporation of Si atoms into aluminophosphate framework generates silicoaluminophosphates (SAPOs) that have been widely used for various applications [2, 3]. In recent years, many flower-shaped metal oxides have been prepared [4–8]. However, the formation of SAPO exhibiting a flower shape has not yet been reported.

Atrane precursors, alumatrane and silatrane, containing trialkanoamine ligands have been synthesized by Wongkasemjit and coworkers [9, 10]. This reaction produces highly pure and moisture-stable metal alkoxides. In the present work, the effects of chemical compositions and reaction conditions were investigated for synthesizing flower-like SAPO morphology using atrane precursors under microwave heating technique. This technique provides many advantages, such as fast crystallization [11],

increased phase purity [12], phase selectivity [13, 14] and narrow particle size distribution [15].

The PROX of CO is an effective method to remove CO remaining in hydrogen as a fuel in proton exchange membrane fuel cells (PEMFC), avoiding degradation for the platinum electrode [16–19]. To study the efficiency of flower-like SAPO as a support in this case, Pt was loaded onto SAPO to purify hydrogen reformed from hydrocarbon fuel on the preferential oxidation (PROX) of CO reaction in H₂-rich, using impregnation method.

6.3 Experimental

6.3.1 Catalyst Preparation

Flower-like SAPO was synthesized by mixing alumatrane, prepared according to reference 9, with 1 M phosphoric acid solution and stirring at room temperature. Silatrane synthesized using the procedure described in reference 10 was added to the synthesis mixture. In the system containing TPABr, 0.1 M TPABr was added. The mixture was stirred until homogenous before microwave heating at a reaction temperature range of 180 °-200 °C for 0.5–2 h. The product was washed and dried, followed by calcining at 600 °C for 7 h. The aging time, pH, and microwave heating time were varied. The impregnation method of the flower-like SAPO with an aqueous solution of (NH₃)₄PtCl₂ (Alfar Aesar, 1, 3, and 5% w/w of Pt) was prepared, followed by drying at 110 °C and calcining at 500 °C for 4 h before testing the catalyst.

6.3.2 Characterization

Morphology was studied on a SEM (JEOL 5200-2AE). XRD patterns were carried out using a Rigaku X-ray diffractometer with CuK α as a source and a scan speed of 5 °/min. The chemical composition was determined by XRF (Philips PW 2400). Hydrothermal crystallization by microwave heating was carried out using Milestone's Ethos Microwave Solvent Extraction Lab-station. TEM (JEOL JEM 2100) was conducted to determine particle size and distribution of Pt metal. BET surface area was

carried out by Autusorb-1 gas sorption system (Quantasorb JR) using nitrogen at 77 K. Samples were degassed at 250 °C under a reduced pressure prior to each measurement. Pt dispersion was determined from CO chemisorption measurement. Prior to pulse chemisorption, sample was purged in purified He at 110 °C for 30 min and then cooled to 50 °C in He atmosphere. The chemisorption of CO was measured by using a thermal conductivity detector (TCD).

6.3.3 Activity Testing on PROX of CO

The catalytic activity was measured in a fixed-bed, U-tube, reactor loading with 100 mg of catalyst. The reaction was carried out in the temperature range of 80 °–300 °C with a total flow rate of 50 ml min⁻¹. A gas reactant consists of 1% CO, 1% O₂ and 40% H₂ balanced in He. The gas compositions were measured by gas chromatography (GC) equipped with thermal conductivity detector (TCD). The conversions of CO and O₂ were calculated from the ratio of the amounts of CO and O₂ used during the reaction to the amounts of CO and O₂ initially present (in volume %), respectively. The selectivity of CO₂ was determined by the oxygen consumed for oxidizing CO to CO₂ divided by the total oxygen reacted (in %volume).

6.4 Results and Discussion

In accordance with our previous works [20, 21], the mixture composition of Al₂O₃:xP₂O₅:0.2SiO₂:750H₂O was employed to study the influence of pH in the synthesis gel on the formation of flower-like SAPO without using any structure-directing agent at the crystallization temperature of 200 °C for 1h. The amount of phosphoric acid, x, was used to adjust the pH of the reaction mixture in a range of 5 to 7. As shown in Figure 6.1, interestingly, the flower-like SAPO morphology, named as SAPO-PPC (Silicoaluminophosphate-Petroleum and Petrochemical College), was formed only in the system having the pH value of 6 (Figure 6.1b). At higher pH levels (Figure 6.1a) an amorphous result was obtained while the sample became agglomerate at a pH lower than 6 (Figure 6.1c). Therefore, a suitable pH of the reaction mixture

adjusted by the phosphate content was necessary for the formation of the flower-like SAPO-PPC.

It can be seen that the flower-like SAPO-PPC, prepared via microwave heating using alumatrane and silatrane precursors, is composed of flower-like particles with six petals extending radially from the center. The average size of the flower-like structure was about 6–8 μm showing a BET surface area of $12 \text{ m}^2\text{g}^{-1}$. Li *et al.* [6] also reported that triethanolamine could be used as a modifying agent for the synthesis of ZnO to obtain a more vivid natural flower shape than shown by those prepared without triethanolamine. Thus, in our case, the precursors containing triethanolamine (TEA) and triisopropanolamine (TIS) generated from the hydrolysis of silatrane and alumatrane, respectively, provide two different structure-directing agents for the formation of the flower-like product, as also reported in the synthesis of K-H zeolite from atrane precursors [22]. Trialkanoamine ligand could also be used as a stabilizing or complexing agent in the synthesis of zeolite [23, 24].

However, when the reaction time was reduced to 0.5 h, an amorphous phase mixed with the flower-like SAPO-PPC was obtained (SEM not shown). If the time was increased to 2 h, the obtained products were similar to those obtained in a 1 h reaction time (Figure 6.1b), indicating that an extension of the reaction time is not beneficial to crystallization. Therefore, crystal growth was completely formed at the crystallization temperature of 200 °C for 1 h. The effect of aging time was also investigated, using different aging times of 6, 16, and 24 h. It was found that a 6 h aging time was not sufficient for a complete formation of the flower-like product (not shown), whereas a 24 h aging time resulted in a misshaped flower-like SAPO. The aging time of 16 h seems to give a perfect flower-like SAPO.

XRF was utilized to determine the mole ratio of SiO_2 to Al_2O_3 of the flower-like SAPO-PPC. The result reveals the contents of silica and aluminum incorporated into the framework equal to 0.22:1:00 $\text{SiO}_2:\text{Al}_2\text{O}_3$. The amount of alumina and silica in the product were close to those of the synthesis gel prepared from 0.20:1.00 mole ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$.

A further study was carried out by the addition of TPABr to the reaction gel. According to our previous work [21], the mixture composition of $\text{Al}_2\text{O}_3:1.5\text{P}_2\text{O}_5:1.5\text{TPABr}:0.2\text{SiO}_2:750\text{H}_2\text{O}$ was selected with 16 h aging time and 1h heating time at

200 °C. As can be seen in Figure 6.1d, the sample prepared in the presence of TPABr was different from the above samples prepared without TPABr. The product shows a flower-like shape with multilayered petals. The TPABr molecule is generally used as a structure-directing agent for synthesis of ZSM-5 zeolite materials [25, 26]. Hence, the mixture of TPABr, TEA, and TIS could be the reason for the formation of flower-like SAPO with multilayered petals.

The XRD pattern of the flower-like SAPO-PPC (Figure 6.2) can be indexed to hexagonal phase (JCPDS no. 50-0302). Beside, the sample prepared in the presence of TPABr indicated the same pattern of XRD (not shown) as those prepared without TPABr.

Pt metal was loaded on flower-like SAPO-PPC to study the catalytic activity. The XRD peaks exhibited at 2θ of 39.8 ° and 46.3 ° are corresponding to the presence of Pt particles, as indicated in references 18 and 19. It can be seen that as the amount of Pt loading increases, the relative intensity of Pt peak in XRD pattern also increases. The average particle size of Pt was estimated from the full width half maximum (FWHM) of the Pt peak according to Scherrer's equation. The particle size was found to be in the range of 13–16 nm. However, the TEM micrograph (Figure 6.3) exhibits the size of the Pt particle less than 10 nm, and shows well dispersed without agglomeration of Pt particles. CO chemisorption measurement (Figure 6.4) of 3%w/w Pt/flower-like SAPO-PPC revealed Pt dispersion value of 11.5%.

Catalytic study on PROX of CO in H₂-rich over 3 % Pt/Flower-like SAPO-PPC (Figure 6.5) illustrates the efficiency of CO conversion, O₂ conversion, and CO selectivity, depending on the reaction temperature. The catalyst exhibited low performance of CO conversion at low temperature because CO strongly adsorbed on Pt metal [28]. As increasing the reaction temperature to 160 °C, CO molecules were partially desorbed. Thus, the conversion started to increase at the reaction temperature was higher, and a maximum of 100 % CO conversion at the reaction temperature of 240 °C was reached. A wide range of the reaction temperature for a complete removal of CO was obtained from the operation temperature range of 240 ° to 280 °C. Above that temperature, CO conversion decreased a little bit, whereas the O₂ conversion still maintained 100 % conversion due to the oxygen used for H₂ oxidation competing reaction [16] and reverse water gas shift (RWGS) giving CO [17], resulting in the

decrease of the CO selectivity. The Pt impregnated flower-like SAPO-PPC could be considered as a good efficient catalyst for PROX of CO because of the wide range of the reaction temperature providing 100 % of CO conversion. The same result was also obtained for 5 % Pt impregnated SAPO (not shown). However, the catalysts prepared with 1 % Pt presented only 87 % maximum CO conversion at 240 °C (not shown). As a conclusion, the 3 % Pt impregnated SAPO gave the best catalytic performance on PROX of CO in H₂-rich feeding gas.

6.5 Conclusions

Alumatrane and silatrane precursors are successfully used as metal alkoxide precursors for the synthesis of SAPO-PPC flower-like structures via microwave heating technique. The results produced a flower-shaped morphology with six petals. The pH value, aging time, and time were crucial factors for the synthesis. Moreover, the addition of TPABr to the reaction gel also affected the morphology of SAPO, producing multilayered petals. 3 % Pt/SAPO-PPC flower-like are useful to completely deplete CO infected in the H₂-rich feed gas. Generally, the operation temperatures of PEMFC are in the range of 200 °–300 °C and the PROX unit has to be set up between water gas shift reaction (WGS) unit (80 °C) and the PEMFC unit, therefore, it can be directly fed from the low temperature WGS unit into the PROX unit without adjusting the temperature.

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6.7 References

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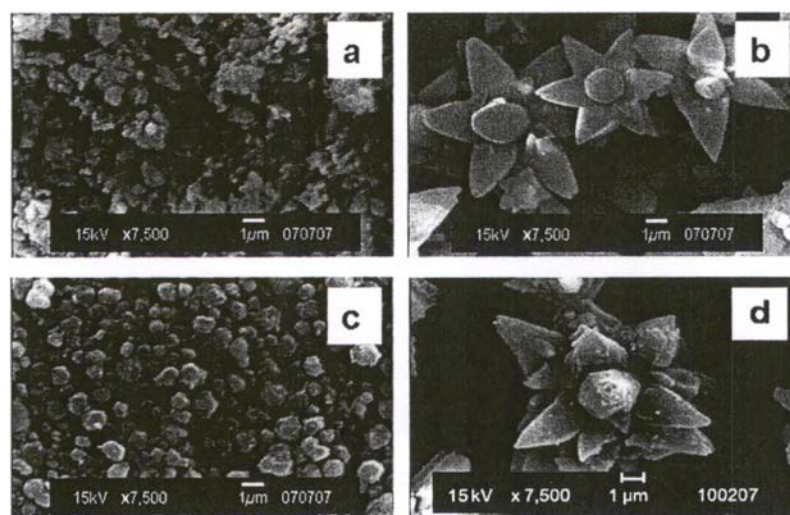


Figure 6.1 SEM images of the samples prepared from the mixture of Al_2O_3 : $x\text{P}_2\text{O}_5$: 0.2SiO_2 : $750\text{H}_2\text{O}$ at $200\text{ }^\circ\text{C}$ for 1h, and the pH of (a) 7, (b) 6, (c) 5, and (d) with TPABr loading.

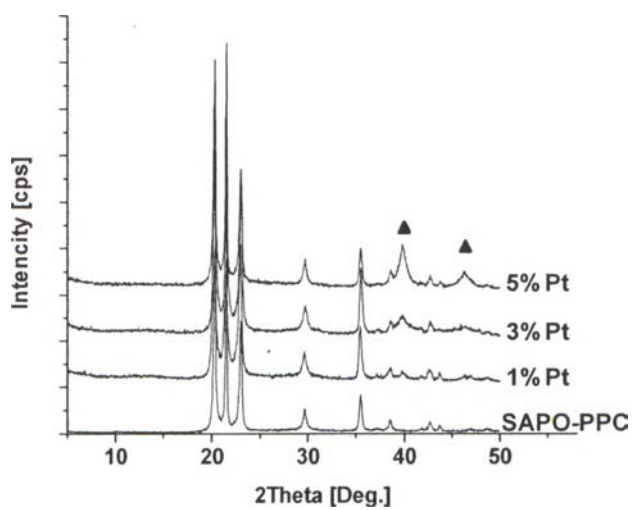


Figure 6.2 XRD patterns of the flower-like SAPO-PPC prepared from the mixture of $\text{Al}_2\text{O}_3:1.5\text{P}_2\text{O}_5:0.2\text{SiO}_2:750\text{H}_2\text{O}$ at pH 6, 200 °C for 1h, with and without Pt impregnation (▲ = peaks of metallic platinum).

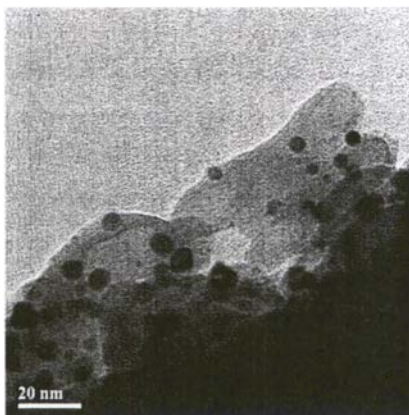


Figure 6.3 TEM micrograph of 3 % Pt impregnated flower-like SAPO-PPC.

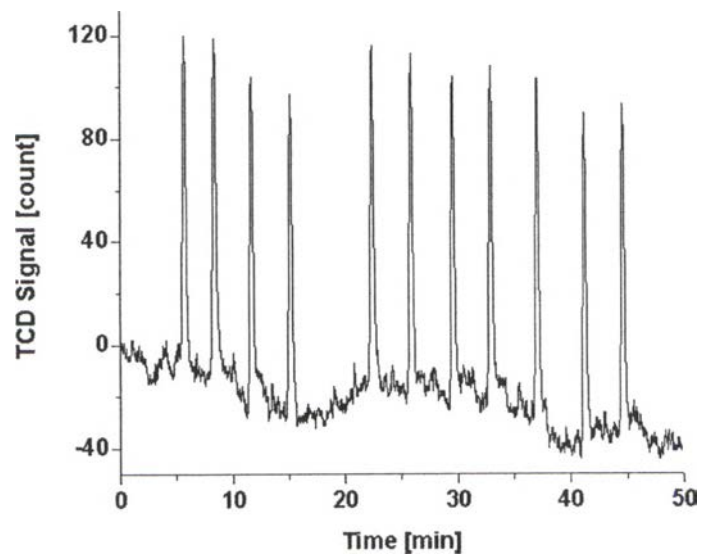


Figure 6.4 CO chemisorption isotherm of 3 % Pt/flower-like SAPO-PPC.

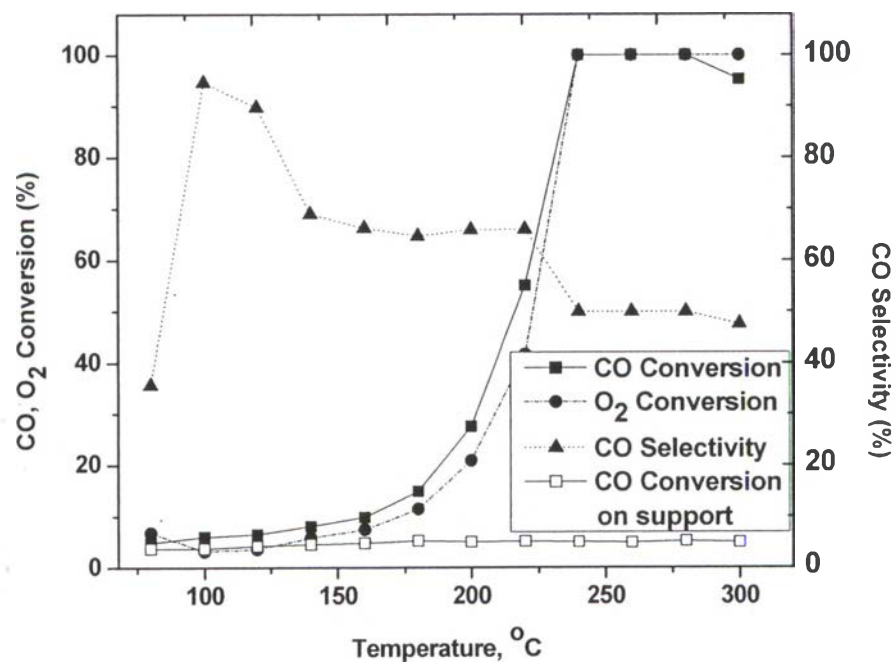


Figure 6.5 The catalytic activity of 3 % Pt/flower-like SAPO-PPC on the PPOX of CO reaction.