$\text{Ga}_x\text{Cs}_{2.5-3x}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ 的固相法制备及其催化正丁烷异构化反应的活性

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摘要: 利用室温固相法制备了一系列掺镓的钨磷酸铯盐催化剂 $\text{Ga}_x\text{Cs}_{2.5-3x}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ ($x = 0.05, 0.1, 0.15$). 与钨磷酸铯盐相比, 掺镓的钨磷酸铯盐催化剂的结构未产生变化, 但其酸强度提高, 在正丁烷异构化反应中催化活性增强, 其中以 $\text{Ga}_{0.1}\text{Cs}_{2.2}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ 和 $\text{Ga}_{0.15}\text{Cs}_{2.05}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ 最为显著.

关键词: 镓; 钨磷酸铯盐; 固相合成; 正丁烷异构化; 酸性

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Solid Synthesis of $\text{Ga}_x\text{Cs}_{2.5-3x}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ Salts and Their Catalytic Activity in the Isomerization of *n*-Butane

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Abstract: $\text{Ga}_x\text{Cs}_{2.5-3x}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ ($x = 0.05, 0.10$, and 0.15) salts were prepared using a solid synthesis method and they showed higher catalytic activity than that of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ for *n*-butane isomerization, which possibly comes from their enhanced acid strength as a result of Ga doping.

Key words: gallium; cesium salt of tungstophosphoric acid; solid synthesis; butane isomerization; acidity

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Keggin-type 12-tungstophosphoric acid, $\text{H}_3\text{PW}_{12}\text{O}_{40}$, is a strong acid and has been used as an efficient catalyst in various acid-catalyzed reactions [1]. The partial substitution of H^+ by Cs^+ improves the properties of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ such as its surface area, porosity, insolubility, and acidity, which are

favorable for the enhancement of its catalytic activity [2,3]. $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ salts prepared using a liquid method were initially reported by Tatematsu et al. [4] and $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ is considered to be the most active acid catalyst among the $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ salts because of its en-

hanced surface acidity [5,6]. The procedure for the liquid method is tedious and also inconvenient for large scale preparation [3]. In a previous study, we reported a solid method for the preparation of $\text{Cs}_x\text{H}_{3-3x}\text{PW}_{12}\text{O}_{40}$ and these prepared salts had the same properties and catalytic activity for *n*-butane isomerization as the salts prepared by the liquid method [6,7]. It has been reported that gallium is an efficient promoter for sulfated zirconia and it can improve the acidity, stability, and catalytic activity of the catalyst during *n*-butane isomerization [8–10]. However, no reports exist about the catalytic activity of a second metal assisted cesium salt of tungstophosphoric acid. Here, we synthesized gallium doped cesium salts of tungstophosphoric acid, $\text{Ga}_x\text{Cs}_{2.5-3x}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$, by the solid method as it is simpler and more convenient to control the molar ratio of Ga/Cs than the liquid method. The products were characterized by X-ray diffraction and nuclear magnetic resonance and their catalytic activities were evaluated in a *n*-butane isomerization reaction.

$\text{Ga}_x\text{Cs}_{2.5-3x}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ (denoted $\text{Ga}_x\text{Cs}_{2.5-3x}\text{-S}$, $x = 0.05, 0.1, \text{ and } 0.15$) were prepared as follows: an appropriate amount of $\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$, CsNO_3 , and $\text{Ga}(\text{NO}_3)_3$ with $\text{Cs}^+/\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$ and $\text{Ga}^{3+}/\text{H}_3\text{PW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$ with molar ratios of $2.5\text{--}3x$ and x , respectively, were ground in a ball mill for 0.5 h and then the solid powder was calcined at 573 K in flowing air for 2 h. For comparison, $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ (denoted $\text{Cs}_{2.5}\text{-S}$) and $\text{Ga}_{0.8}\text{H}_{0.6}\text{PW}_{12}\text{O}_{40}$ (denoted $\text{Ga}_{0.8}\text{-S}$)

were also prepared using the same method.

The activity of the catalysts for the *n*-butane isomerization reaction was evaluated by ^{13}C MAS NMR using $1\text{-}^{13}\text{C}\text{-}n\text{-butane}$ as the reactant. Figure 1 shows the evolution of reactant and product content with reaction time during the skeletal isomerization of $1\text{-}^{13}\text{C}\text{-}n\text{-butane}$ at 373 K over $\text{Cs}_{2.5}\text{-S}$ and $\text{Ga}_x\text{Cs}_{2.5-3x}\text{-S}$. All the catalysts show similar kinetic curves. In the initial stage of the reaction over the $\text{Cs}_{2.5}\text{-S}$ and $\text{Ga}_x\text{Cs}_{2.5-3x}\text{-S}$ catalysts, only the products of $2\text{-}^{13}\text{C}\text{-}n\text{-butane}$ and the ^{13}C -isobutanes were observed. The total ^{13}C intensity was close to 100% indicating that the monomolecular mechanism is at work because no noticeable amount of NMR ‘invisible’ oligomers formed from the alkenes through the bimolecular mechanism. With an increase in the reaction time, the intensity of $2\text{-}^{13}\text{C}\text{-}n\text{-butane}$ reaches a plateau and then decreases, which suggests that $2\text{-}^{13}\text{C}\text{-}n\text{-butane}$ is a product of ^{13}C scrambling and is also an intermediate for further isomerization [11]. The quantity of the ^{13}C -propane and ^{13}C -isopentane byproducts increased gradually with an increase in the reaction time after the initial reaction period indicating that the bimolecular mechanism becomes significant. These results indicate that the isomerization of $1\text{-}^{13}\text{C}\text{-}n\text{-butane}$ proceeds over $\text{Ga}_x\text{Cs}_{2.5-3x}\text{-S}$ mainly by the monomolecular mechanism in the initial stage of the reaction, and then the bimolecular mechanism becomes dominant [6,7,11].

The conversion of $1\text{-}^{13}\text{C}\text{-}n\text{-butane}$ and the yield of

Fig. 1. Isomerization of $1\text{-}^{13}\text{C}\text{-}n\text{-butane}$ at 373 K over $\text{Cs}_{2.5}\text{-S}$ (a), $\text{Ga}_{0.05}\text{Cs}_{2.35}\text{-S}$ (b), $\text{Ga}_{0.1}\text{Cs}_{2.2}\text{-S}$ (c), and $\text{Ga}_{0.15}\text{Cs}_{2.05}\text{-S}$ (d).

^{13}C -isobutanes in the $1\text{-}^{13}\text{C}$ - n -butane isomerization reaction over different catalysts at 373 K after 50 min are listed in Table 1. Both the conversion and yield over $\text{Cs}_{2.5}\text{-S}$ are lower than that over $\text{Ga}_x\text{Cs}_{2.5-3x}\text{-S}$, especially when $x = 0.1$ and 0.15. The introduction of Ga accelerates the n -butane isomerization reaction. $\text{Ga}_{0.1}\text{Cs}_{2.2}\text{-S}$ and $\text{Ga}_{0.15}\text{Cs}_{2.05}\text{-S}$ show similar catalytic activity in the n -butane isomerization reaction at 373 K. These results indicate that the catalytic activity of $\text{Cs}_{2.5}\text{-S}$ in the n -butane isomerization reaction can be enhanced over a relatively wide range of gallium content. To the best of our knowledge, this catalytic phenomenon along with the preparation of $\text{Ga}_x\text{Cs}_{2.5-3x}\text{-S}$ using the solid method has not been reported previously. In contrast, $\text{Ga}_{0.8}\text{-S}$ shows nearly no catalytic activity for the n -butane isomerization reaction at 373 K, which indicates the promotion role of gallium. The synergistic effect between Cs^+ and Ga^{3+} accounts for the improved catalytic performance of $\text{Ga}_x\text{Cs}_{2.5-3x}\text{-S}$ compared with that of $\text{Cs}_{2.5}\text{-S}$. Moreover, the catalysts prepared in different batches exhibit the same catalytic activity towards the n -butane isomerization reaction, indicating the reliability of the solid synthesis method.

Table 1 The conversion of $1\text{-}^{13}\text{C}$ - n -butane and the yield of ^{13}C -isobutanes during the isomerization of $1\text{-}^{13}\text{C}$ - n -butane over the catalysts at 373 K after 50 min

Catalyst	Conversion of $1\text{-}^{13}\text{C}$ - n -butane (%)	Yield of ^{13}C -isobutanes (%)
$\text{Cs}_{2.5}\text{-S}$	38	15
$\text{Ga}_{0.05}\text{Cs}_{2.35}\text{-S}$	47	18
$\text{Ga}_{0.1}\text{Cs}_{2.2}\text{-S}$	61	26
$\text{Ga}_{0.15}\text{Cs}_{2.05}\text{-S}$	62	25

The XRD patterns (Fig. 2(a)) of the samples show that $\text{Cs}_{2.5}\text{-S}$ and $\text{Ga}_x\text{Cs}_{2.5-3x}\text{-S}$ have an identical crystalline phase, similar to that reported for $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ in the literature [3,7]. The ^{31}P MAS NMR spectroscopy was used to characterize the environment of the ^{31}P nucleus in the samples and

the results show that the ^{31}P MAS NMR spectra of $\text{Cs}_{2.5}\text{-S}$ and $\text{Ga}_x\text{Cs}_{2.5-3x}\text{-S}$ (Fig. 2(b)) all mainly contain an intense signal at $\delta = -15$. XRD and ^{31}P MAS NMR give similar results and this shows that the addition of gallium has little influence on the structure of $\text{Cs}_{2.5}\text{-S}$.

Generally, the acidity of a catalyst plays a significant role in the skeletal isomerization of n -butane. To investigate the influence of the possible variation of acidity on catalyst activity, trimethylphosphine (TMP) was used as a basic probe molecule to characterize the acidity of the catalysts [12,13]. The formation of a TMPH^+ complex from the interaction between TMP and the Brönsted acid sites gives rise to a ^{31}P NMR resonance at $\delta = 0$ to -5 while the interaction between TMP and Lewis acid sites leads to ^{31}P resonances ranging from $\delta = -30$ to -60 . Figure 3(a) shows typical ^1H -decoupling ^{31}P MAS NMR spectra of adsorbed TMP molecules on $\text{Cs}_{2.5}\text{-S}$ and $\text{Ga}_{0.1}\text{Cs}_{2.2}\text{-S}$. The resonance at $\delta = 0$ to -5 results from the interaction between TMP and the Brönsted acid sites over the catalyst and the residual resonances range from $\delta = -10$ to -16 and these are assigned to the ^{31}P nucleus in the Keggin unit of the catalyst. No signal in the region of $\delta = -30$ to -60 was detected. Therefore, both $\text{Cs}_{2.5}\text{-S}$ and $\text{Ga}_{0.1}\text{Cs}_{2.2}\text{-S}$ mainly contain Brönsted acid sites. Based on a quantitative analysis, the density of the Brönsted acid sites are estimated to be 94 and 17 $\mu\text{mol/g}$ for $\text{Cs}_{2.5}\text{-S}$ and $\text{Ga}_{0.1}\text{Cs}_{2.2}\text{-S}$, respectively. As the ^{31}P chemical shift of TMPH^+ is not sensitive to the acid strength, the $J_{\text{P-H}}$ coupling constant is normally used to estimate the acid strength and a larger $J_{\text{P-H}}$ coupling constant indicates stronger Brönsted acidity [13]. Non- ^1H decoupling ^{31}P MAS NMR spectra of the TMP adsorbed on the catalysts are shown in Fig. 3(b). The ^{31}P resonance at $\delta = 0$ to -5 shown in Fig. 3(a) splits into a doublet because of $J_{\text{P-H}}$ coupling. The $J_{\text{P-H}}$ constant for $\text{Cs}_{2.5}\text{-S}$ and $\text{Ga}_{0.1}\text{Cs}_{2.2}\text{-S}$ is 500 and 584 Hz, respectively, indicating that the introduction of gallium leads to an increase in the overall Brönsted acid

Fig. 2. XRD patterns (a) and ^{31}P MAS NMR spectra (b) of different catalysts. (1) $\text{Cs}_{2.5}\text{-S}$; (2) $\text{Ga}_{0.05}\text{Cs}_{2.35}\text{-S}$; (3) $\text{Ga}_{0.1}\text{Cs}_{2.2}\text{-S}$; (4) $\text{Ga}_{0.15}\text{Cs}_{2.05}\text{-S}$.

Fig. 3. ^1H -decoupling (a) and non- ^1H -decoupling (b) ^{31}P MAS NMR spectra of adsorbed TMP on $\text{Cs}_{2.5}\text{-S}$ (1) and $\text{Ga}_{0.1}\text{Cs}_{2.2}\text{-S}$ (2) catalysts.

strength. To further obtain information on the acid sites with different strength, especially the strong sites, 2- ^{13}C -acetone was used as a basic probe molecule. The ^{13}C chemical shift of the 2- ^{13}C -acetone adsorbed on an acid catalyst is known to increase with an increase in acid strength [13–15]. Both $\text{Cs}_{2.5}\text{-S}$ and $\text{Ga}_{0.1}\text{Cs}_{2.2}\text{-S}$, after the adsorption of 2- ^{13}C -acetone, show strong acid peaks at $\delta = 243.8$ and 244.4 in their ^{13}C MAS NMR spectra (not shown) with acid densities of 4.7 and 0.4 mol/g, respectively. Therefore, $\text{Ga}_{0.1}\text{Cs}_{2.2}\text{-S}$ shows a higher acid strength but a lower acid density than $\text{Cs}_{2.5}\text{-S}$, particularly for strong acid sites. Based on the catalytic results discussed above, it seems that high acid strength plays a more significant role in the *n*-butane isomerization reaction. Similar conclusions were also obtained in a study where a correlation between the acidity and the activity of a catalyst for an alkane isomerization reaction was obtained. Iglesia et al. reported that the activity of the catalyst for *n*-hexane isomerization increases exponentially with an increase in the acid strength of the catalysts [16,17].

In conclusion, $\text{Ga}_x\text{Cs}_{2.5-3x}\text{-S}$ salts were successfully prepared by a solid synthesis method. The introduction of gallium accelerates the isomerization of *n*-butane over $\text{Cs}_{2.5}\text{-S}$, especially when $x = 0.1$ to 0.15. $\text{Ga}_{0.1}\text{Cs}_{2.2}\text{-S}$ has higher acid strength but lower acid density compared with $\text{Cs}_{2.5}\text{-S}$. The higher catalytic activity of $\text{Ga}_{0.1}\text{Cs}_{2.2}\text{-S}$ may thus arise from its higher acid strength. The promotion effect of gallium on the cesium salt of tungstophosphoric acid should be further investigated.

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