NATURE AND CATALYTIC PERFORMANCE OF PtSAPO-5 MOLECULAR SIEVE CATALYST SYNTHESIZED BY ONE STEP

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Abstract – Pt catalysts supported on silicoaluminophosphate molecular sieves were synthesized by adding platinum salts directly to the gel mixture of SAPO. The synthesized products were marked as PtSAPO-5, in order to distinguish with the SAPO-5 supported platinum catalyst prepared by impregnation, which was marked as Pt/SAPO-5. The as-synthesized and calcined PtSAPO-5 samples were characterized by XRD, ^{29}Si MAS NMR, ^{129}Xe NMR and NH$_3$-TPD, and their catalytic activities were evaluated by the hydroisomerization of n-hexane. The results revealed that in PtSAPO-5, the platinum could catalyze the removal of the templates entrapped in the as-synthesized samples. The presence of Pt in the gel mixture can increase silicon content in the framework of SAPO-5, and the acid sites. In the activated PtSAPO-5 catalyst, Pt was highly dispersed in the channel of SAPO-5 molecular sieve. Pt exists in the form of big particles outside of the channel of Pt/SAPO-5 prepared by impregnating method, and impregnation with H$_2$PtCl$_6$ improved the strength of acid sites. PtSAPO-5 has a higher activity and selectivity than Pt/SAPO-5 in the hydroisomerization of n-hexane. This is because the former has medium acid sites and high dispersion of Pt, while the channel of Pt/SAPO-5 is somewhat retarded by the big platinum particles, and the acid sites are stronger than the former.

Key words : PtSAPO-5, Synthesis by One Step, NMR Characterization, Catalytic Activity, Hydroisomerization of n-Hexane

INTRODUCTION

Bifunctional catalysts with acidic sites and metallic sites are widely used in the petroleum processing industry. However, up to now, their main preparation methods have been impregnation or ion exchange. After impregnation or ion exchange, a large amount of used solution containing a little noble metal salts or some other substance like ammonia is discharged, which often generates waste and severely pollutes the environment. Above all, these methods have complex procedures and are time consuming, so it is difficult to control the nature and performance of catalysts. To prepare ideal bifunctional catalysts and to decrease waste discharge, new techniques need to be developed.

In recent years, a large number of molecular sieves based on aluminophosphates have been synthesized and identified. It is shown that as one of the new aluminophosphate molecular sieve materials, SAPO-5 can combine pore shape variability and somewhat adjustable acidity, and can be synthesized in a relatively wide range of pH values [Lok 1984; Xiao 1993]. Recently, we have developed a new way to synthesize bifunctional catalysts of SAPO-5 supported noble metal by cocrystallizing the gel mixture of SAPO with platinum salts directly, which not only simplifies the preparation procedures of bifunctional catalyst and causes less waste, but also helps to design the property and performance of such catalysts [Xiao,

1995]. The objective of the present work is to prepare PtSAPO-5 catalyst by one step and compare the character and catalytic performance of PtSAPO-5 with those of Pt/SAPO-5 catalyst prepared by impregnating method, using n-hexane hydroisomerization as a model reaction.

EXPERIMENTAL

1. Catalyst Preparation

The SAPO-5 supported platinum catalysts were synthesized as follows: the reactants were added in a ratio 1.2NEt$_3$: Al$_2$O$_3$: P$_2$O$_5$: 0.3Si(OEt)$_4$: xH$_2$PtCl$_6$: 60H$_2$O, the sources of Al, Si and P were pseudoboehmite, Si(OEt)$_4$ and 85 wt% H$_3$PO$_4$ receptively. Pseudoboehmite was mixed with H$_3$PO$_4$ at room temperature by vigorous stirring, then Si(OEt)$_4$ and some water were added with stirring; afterwards, Et$_3$N as the template was added. A homogeneous gel mixture was thus obtained. H$_2$PtCl$_6$ solution (pH=2, 0.0102 gPt/ml) was added at Pt/(Pt+Al+Si+P) ratios of 0.1 %, 0.5 %, and 1.0 % (in wt%), respectively. The mixtures were poured into Teflon-coated stainless-steel autoclaves. Heating was maintained for 24 h at 195 °C. When used as catalysts, the SAPO-5 sample was dried at 120 °C, and activated by calcining at 550 °C for 5 h; the PtSAPO-5 is further activated by reduction with H$_2$ at 400 °C for 4 h after calcination.

Pt/SAPO-5 catalyst was prepared by dipping the calcined SAPO-5 molecular sieve in H$_2$PtCl$_6$ solution. After being dipped for 24 h, the materials were dried in air at 120 °C for 5 h, then calcined at 500 °C for 2 h and subsequently reduced with

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H₂ at 400°C for 4 h.

2. Characterization

XRD patterns were obtained to identify the structure of the synthesized products on a D/MAX-12kV X-ray Diffractometer (XRD). The noble metal contents in the synthesized samples and the aged solution were measured by inductively coupled plasma atomic emission spectrometry (ICP). The framework element contents were measured by X-ray disperse spectroscopy (EDS), and the coordination environment of Si was analyzed by MAS NMR, using TMS as references. The measurements were carried out at a spinning rate of ca. 3000 Hz/s.

The distribution and dispersion of Pt in reduced PtSAPO-5 were characterized by ^{129}Xe NMR. The catalyst samples were degassed at 400°C to 1.3×10^{-3} Pa and kept for 2 h, then cooled to room temperature, and xenon was conducted to the sample tube and the pressure of xenon was kept at 13,332 Pa for 10 min, then sealed the tube. The chemical shifts refer to the extrapolated shift of bulk xenon at P=0. A second standard of xenon adsorbed in NaY in equilibrium with gas at 78,647 Pa was used for calibration. All the NMR spectra were recorded with a Brucker MSL-400k spectrometer.

The acidity of the catalysts was measured by NH₃-TPD using a static method. NH₃ was adsorbed on the catalyst at 100 °C, and the temperature was raised at a rate of 5°C/min.

The performance of the catalyst was evaluated by the hydroisomerization of n-hexane at 350°C. The pressure of H₂ was 300,000 Pa; the flow rate of liquid n-hexane was 1.0 cm³/h. The reactor effluent was collected for 2 h and analyzed by high resolution gas chromatography equipped with a 100 m × 0.25 mm fused silica capillary column. Helium was used as carrier gas, and the flowing rate was 20 ml/min.

RESULTS AND DISCUSSIONS

The chemical compositions and Pt contents in PtSAPO-5 and Pt/SAPO-5 are listed in Table 1, which shows that with increasing Pt salt in the gel mixture, the amount of Si in the PtSAPO-5 is gradually increased, suggesting that addition of Pt salt to the gel mixture helps the silicon enter the framework of SAPO-5. Table 1 also shows that almost all the added Pt in the gel mixture can be loaded in SAPO, and little Pt is left in the mother solution after PtSAPO-5 synthesis. However, in preparation of Pt/SAPO-5 by impregnating method, Pt concentration in the solution is 0.005 % at the beginning, and becomes 0.0012 % after 24 h at room temperature, suggesting that Pt in the solution cannot be fully supported
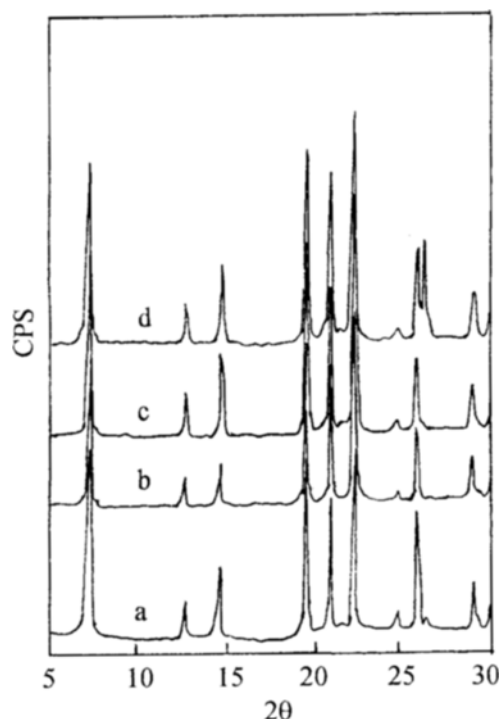

Fig. 1. XRD patterns of the synthesized samples from the mixture of SAPO gel with Pt content, (a) 0 wt%, (b) 0.1 wt%, (c) 0.5 wt%, and (d) 1.0 wt%.

on SAPO-5 molecular sieve by impregnation method.

The X-ray diffraction patterns of the synthesized samples are shown in Fig. 1. It can be seen that the XRD patterns of the PtSAPO-5 with Pt contents of 0.1 wt% and 0.5 wt% are always fully coincident with those of SAPO-5 reported in the literature [Xiao, 1993; Das, 1992], which suggests that addition of platinum salt to the gel mixture of SAPO-5 does not change the structure of SAPO-5 within Pt content of 0.5 wt%. In Fig. 1b and c, no diffraction peaks of Pt are displayed in the XRD patterns, probably owing to Pt being highly dispersed in SAPO-5. However, for the PtSAPO-5 with Pt content of 1.0 wt%, a peak at 27.5° appears, which is probably the diffraction peak of Pt compounds. These results show that when Pt salt content is up to 1.0 wt% of SAPO, some crystalline phases of Pt compounds exist in PtSAPO-5.

The results of TG-DTA show that template-removal in SAPO-5 starts at 350°C, and completes at 1,000°C; the template is removed in four stages. In PtSAPO-5 sample with 0.1 % Pt, the template starts to decompose at 335°C, and the de-

Table 1. Chemical composition of the SAPO-5 supported Pt and Pt concentration (wt%) in liquid phases

Sample	Chemical composition of SAPO-5*			Pt (wt%) in liquid**	
	Al	P	Si	Start	End
SAPO-5	0.49	0.46	0.05	0.000	~0
PtSAPO-5(0.1wt%)	0.487	0.45	0.063	0.001	~0
PtSAPO-5(0.5wt%)	0.485	0.449	0.066	0.005	~0
PtSAPO-5(1.0wt%)	0.485	0.446	0.069	0.0095	~0
Pt/SAPO-5(0.5wt%)	0.486	0.46	0.054	0.005	~0.0012

*The analysis was carried out by EDS.
**The results were obtained by ICP.
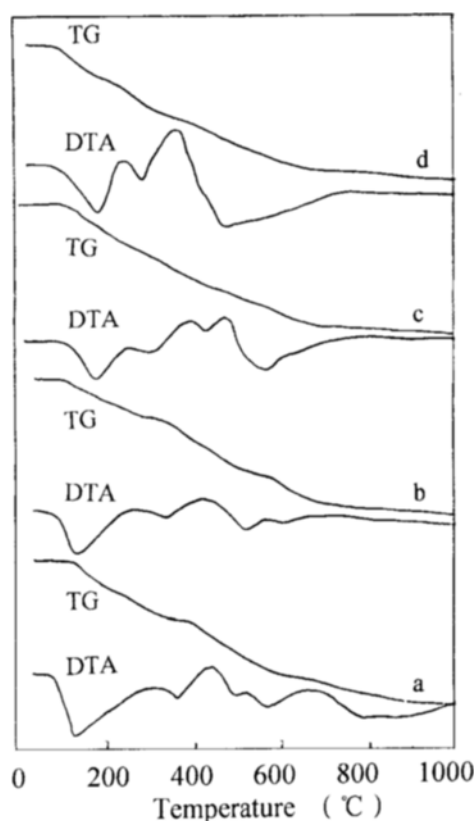
Fig. 2. TG-DTA curves of the as-synthesized PtSAPO-5 with different Pt content, (a) 0 wt%, (b) 0.1 wt%, (c) 0.5 wt%, and (d) 1.0 wt%.

Fig. 3. ^{29}Si MAS NMR spectra of the synthesized PtSAPO-5 with different Pt content, (a) 0 wt%, (b) 0.1 wt%, (c) 0.5 wt%, and (d) 1.0 wt%.

composition of the template undergoes only three stages. The end of template-removal is at 700 °C, nearly 300 °C lower than that of SAPO-5 with no Pt (Fig. 2b). These results suggest that the presence of Pt in the as-synthesized PtSAPO-5 can catalyze the removal of the template in the molecular sieves. When Pt content is up to 0.5 % and 1.0 % in PtSAPO-5, from Fig. 2c and d, it can be seen that the temperature of template removal moves lower and the template is decomposed in two stages. This result implies that Pt in PtSAPO-5 changes the existing state of the template in the molecular sieve, and shows that Pt in PtSAPO-5 plays a catalytic role in decomposition of the template.

Fig. 3 is the ^{29}Si MAS NMR spectra of the as-synthesized SAPO-5 and PtSAPO-5 samples. It is shown that SAPO-5 has a main NMR line at − 94 ppm, corresponding to the state of Si(OAl)$_4$ in SAPO-5, which implies that Si is uniformly distributed in the framework of SAPO-5 [Blackwell, 1988]. For PtSAPO-5 sample, besides the peak of − 94 ppm, two little peaks at − 85 ppm and − 105 ppm also appear, which grow with increasing Pt content in PtSAPO-5. The peak at − 85 ppm can be assigned to the Si(OAl)$_4$ in the SA domain in SAPO, and the peak at − 105 ppm to the framework Si in the state of Si(OSi)$_4$ in SA domain [Blackwell, 1988; Wang, 1991]. These results show that addition of Pt salt to the gel mixture of SAPO increases the SA domain in PtSAPO-5, and addition of Pt salt in the gel mixture of SAPO makes the Si unevenly distribute in the framework of SAPO-5. Ac-
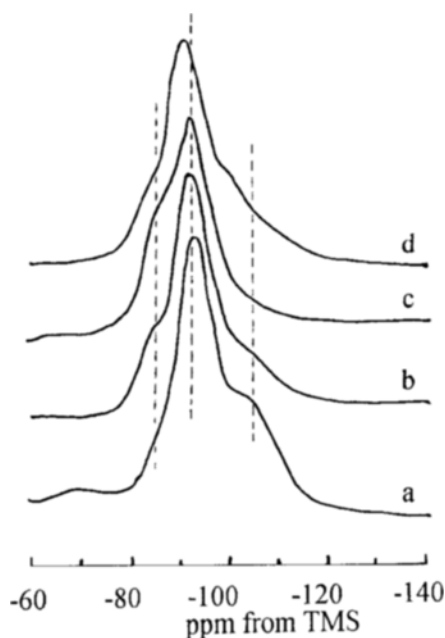
cording to references [Lok, 1984; Wang, 1991; Ojo, 1992], SA domain in SAPO-5 results from two silicon atoms replacing a pair of Al and P in the framework of SAPO. Hence it can be concluded that the existence of Pt salt in the gel mixture can help the process of two Si atoms replacing a pair of P and Al rather than that of a silicon atom replacing a P in the framework of AlPO$_4$-5, which thus favors Si entering the framework. Therefore, there are more silicon-rich domains in the PtSAPO-5.

Fig. 4 gives the NMR spectra of xenon adsorbed in the catalyst samples. The NMR spectrum of xenon adsorbed on SAPO-5 contains only a single resonance line at 73.5 ppm, which indicates that the framework elements of Al, Si and P are evenly distributed in SAPO-5. The result is in agreement with that of NMR measurement [Blackwell, 1984]. However, for some residue "coke" is probably generated and exists in the channel of SAPO-5 during calcination of the template; the peak of ^{129}Xe is not totally symmetrical. For PtSAPO-5 catalyst with Pt content of 0.1 wt%, a single symmetrical line at 79.4 ppm is observed (Fig. 4a), implying that the platinum particles are highly and evenly dispersed in the channel of SAPO-5 molecular sieves [Xiao, 1995; Du, 1991]. The chemical shift of ^{129}Xe NMR in PtSAPO-5 is 2.3 ppm higher than that in PdSAPO-5, which is probably due to the fact that Pt has a greater ability to donate an electron than Pd. With the Pt content increasing from 0.1 wt% to 0.5 %, chemical shift of ^{129}Xe NMR keeps almost the same, and the line becomes more symmetrical, suggesting that the channel environment becomes more even, and Pt metal is distributed more uniformly in PtSAPO-5 with Pt content of 0.5 wt%. When Pt content is up to 1.0 wt% in PtSAPO-5 catalyst, the line of ^{129}Xe NMR becomes broad and unsymmetrical, showing that some Pt particles are distributed unevenly in the channel of SAPO-5.
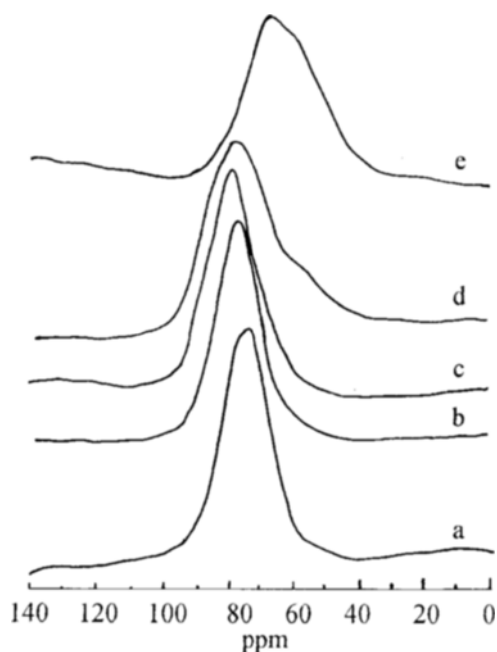
Fig. 4. ^{129}Xe NMR spectra of PtSAPO-5 with different Pt contents, (a) 0 wt%, (b) 0.1 wt%, (c) 0.5 wt%, (d) 1.0 wt%, and (e) Pt/SAPO-5 catalyst with 0.5 wtPt%.
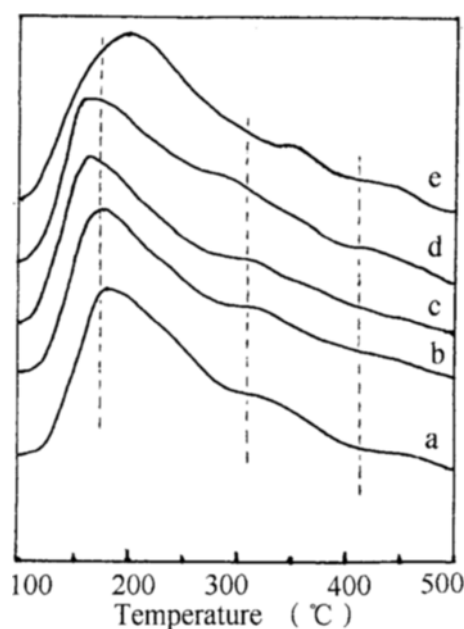

Fig. 5. NH$_3$-TPD profiles of PtSAPO-5 with different Pt contents, (a) 0 wt%, (b) 0.1 wt%, (c) 0.5 wt%, (d) 1.0 wt%, and (e) Pt/SAPO-5.

Table 2. Activity and selectivity of hydroisomerization of n-hexane* on different SAPO-5 supported Pt catalysts

Catalyst	PtSAPO-5 (0.5 %)	Pt/SAPO-5 (0.5 wt%)
Conversion	70.6 %	54.8 %
Selectivity**	36.0 %	11.5 %

Reaction conditions: T=350 °C, P$_{H2}$=300,000 Pa, Reaction time: 120 min.

In the catalyst of Pt/SAPO-5 prepared by impregnating SAPO-5 with H$_2$PtCl$_6$ solution, the line of ^{129}Xe NMR is broad, and two peaks appear at 74.2 ppm and 63.8 ppm (Fig. 4e); when Pt content is still as low as 0.5 wt%, the resonance line is not well symmetrical, the chemical shift moves to the upward of the magnetic field. These results reveal that Pt metal in Pt/SAPO-5 catalyst prepared by impregnating method cannot be highly and evenly dispersed in SAPO-5 molecular sieve.

The acidity (sum of Bronsted and Lewis sites) was measured by TPD using NH$_3$ as a probe molecule as shown in Fig. 5. It can be seen that in SAPO-5 molecular sieve, NH$_3$ desorbs at 168 °C and 305 °C, corresponding to the weak and medium acidic sites, respectively. In PtSAPO-5 with Pt content of 0.1 wt%, the weak and medium acidic sites still exist, and the amount of desorbed NH$_3$ is almost the same with that desorbed from SAPO-5, while the desorption temperatures are a little lower, which suggests that existence of Pt in PtSAPO-5 weakens the acidic strength but does not decrease the acidic sites. The temperatures corresponding to the desorption peaks of NH$_3$ from PtSAPO-5 move lower with increasing Pt content (Fig. 5b, c, d). This result shows that for PtSAPO-5 catalysts, the higher Pt content is, the weaker the acidic sites are, which also demonstrates that the Pt metal is evenly dispersed in the acidic sites in the PtSAPO-5 catalysts. The reason is that Pt acts as an electron donor to the acidic sites, and thus weakens the acidity of SAPO-5. The NH$_3$-TPD profile for Pt/SAPO-5 catalyst is different from those of SAPO-5 and PtSAPO-5. The desorption peaks of NH$_3$ from Pt/SAPO-5 appears at higher temperature, and the weak and medium acidic sites decrease while strong acidic sites increase, which is owing to the fact that the acidity of PtSAPO-5 is enhanced by H$_2$PtCl$_6$ acid.

The conversion of n-hexane hydroisomerization on PtSA-PO-5 catalyst at 350 °C and 300,000 Pa of hydrogen reaches 74 %, 20 % higher than that on Pt/SAPO-5, and the selectivity of dibranched isomers of hexane on PtSAPO-5 is up to 36 %, 25 % higher than that on Pt/SAPO-5. The comparison of the catalytic performances of the catalysts is shown in Table 2.

The above results can be explained by the degree of dispersion of Pt particles and the strength of acidity of the catalysts. Generally speaking, the main steps in the catalytic hydroconversion are the following: (1) dehydrogenation of n-hexane to n-hexene on metallic sites, (2) isomerization of n-hexene to isohexenes on acid sites, and (3) hydrogenation of isohexenes to isohexanes on metallic sites [Compelo, 1995]. It has been shown that dehydrogenation mainly happens on the highly dispersed metal sites, the higher dispersion of the Pt in the catalyst, the easier step (1) takes place. Hence on PtSAPO-5 catalyst, more n-hexene is produced during the reaction. During isomerization of n-hexene, acidic sites are needed. However, if the acidity of the catalyst is too strong, the isohexenes probably crack on the strong acidic sites, which lowers the selectivity of the isomerization, and generates more cracking products. According to the previous results, PtSAPO-5 has a high dispersion of Pt and moderate acidic sites, so the activity and selectivity for isomerization are high rela-

tively to those of Pt/SAPO-5.

CONCLUSION

Synthesis of PtSAPO-5 catalyst by one step can simplify the preparation procedures of bifunctional catalysts, causes less waste and makes the noble metal fully support on the molecular sieves. The addition of Pt salts to the gel mixture does not change the structure of the molecular sieve, but increases silicon content and catalyzes the removal of template. The Pt particles in PtSAPO-5 synthesized by one step was distributed highly and evenly in the channel of SAPO-5. The PtSA-PO-5 catalyst has more medium acidic sites and Pt is highly dispersed in it; hence it has a higher activity and selectivity in the hydroisomerization of n-hexane than that of Pt/SAPO-5 catalysts.

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