Influence of operating conditions, Si/Al ratio and doping of zinc on Pt-Sn/ZSM-5 catalyst for propane dehydrogenation to propene

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Abstract−The direct catalytic dehydrogenation of propane to propene is an important route to enhance propene production. In the present experimentation the focus was to investigate the influence of incipient operating conditions, Si/Al ratio of zeolite support and effect of zinc doping on Pt-Sn/ZSM-5 catalyst performance. The catalysts were extensively investigated by reaction tests in a continuous plug-flow quartz micro-reactor. The experimental data shows that the manipulation of operating parameters significantly improves the reaction performance, while huge dynamicity is observed in product distribution. Reaction temperature, 600 °C is found to be most suitable, while increasing the weight hourly space velocity (WHSV), propene selectivity improves at the expense of lower conversion. The OPE was drawn to observe overall reaction network. It was found that the acidity of zeolitic support plays a more important role in achieving desired product selectivity than additional metallic content. Accordingly, the Si/Al ratio of the ZSM-5 zeolite the pro- pene selectivity was enhanced, leading to remarkable improvement in the total olefins selectivity which was remarkably improved owing to a suppression of secondary reactions. At Si/Al ratio 300, the selectivity of propene and total olefins becomes stable at 73% and 90% respectively. The doping of Zn on Pt-Sn/ZSM-5 improves only propene selectivity, but is severely affected by quick deactivation.

Key words: Propene, Direct Dehydrogenation, ZSM-5 Zeolite, Support, Selectivity

INTRODUCTION

Light alkane dehydrogenation to propene has acquired significant importance in recent days, as growing demand of propene is continuously increasing by 5.3% annually [1] and is expected to be 75 millions t/yr in 2010 [2]. Presently, two-third of the propene is produced from thermal steam cracking of liquid feed stock (naphtha) and about 28% propene is from FFC units [3]. Moreover, UOP has forecast that in future propene production from steam crackers will be reduced largely [4]. To meet the gap of demand and productivity, much emphasis has been given to propene technologies like methanol-to-olefin (MTO) and propane dehydrogenation [5]. The direct catalytic dehydrogenation of light alkane significantly suffers from equilibrium limitation and thermo-dynamical constraints [6]. On the other hand, lower propene selectivity at higher conversion was observed during oxidative dehydrogenation [7,8] acting as catalyst in development of direct propane dehydrogenation technology revel HAZOP issues. The higher temperature enhances dehydrogenation, while on the other hand favors thermal cracking to coke and leads to lower olefins selectivity.

Platinum-tin-alumina-supported catalysts have been widely used [9] in many refinery processes including paraffin dehydrogenation. Zeolite as a catalyst is becoming popular with prominent figures in its use in petrochemical industry. Distinct features like shape selectivity and ring structure have led to this popularity [10-14]. Both chromium- and platinum-based catalysts enhance stability and selec-

tivity for paraffin dehydrogenation to olefins, while reasonably suppressing coke formation [15-20]. Improvement in catalytic activity has been reported by using Pt-Sn on Al_2O_3 [9] and ZSM-5 as support [21-25]. The interaction of tin on the performance of Pt-Sn catalysts has been extensively investigated [26-32]. Tin modifies the electronic density of Pt [33] and decreases the size of platinum leading to reduction in coking formation [34-36].

ZSM-5 was selected as a support because of its better conversion ability and better resistance to coke formation due to well defined 10 member ring structures. The possibilities of pore blocking in ZSM-5 are also less due to the intercrossed connected channels [37,42]. However, comparatively few studies are focused on the effect of operating conditions in propane dehydrogenation using Pt-Sn/ZSM-5 catalyst. For propane dehydrogenation reaction, no information is available through open access regarding zinc doping as third metallic content on Pt-Sn/ZSM-5 catalyst. In this work, the performance of Pt-Sn/ZSM-5 catalyst with different Si/Al ratios was investigated for selective propane dehydrogenation to propene. As previously, large emphasis has been given to characterize the catalysts by hiding their actual behavior; therefore, our focus is not to characterize the catalyst, but to find operational suitability. Moreover, the influence of the zinc addition to ZSM-5 supporting Pt-Sn catalysts for the propane dehydrogenation reaction was analyzed.

EXPERIMENTAL

1. Catalyst Preparation

The bimetallic Pt-Sn/ZSM-5 catalyst was prepared by sequential impregnation [17] with powder H-ZSM-5 of specific surface area

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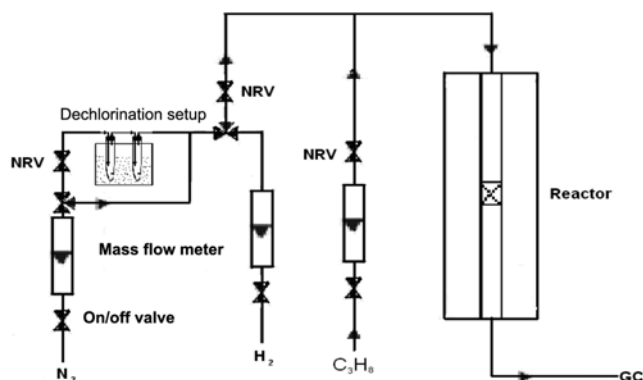E-mail: zeeshan@mails.tsinghua.edu.cn

Fig. 1. Systematic PFD of reaction setup.

354.1 m²/g (provided by Nankai Catalyst Company, Tianjin, China). At first, the powder H-ZSM-5 zeolite was co-impregnated with 0.16 M SnCl₂·2H₂O at 80 °C to make 1 wt% Sn in the catalyst and dried at 100 °C for 4 h. Then samples were calcined at 500 °C in muffle furnace for 4 h. The 0.03 M solution of H₂PtCl₆ was made for 0.5 wt% Pt and co-impregnated with powdered Sn/ZSM-5 at 60 °C. Afterward, prepared samples were dried at 100 °C for 4 h and calcined at 500 °C for 4 h.

In case of tri-metallic Pt-Sn-Zn/ZSM-5, 1 wt% of Zn was doped first in similar way followed by Sn and Pt impregnation sequentially. Both bi- and tri-metallic catalysts were crushed and de-chlorinated at 490 °C for 4 h with steam. Prior to the reaction tests, all of the catalyst samples were reduced by H₂ at 505 °C over night. The nominal composition of each content in every sample was about 0.5 wt% Pt, 1 wt% Sn and 1 wt% Zn. Similarly, bimetallic catalyst of three different Si/Al ratios of ZSM-5, 50, 140 and 300, were prepared. The metallic content of catalytic samples was verified by scanning electron microscope equipped with energy dispersive spectroscopy (JSM 7401F).

2. Reaction Setup

Catalytic samples were tested for direct propane dehydrogenation in a continuous plug-flow quartz micro-reactor at atmospheric pressure and setup as shown in Fig. 1. The 99.5% pure propane feed made available by Zhong Ke Hui Jie (HJAT), Beijing, China was used. Measured amounts of samples were loaded to maintain desired WHSV (i.e., 3, 5.9, and 9) and reduced under flowing H₂ (8 ml/min) at 500 °C for 10 h prior to reaction test. The reaction mixture composed of H₂/C₃H₈ (molar ratio 0.25) was charged to the reactor and product composition was analyzed through an online gas chromatograph with FID detector (GC7890II).

RESULTS AND DISCUSSION

1. Effect of Operating Conditions

The increase in temperature has an obvious effect on propane conversion and propene yield; however. propene selectivity first decreases and then increases to a maximum with running time (see Fig. 2). The product distribution analysis indicates that this initial decrease in propene selectivity is because of further cracking of propene to methane, ethane and ethene at higher temperatures, as shown in Fig. 3. Therefore, at lower temperatures a steady increase in propene selectivity was noted. The product distribution and tempera-
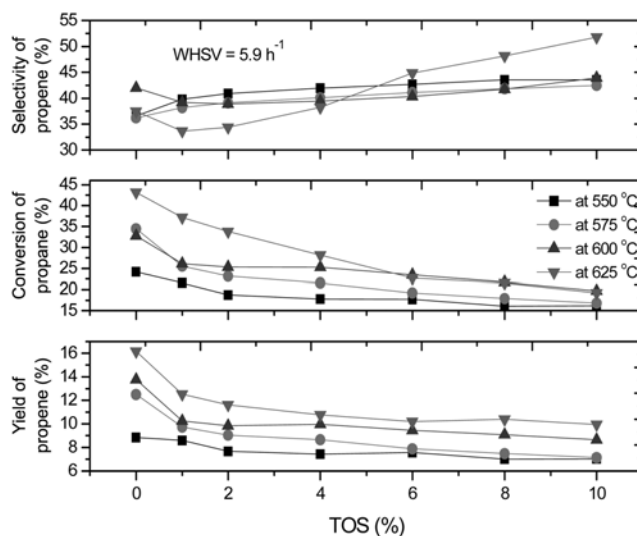

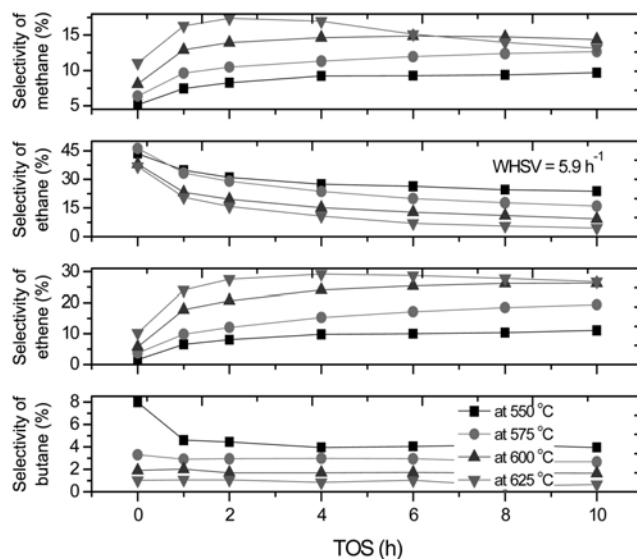Fig. 2. Effect of temperature on propane dehydrogenation over Pt-Sn/ZSM-5 of Si/Al=140.

Fig. 3. Effect of temperature on product distribution using Pt-Sn/ZSM-5 of Si/Al=140.

ture equaled the adiabatic equilibrium values [39]. The presence of methane, ethane and ethene in the system clearly demonstrates that at all temperatures and time on stream some amount of propene or propane is cracked. This phenomenon was verified by olefins performance envelope (OPE). The optimum propane dehydrogenation temperature with respect to discussed constraints was observed to be 600 °C.

The variation in weight hourly space velocity (WHSV) has a significant influence on the performance of Pt-Sn/ZSM-5 catalyst for propane dehydrogenation to propene. Increase in the WHSV markedly increases the propene selectivity at the cost of decrease in conversion, while the yield pattern is almost the same (see Fig. 4). The complete experimental picture of propane dehydrogenation over Pt-Sn/ZSM-5 at optimum temperature was obtained from the OPE plot and shown in Fig. 5. The best conversion range for propane to
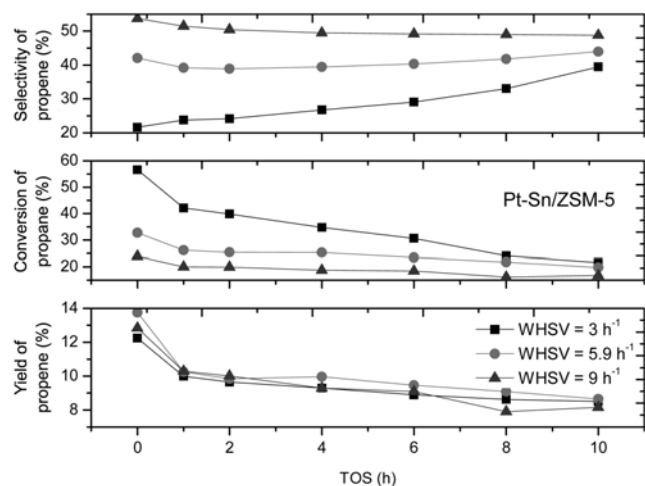
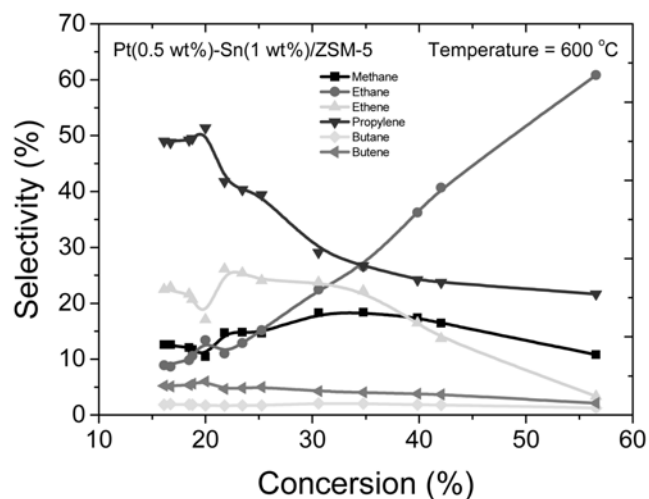**Fig. 4. Influence of WHSV on propane dehydrogenation to propylene at 600 °C.**

Fig. 5. OPE of propane dehydrogenation reaction.

Fig. 6. Effect of Si/Al ratio of ZSM-5 support on the performance of bi-metallic catalyst for propane dehydrogenation to propene.

(see Fig. 6). Consequently, there was an obvious increment in total olefins selectivity. The increase in Si/Al ratio of ZSM-5 decreases the acidity that is unfavorable for also disfavoring the hydrogen transfer reaction. The main work in propane dehydrogenation, which is to adsorb hydrogen from alkane, which is the rate-limiting step, was conducted by Pt metal. On the other hand, if a support is used for alkane dehydrogenation, relatively stronger acidity is needed to activate the alkane molecules, while secondary reaction of the produced alkene is also prompted, resulting in lower alkene selectivity. But using ZSM-5 itself or as a metallic support, it has been observed that with an increase in the Si/Al ratio, the stability of the catalyst was strongly effective and resulted in the quick deactivation. For the Pt-Sn/ZSM-5 zeolite with an Si/Al ratio of 300, the conversion decreased from an initial value of 32.2% to 15.1% at 10 h of running, 16.1% lower; while on the Pt-Sn/ZSM-5 with an Si/Al ratio of 50 the conversion changed from 34 to 23% (see Fig. 6).

3. Influence of Zn Addition on Pt-Sn/ZSM-5

The curiosity of achieving higher propene selectivity at higher conversion leads to dope third metallic content on Pt-Sn/ZSM-5. Previously, many combinations using different alkali and alkaline earth metals were tried [41-45], but we observed that both alkali and alkaline earth metals doped zeolite catalysts were severely affected during hydrothermal treatment. Therefore, in the current experimentation we tried transition metal 'zinc' and the results indicated that the addition of zinc had an obvious impact on the propylene selectivity. It had been reported earlier that Pt/ZnO catalysts have higher hydrogenation and dehydrogenation capabilities [46,47] and the strong interactions between Zn and Pt changes electronic property and weakens the strength of the Pt-(C-C) bond to promote olefin desorption [48]. However, no literature has been found on the effects of zinc on ZSM-5 supported platinum catalysts in propane dehydrogenation.

The addition of Zn prevented the propene yield and showed higher

propene is around 20% conversion, where propene selectivity was high, while higher conversions favor ethane formation.

2. Influences of Si/Al Ratio of Support

As discussed above, the Pt-Sn supported on ZSM-5 zeolite exhibited good stability and relatively low hydrogen transfer reaction possibilities during propane dehydrogenation. Therefore, the ZSM-5 zeolite support was selected for further study to see the influence of the Si/Al ratio on propane conversion and product distribution. NH₃-TPD and FT-IR spectroscopy profiles of different Si/Al ratios ZSM-5 zeolites have been characterized by Xiangxue et al. [40]. In the NH₃-TPD profile the increase in Si/Al ratio of the HZSM-5, both strong and weak acid sites were decreased and a similar pattern was reported for FT-IR spectroscopy [40]. Therefore, the acid strength of support is directly associated with Si/Al ratio.

The effects Si/Al ratio of support on propane dehydrogenation are shown in Fig. 6. It can be seen that with increase in the Si/Al ratio, propane conversion decreased steadily due to the decrease in acidity. The propene selectivity and yield increased with the increase in Si/Al from 50 to 300 and remained almost unchanged with TOS
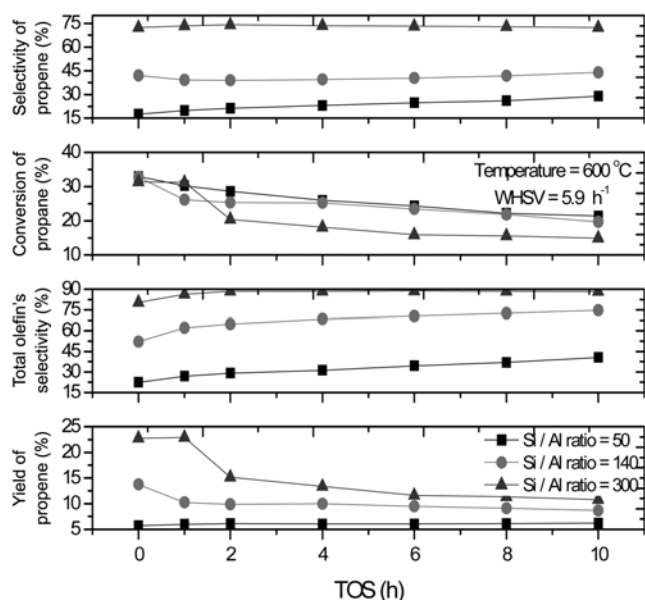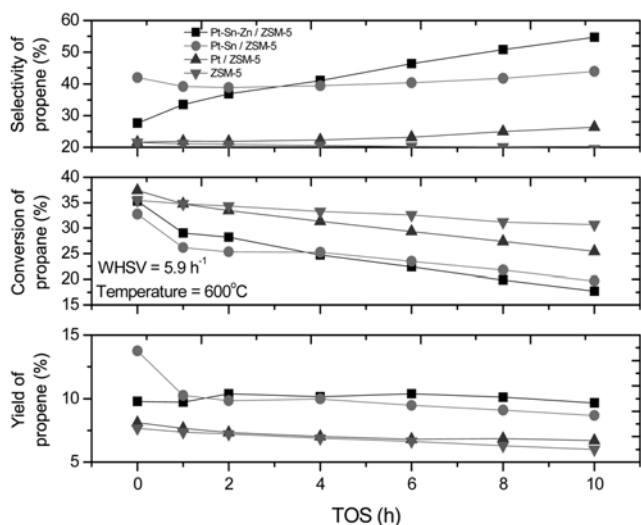
Fig. 7. Effect of Zn doping on reaction performance.

Table 1. Deactivation rate of zeolite supported catalysts of Si/Al=140

Catalyst	X_0	X_f	Deactivation rate
ZSM-5	35.13	31.94	9.99
Pt/ZSM-5	36.11	25.63	29.02
Pt-Sn/ZSM-5	32.75	19.7	39.85
Pt-Sn-Zn/ZSM-5	35.33	17.66	50.01

selectivity. However, over Pt-Sn-Zn/ZSM-5 catalyst, a part of Zn may be reduced to metallic Zn to form Pt-Zn alloy, which results in a great increase in the selectivity towards propene, but may produce some aromatics. The comparative experimental results of different catalysts at optimum WHSV and temperature are shown in Fig. 7. It is found that the selectivity and yield of Zn doped Pt-Sn/ZSM-5 is suited at the expense of lower conversion. Table 1 shows the activity decay with respect to time-on-stream of different catalysts. The deactivation rate was calculated by using the following relationship, where X_0 is the initial propane conversion at 1 minute and X_f is the final propane conversion at 10 h. It was observed that with the addition of metallic content only the selectivity was improved but it decreased the conversion.

$$\text{Deactivation rate}=[X_0-X_f]\times100/X_0 \qquad (1)$$

CONCLUSION

Direct dehydrogenation catalysts are available with their distinct characteristics, but neither a blind reliance on, nor an unfounded distrust of, their results should lead one into errors of reactor design, and therefore in this paper we characterize propane dehydrogenation reaction using zeolite supported catalyst in all respects. The increase in temperature has an obvious effect on feed conversion, while propene selectivity initially deceases and then increases with running time due to propene further cracking at higher temperature. Therefore, the optimum propane dehydrogenation temperature was estimated to be 600 °C. The higher weight hourly space velocity

(WHSV) has significantly improved propene selectivity at the cost of lower conversion. The OPE suggests that the best conversion range for propane to propene is around 20% conversion, where propene selectivity was as high as 53%, while higher conversion favors ethane. Increasing the Si/Al ratio of ZSM-5 zeolite (support) the acidity will decrease and favor propene selectivity by retarding hydrogen transfer reaction. While at higher Si/Al ratio 300 of support, high and stable selectivities of propene and total olefin were recorded, i.e., 73% and 95%, respectively. The improvement in propane selectivity is obtained over zinc-doped Pt-Sn/ZSM-5 catalysts with lower conversion and higher deactivation rate. Moreover, it is apparent that increasing the Si/Al ratio has a more distinct effect on performance of propane dehydrogenation than addition of zinc.

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