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STUDIES ON PROPANE DEHYDROGENATION TO PROPYLENE IN A GAS-SOLID-SOLID FLUIDIZED BED REACTOR

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ABSTRACT

Platinum and tin deposited on mixed support of SAPO-34 and alumina oxide at certain proportion constitute a new catalyst of good catalytic performance. The catalyst was tested in a Gas-Solid-Solid fluidized bed reactor. Cold model experiment was carried on to obtain fluidization curves and characteristic velocities. Reaction results in the GSS-FBR showed that propylene yield was improved by 5 % compared with that in micro fixed bed reactor.

INTRODUCTION

Light alkenes such as propylene are indispensable raw material in numerous (petro)chemical applications. To comply with the development of downstream industries, propylene demand has been growing quickly (1). On-purpose propylene production technologies such as direct propane dehydrogenation (PDH) have been focused on as one of major process to make up the shortfall of propylene supply left by catalytic and steam cracking of naphtha in which propylene is called a by-product (2, 3, 4).

Nowadays, chromia-alumina catalysts and platinum based catalysts are used in commercial dehydrogenation plants. In the late 1980s, Catofin technology applying chromia-alumina catalyst was commercialized by ABB Lummus (6). Then during the 1990s, UOP (Universal Oil Products, USA) developed Oleflex process. In Oleflex process, Pt-Sn/Al_2O_3 catalyst was used (7). The effect of support has been discussed by many researchers. Traditional catalysts with Al_2O_3 support had problems in application especially of stability and selectivity. As a result a variety of catalysts in which Pt-Sn was supported on various supports like SiO_2, Y-zeolite, Beta, SBA-15, MgAl(O), ZSM-5 were studied in an effort to find an optimum catalyst (5, 8, 9, 10). In our work, a kind of silicoaluminophosphate zeolite called SAPO-34 is chosen as catalyst support which is a microporous sieve with chabasite-like structure. This

zeolite has good thermal stability and is inherently resistant toward hydrothermal treatment (5), making it possible for support of the propane direct dehydrogenation catalyst.

As a highly endothermic reaction, direct dehydrogenation process is suitable to be operated in a fluid bed reactor which offers a lot of advantages such as high rate of mass and heat transfer and solids mobility. The mobility of catalyst particles gives the deactivate catalyst a chance to be regenerated. In PDH process, because of the high temperature and olefins product, coke deposited rate is high resulting in deactivation of the catalyst. In Circulating Fluidized Bed, catalysts can move into the regenerator continuously making sure of the continuous operation.

While the particle attrition rate in a fluidized bed is much faster than fixed bed reactor, to save the noble metal Pt of the PDH catalysts, an idea of binary particles fluidized bed reactor (Gas-Solid-Solid fluidization, GSS) is proposed (11). In our previous work, mechanical attrition behavior in binary fluidization was examined. The negligible attrition of large particles in the experiment indicated that GSS fluidized reactor was applicable for platinum based catalytic process (12).

This paper presents some experimental results from a study of Pt-Sn catalysts supported on SAPO-34 and specially pelletized supports making up of SAPO-34 zeolite and alumina oxide binder. Effect of the improvement in catalyst supports on catalytic activity is tested in a micro fixed bed reactor. And then in a cold model, fluidization characteristics of pelletized catalysts are studied. Finally, the process is operated in a lab-scale Gas-Solid-Solid fluidized bed reactor.

EXPERIMENTAL SECTION

Catalyst Preparation

Three kinds of supports were used in this article to compare their activity in propane direct dehydrogenation. Besides pure SAPO-34 zeolite, γ-Al_2O_3 and their mixture were also used. The specially pelletized support made up of SAPO-34 and Al_2O_3 at certain proportion was produced by a manufactory named Hui er green chemical technology corporation, Beijing.The Pt-Sn based catalyst was prepared by sequential impregnation method (5). For the three kinds of catalysts made with different supports, metallic composition was the same by 0.5, 1.0 wt % of Pt, Sn.

Catalytic Tests in a Micro Fixed Bed Reactor

The catalytic tests of different catalysts were performed using a micro fixed-bed plug

flow reactor working at atmospheric pressure. The reactor was a 8 mm i.d. and 240 mm long quartz tube placed inside an electrical furnace. Mass flow controllers were used to adjust the amount of inlet gas. The product analysis was accomplished by an online gas chromatograph. The deposited coke content in the catalyst sample was analyzed by thermal gravimetric analysis (TGA) using Netzsch STA 409.

Catalytic Tests in a Gas-Solid-Solid Fluidized Bed Reactor

Cold model fluidization experiment

To be used in the Gas-Solid-Solid fluidized bed reactor, prepared catalysts were pelletized to coarse particles with diameter of 590~840μm (20~30 mesh). SiO_2 particles of average diameter 87.76μm that had similar physical properties with FCC catalyst were used as small particles. The fluidization characteristics of that system were studied in a cold model Perspex equipment with dimensions of diameter 5 cm and height 100 cm. Pure nitrogen was used as fluidization medium.

Reactive fluidization experiment

Figure 1 shows a scheme of the Gas-Solid-Solid fluidized bed reactor used in this work. The fluidized bed reactor was a steel tube with inner diameter 50 mm and height 600 mm. Inside the tube several fins were added in order to enlarge the heat transfer area and improve the fluidization state.

Typically 50 g pelletized Pt-Sn based catalyst and 100 g small particles were charged in the fluidized bed reactor. Preheated propane and hydrogen, sometimes including inert fluidization medium nitrogen, were let into the reactor from the bottom. The flow rate of hydrogen changed as to keep the reactant ratio H_2/C_3H_8 0.25.

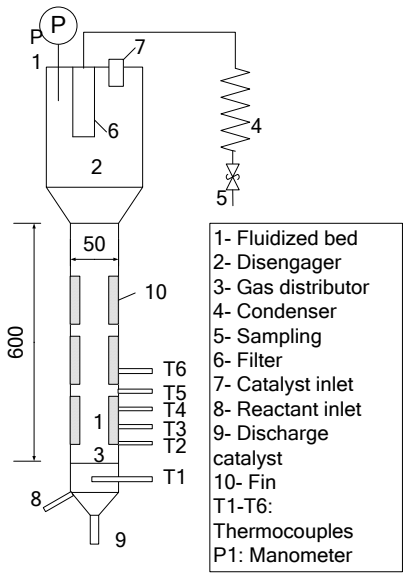

Figure 1 Scheme of the reactive fluidized bed reactor

RESULT AND DISCUSSION

Influence of Supports on Catalyst Performance

Figure 2 shows the experimental result of different catalysts in a micro fixed-bed reactor. It can be drawn that using SAPO-34 as support can largely improve propylene selectivity as has been mentioned in our previous work (5). By adding Al_2O_3 into SAPO-34 at a certain proportion as binder, the specially pelletized catalyst made a great improvement in both propane conversion and propylene selectivity.

The coke deposited catalysts were analyzed by TGA to measure the amount of coke produced during five hours' reaction. The calculated data was listed in Table 1. By comparing the coke selectivity of Pt-Sn/SAPO-34 and Pt-Sn/mixed supports, it's clear that coke selectivity decreased significantly through specially pelletization of the support. The low rate of coke deposition is one of the reasons why catalysts' activity and stability improved by using the specially pelletized support.

Figure 3 shows the different curves of TGA results of coke deposited catalysts after five hours' reaction. The position of peaks which was in accordance with literatures (5, 13) showed that coke deposited on the catalyst was of different forms. The peak at 450^{o}C shows coke deposit on Al_2O_3 support while the peak at 630^{o}C represents coke deposit on SAPO-34 support. In the mixed carriers, two kinds of coke existed simultaneously.

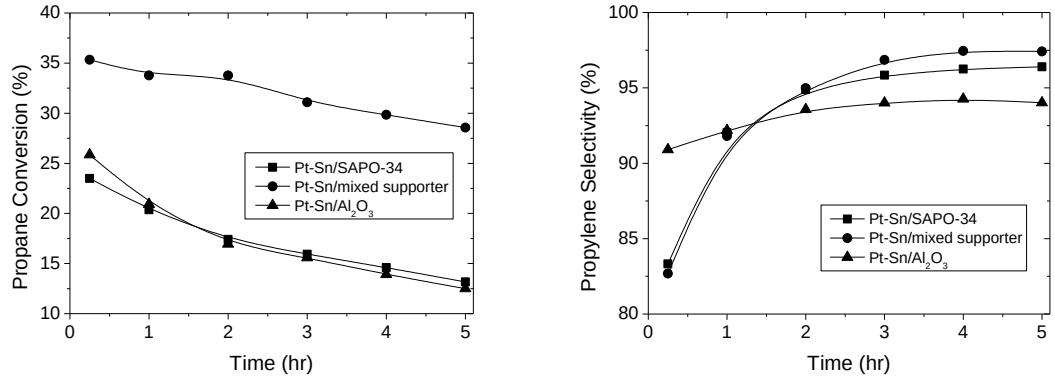

Figure 2 Evolution of catalyst performance with time in micro fixed bed reactor. T=863K; WHSV=2.8 h^{-1}; $m_{catalyst}$=200mg; Q_{C3H8}=5.5 ml/min; Q_{H2}=0.25 Q_{C3H8} .

Table 1 The amount of coke formed after five hours' on-stream and selectivity for coke of the three kinds of catalyst calculated from TGA results

Catalyst	C, wt%	S_{coke}, %
Pt-Sn / SAPO-34	7.68	4.11
Pt-Sn / mixed support	10.73	2.98
Pt-Sn / Al_2O_3	5.3	2.90
Pt-Sn / mixed support*	8.25	1.06

* This catalyst was tested in the GSS-FBR.

Fluidization Properties of Binary Mixtures in the GSS-FBR

To determine the proper range of operating parameters, experiments in a cold model of same diameter to the hot model reactor were done using 50 g pelletized Pt-Sn based catalyst and 50 g SiO_2 particles. Figure 4 shows the fluidization curve and the calculated minimum fluidization velocity is 0.035 m/s.

Fluidization of binary particles with significhant difference had been studied decades of years and several formulas to calculate U_{mf} had been described. In this work a semi-empirical formula presented by Noda was chosen to calculate the minimum fluidization velocity (14). Calculative process was as follows:

Calculation of the average density and diameter of the mixture:

$$\frac{1}{\rho_m}=\frac{\omega_f}{\rho_f}+\frac{\omega_p}{\rho_p};\qquad \frac{1}{d_m\rho_m}=\frac{\omega_f}{d_f\rho_f}+\frac{\omega_p}{d_p\rho_p}$$

Calculation of U_{mf} with the following equation:

$$Ar=A\mathrm{Re}_{mf}^2+B\mathrm{Re}_{mf}$$

In which,

$$Ar=\frac{d_m^3\rho'(\rho_m-\rho')g}{\mu^2};\qquad \mathrm{Re}_{mf}=\frac{d\rho' u_{mf}}{\mu}$$

$$A=36.2\left(\frac{d_p}{d_f}\cdot\frac{\rho_f}{\rho_p}\right)^{-0.196};\qquad B=1397\left(\frac{d_p}{d_f}\cdot\frac{\rho_f}{\rho_p}\right)^{0.296},\ if\quad d_p/d_f>3$$

By using formula listed above, the U_{mf} of our fluidization system can be calculated and its value was 0.041 m/s. There were some difference between the experimental result and the calculated result. This had something to do with the wide diameter distribution of the large particles as well as the limitation of applicable range of the formula.

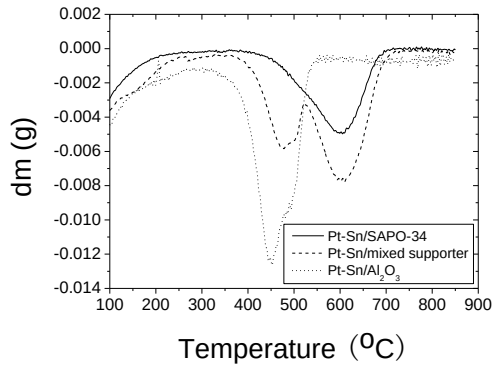

Figure 3 TGA results of coke deposited catalysts

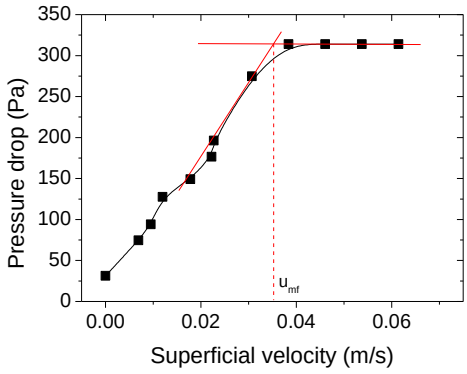

Figure 4 Cold model fluidization result of the binary mixture

Reactive Fluidization Experiment

Figure 5 shows the evolution of propane conversion and propylene selectivity with time in the micro fixed bed reactor and in the Gas-solid-solid fluidized bed reactor. The experiments used the same specially pelletized catalysts and were run under the same temperature, weight hourly space velocity of propane and H_2/C_3H_8 ratio that had been optimized in micro fixed bed reactor previously (15). It can be seen that propane conversion was more stable in the fluidized bed reactor compared to the fixed bed reactor. After six hours' reaction, the remaining conversion was about 60 % of the initial in fixed bed reactor while in fluidized bed reactor that percentage was about 95 %. For selectivity of propylene, in both reactors, trend of two curves was identical that in the initial period a significant increase existed and finally a stable state of higher than 96 % can be achieved. In the GSS-FBR, though the growth speed of selectivity was slower, high selectivity of 97 % remained steady in the later 4 hours. Propylene yield was improved by 5 % in the GSS-FBR than the fixed bed reactor.

This improvement in propylene yield profits from the high value of heat transfer coefficient in the fluidized bed reactor. Due to uniform bed temperature in the reactor, the selectivity of coke deposition and byproduct like methane and ethylene resulting form propane cracking would decrease. The value of coke deposited on catalyst after five hours' reaction in the GSS-FBR was measured by TGA and listed in Table 1. Coke selectivity was found to be much lower than that of the same catalyst tested in fixed bed reactor.

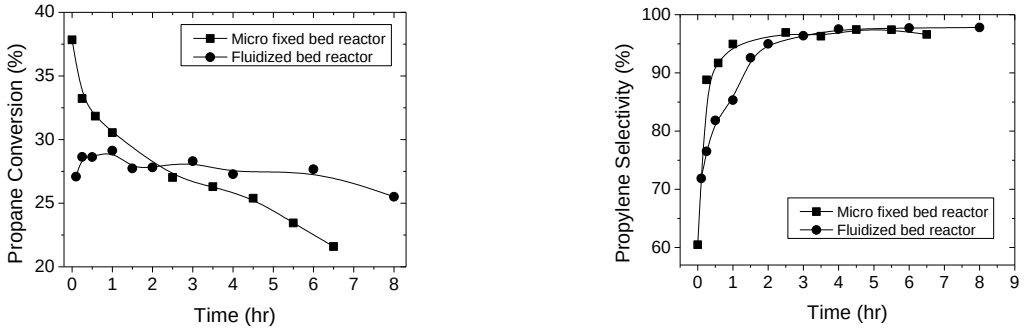

Figure 5 Comparison of catalytic performance in fixed bed reactor and fluidized bed reactor.T=863K; WHSV=5.6 h^{-1}; In micro fixed bed reactor: $m_{catalyst}$=100mg ; Q_{C3H8}=4.75 ml/min; Q_{H2}=0.25 Q_{C3H8}. In fluidized bed reactor: $m_{catalyst}$ = 50 g; Q_{C3H8} = 2.38 L /min; Q_{H2} = 0.25 Q_{C3H8}.

CONCLUSION

Pt-Sn based catalysts were tested in a micro fixed bed reactor and the specially pelletized catalyst of higher conversion, better stability and lower coke selectivity than others was chosen to be tried in the Gas-solid-solid fluidized bed reactor. Cold model experiment was run to study the fluidization characteristics of binary particles mixture with significant size difference obtaining fluidization curves and minimum fluidization velocity. Finally, using the chosen catalyst as big particle and inert substance SiO_2 as small particle, propane dehydrogenation reaction was tried in a fluidized bed reactor. Stable propane conversion and high propylene selectivity were achieved. The reaction result in the GSS-FBR indicated that this design of fluidized bed reactor was practicable for PDH process.

NOTATION

GSS-FBR: Gas-solid-solid fluidized bed reactor
TGA: Thermal gravimetric analysis
WHSV: Weight hourly space velocity, h^{-1}
U_{mf}: Minimum fluidization velocity, m/s
ρ_m: Density of mixed particles, kg/m^3
d_m: Diameter of mixed particles, m
ω_f: Mass fraction of fine particle,
ω_p: Mass fraction of large particle
ρ_f: Density of fine particle, kg/m^3
ρ_p: Density of large particle, kg/m^3
d_f: Diameter of fine particle, m

d_p: Diameter of large particle, m
ρ': Density of gas, kg/m^3
μ: Viscosity of gas, Pa•S
g: Acceleration due to gravity, m/s^2

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