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Metathesis of ethylene and butylene-2 to propylene with Mo on Hβ-Al_2O_3 catalysts

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Abstract

Reaction performance, acidic and basic properties, as well as reduction properties of various supported molybdenum catalysts for the metathesis of ethylene and butylene-2 to propylene were investigated by TPR and NH_3-TPD techniques in a flow-reactor. Besides temperature, space velocity and pressure, the stability of a Mo/(Hβ-Al_2O_3) catalyst is strongly affected by the Mo loading, the calcination temperature and the hydrothermal treatment conditions. A suitable molybdenum loading on Hβ-Al_2O_3 is favorable to the stability of the catalyst that possesses suitable amount of acidity, which was determined by NH_3-TPD measurements. The optimum preparation conditions of the Mo/(Hβ-Al_2O_3) catalyst are as follows: molybdenum content 3 wt.%, hydrothermal treatment and calcination at 550 °C for 2 h and 700 °C for 2 h, respectively. Thus, the optimal catalyst of 3Mo/(Hβ-Al_2O_3), designated as 3Mo/Hβ5502700, could keep a conversion of C_4H_8-2 at about 82% during 22 h of reaction time-on-stream under the following conditions: $N_2/C_2H_4 = 1.5$, $C_2H_4/C_4H_8\text{-}2 = 3/1$, $\mathrm{WHSV}(C_2H_4 + C_4H_8\text{-}2) = 1\,h^{-1}$, $T = 120\,°C$, and $P = 1.0\,MPa$. In addition, a suitable pressure, such as 0.5–1.0 MPa, and a low temperature, such as 35 °C, are beneficial for keeping the stability of the 3Mo/Hβ5502700 catalyst.

Keywords: NH_3-TPD techniques; Mo/(Hβ-Al_2O_3) catalyst; Hydrothermal treatment

1. Introduction

A large number of solid catalysts have been reported as active for the metathesis of alkenes. The most superior catalysts are those based on rhenium, molybdenum and tungsten [1]. Of these, Re_2O_7 catalysts supported on alumina or silica-alumina are the most interesting ones, as they are highly active and selective even at room temperature. However, the costs of rhenium compounds are high, and catalysts with low rhenium loadings have only negligible activities [2]. Supported molybdenum oxide catalysts have received much attention because they are widely used in industrial petrochemical processes, including metathesis of alkenes. Their surface properties and catalytic activities are strongly dependent on the specific oxide support, the surface Mo-oxide content, and the calcination temperature, etc. In the present work, molybdenum based catalysts have been investigated for the metathesis of propylene to ethylene and butylene-2. The catalysts studied included MoO_3/SiO_2, MoO_3/TiO_2, $MoO_3/SiO_2{\cdot}Al_2O_3$, MoO_3/Al_2O_3, MoO_3/MgO and MoO_3/ZrO_2, etc. [1]. Moreover, we have reported that Mo/(Hβ-Al_2O_3) catalyst is the best catalyst among the catalysts evaluated, namely, Mo/MgO, Mo/Al_2O_3, Mo/MCM-22, Mo/ZSM-35, Mo/Silicate and 6Mo/SAPO-11 [3]. In this paper, besides reaction temperature, pressure and space velocity, the influence of Mo content as well as hydrothermal and calcination conditions on the reaction performance of the Mo/(Hβ-Al_2O_3) catalyst are reported.

2. Experimental

2.1. Preparation of the catalyst and its reaction performance

The zeolite support Hβ-A (specific surface area: 494 m^2/g) was obtained from the Second Refinery of Fushun

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Petrochemical Corporation of China, which was prepared by first binding the pure zeolite Hβ ($Si/Al_2 = 30$) and Al_2O_3 (20 wt.%) together, then calcining in air at 550 °C for 2 h before impregnation.

The molybdenum catalyst was prepared by impregnating the Hβ-A with an appropriate amount of $(NH_4)_6Mo_6O_{24}\cdot 4H_2O$ for 24 h, then drying at 120 °C, and calcining in air at 400–850 °C [3]. Hereafter, the Mo/support catalysts are denoted as x Mo/support, where x is the Mo loading in weight percent.

The catalysts were tested in a fixed-bed flow microreactor of 10 mm internal diameter, and 5 g of catalyst with an average particle size of 0.56–1.3 mm was loaded. An EU-2 type thermocouple was fixed in the middle position of the catalyst bed at the outside of the steel reactor to measure the temperature of the electric furnace, which was taken as the reaction temperature. After the catalyst was pretreated in situ at 500 °C and 0.1 MPa with high purity N_2 (30 ml/min) for 1 h, it was cooled to the reaction temperature in flowing N_2. The catalyst was then used for the metathesis of ethylene and butylene-2 to propylene. The reaction conditions are as follows: temperature = 35–150 °C, pressure = 0.1–3.0 Mpa, $N_2/C_2H_4 = 1.5$, $C_2H_4/C_4H_8\text{-}2 = 3$, WHSV($C_2H_4 + C_4H_8$-2) = 0.2–4 h^{-1}, and catalyst = 5.0 g. The reaction products are analyzed by a gas chromatograph with a TCD detector. The conversions of ethylene and butylene-2 are calculated on the basis of carbon number.

2.2. Characterization of catalyst

NH_3-TPD measurements were performed in a conventional flow apparatus using a U-shaped microreactor (4 mm i.d.) made of stainless steel, with helium (He) as the carrier gas. The NH_3-TPD process was monitored by a gas chromatograph with a TCD detector. A catalyst sample of 0.140 g, after pretreatment at 600 °C for 0.5 h in a He stream with a flow rate of 25 ml/min, was cooled to 150 °C. It was then saturated with an NH_3-containing He stream for 10 min. The sample was purged with a He stream for a certain period of time, until a constant baseline was attained. NH_3-TPD was carried out in the range of 150–700 °C at a heating rate of 18.8 °C/min [4].

H_2-TPR profiles were recorded by an on-line computer at a programmed temperature rate of 14 °C/min in a 10% H_2/Ar flow after the samples had been pretreated in an Ar flow at 500 °C for 30 min.

3. Results and discussion

The metathesis of mixtures of ethylene and butylene-2 ($CH_2{=}CH_2 + CH_3{-}CH{=}CH{-}CH_3 {=} 2CH_3{-}CH{=}CH_2$) is an equilibrated reaction, which is slightly exothermic ($-\Delta H \sim 1.7$ kJ/mol). Besides the main metathesis reaction, butylene-2 contains an equilibrium amount of butylene-1, which will enter into the secondary metathesis reactions, leading to the formation of byproducts. The reaction between butene-1 and butylene-2 produces propylene and pentylene-2. Another reaction is the butylene-1 itself, leading to ethylene and hexane-3. The latter reaction is less important due to the lower reactivity of butylene-1, so that hexenes are observed only in trace amounts [5]. In our experiments for the metathesis over the Mo supported on Hβ-A, the products are C_3H_6, C_5H_{10}, C_6H_{12}, C_7H_{14}, and C_8H_{16}, etc. The C_3H_6 selectivity is above 90%, and the conversion of C_2H_4 increases with that of C_4H_8-2. Hereafter, we use the C_4H_8-2 conversions to represent the catalytic activities.

3.1. Reaction performance of catalysts with different Mo contents on the Hβ-A support

Mo/Al_2O_3 and Re/Al_2O_3 samples are reported to be good catalysts for the metathesis of ethylene and butylene to propylene [1]. In this work, we have compared the reaction performances of $6Mo/Al_2O_3$, $9Re/Al_2O_3$ and 6Mo/Hβ-A catalysts under the same reaction conditions. The results show that the $6Mo/Al_2O_3$ is the worst among the three catalysts, while the reaction performance of 6Mo/Hβ-A is similar to that of $9Re/Al_2O_3$, which indicates that the Mo/Hβ-A catalyst is a suitable catalyst for the process.

Based on the above results, the reaction performance as a function of molybdenum loading on Hβ-A support was investigated. As shown in Fig. 1, there is almost no C_4H_8-2 conversion on the Hβ-A support. The initial C_4H_8-2 conversion increases with the Mo loading on the Hβ-A support from 1 to 3 wt.%, arriving a plateau as the Mo loading was between 3 and 9 wt.%, then decreases with the increase of the Mo content to above 12 wt.%. Thomas and Moulijin [6] have reported that the catalytic activity of MoO_3/Al_2O_3 is highly dependent on the molybdenum loading of the catalysts. The catalytic activity first increases with the surface coverage of molybdenum, then passes through a maximum. In addition, as shown in Fig. 1, the stability of the catalyst is also affected by the Mo loading on Hβ-A. The stable time on stream drops distinctly with the increment of the molybdenum loading from 3 to 12 wt.%.

The interaction between the Mo and the Hβ-A support was investigated by the H_2-TPR technique. The H_2-TPR profiles of Mo/Hβ-A samples with different Mo loadings are shown in Fig. 2. The Hβ-A support has no H_2 reduction peaks (not shown). The three peaks, denoted as l, m and h, centered at about 550, 650 and 900 °C, respectively, can be observed obviously on the 12Mo/Hβ-A catalyst. According to Refs. [7,8], the l, m and h peaks correspond to the reduction of polymolybdate or multilayered Mo oxide to MoO_2, $Al_2(MoO_4)_3$ and microcrystalline MoO_3 to MoO_2, and MoO_2 to Mo, respectively. As shown in Fig. 2, the amount of H_2 consumption decreases with the molybdenum loading on the Hβ-A support. Besides, the l peak shifts to a lower temperature.

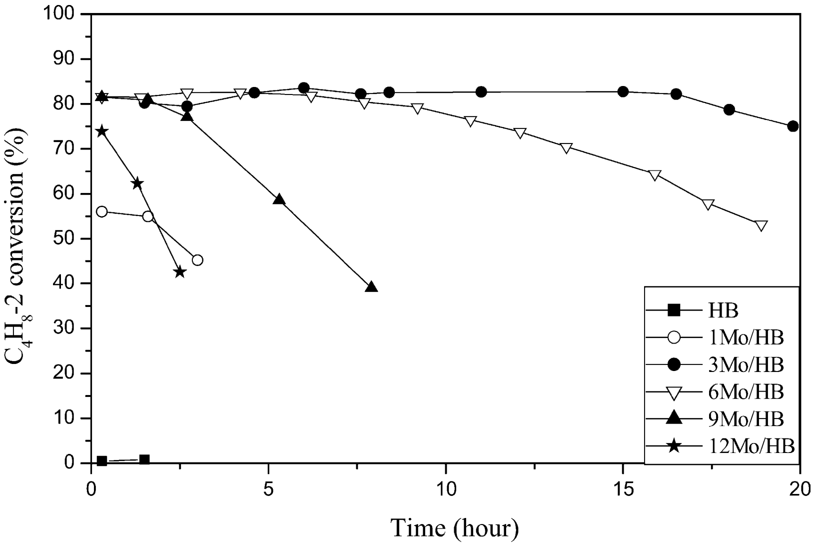

Fig. 1. C_4H_8-2 conversion as a function of Mo loading on the Hβ-A support for the metathesis of ethylene and butylene-2 to propylene (HB in the figure represents Hβ-A) $N_2/C_2H_4 = 1.5$, $C_2H_4/C_4H_8\text{-}2 = 3/1$, WHSV$(C_2H_4 + C_4H_8\text{-}2) = 1\,h^{-1}$, $T = 120\,°C$, $P = 1.0$ MPa.

When a catalyst such as 3Mo/Hβ-A was first pretreated in H_2 at 550 or 650 °C for 2 h, then the pretreatment gas H_2 was switched to the feed of ethylene and butylene-2, rather poor activity and stability were observed. When the pretreatment gas H_2 was replaced by N_2, the 3Mo/Hβ-A catalyst demonstrated a good reaction performance, as shown in Fig. 1. This indicates that the molybdenum species which are in an oxidation state, such as MoO_3 and $Al_2(MoO_4)_3$, are probably the reaction centers. However, too much molybdenum species existing in the oxidation state would deteriorate the catalyst stability (Figs. 1 and 2), owing to the oligomerization of the olefins present, and results in a faster rate of catalyst deactivation (more than three orders of magnitude) [9]. From the above results, we can conclude that the 3Mo/Hβ-A catalyst is the best one among the catalysts evaluated, which possesses a suitable Mo loading on the support, and could keep a conversion of C_4H_8-2 at about 82% during the 16 h of time-on-stream.

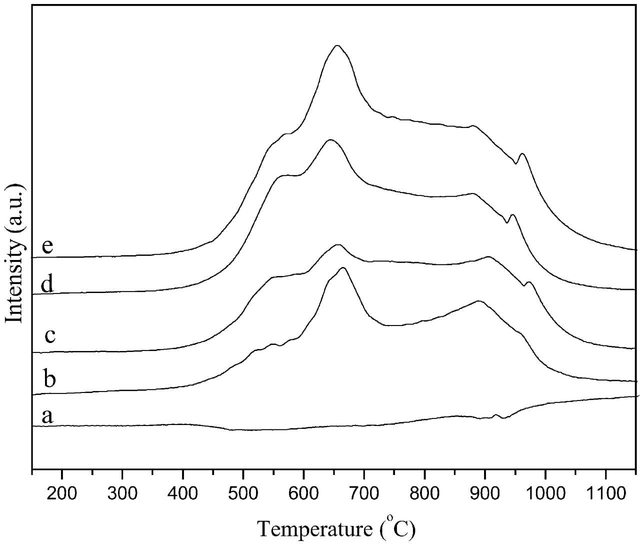

Fig. 2. TPR profiles of: (a) 1Mo/Hβ-A, (b) 3Mo/Hβ-A, (c) 6Mo/Hβ-A, (d) 9Mo/Hβ-A, (e) 12Mo/Hβ-A.

3.2. *Effects of hydrothermal treatment condition and calcination temperature on reaction performance of the 3Mo/Hβ-A catalyst*

The effect of hydrothermal treatment condition on the catalytic activity and stability was also compared. Dealumination of Hβ-A was realized by a steaming method, resulting in a series of dealuminated samples. The steam treatment conditions (temperature/°C, pressure of water/mmHg, and time/h) of a series of Hβ-A were (450, 290, 2), (550, 290, 2), (650, 290, 2) and (550, 290, 6), respectively. After the steam treatment, the samples were directly impregnated with an aqueous solution of ammonium heptamolybdate. Then, the catalysts were dried at 120 °C for 4 h, and calcined in air at 600 °C for 2 h. In Figs. 3 and 4, 3Mo/Hβ5502600 means that the Hβ-A support was treated under a steam flow at 550 °C for 2 h, and the 3Mo/Hβ5502 sample was calcined at 600 °C for 2 h. The sample after hydrothermal treatment at 450 or 550 °C for 2 h shows better stability than that without any hydrothermal treatment (3Mo/Hβ0000600 in Fig. 3), but too severe dealumination of the Hβ-A results in a decrease of stability of the catalyst, as shown by comparing 3Mo/Hβ6502600 and 3Mo/Hβ5506600 with 3Mo/Hβ0000600 in Fig. 3.

Similarly, the effect of calcination temperatures of the catalysts on their reaction performances were also investigated. As shown in Fig. 4, under the same hydrothermal treatment condition (550 °C for 2 h), the catalyst stability increases with the calcination temperature from 450 to 700 °C. The stable time is 9, 12, 20 and 22 h when the calcination tem-

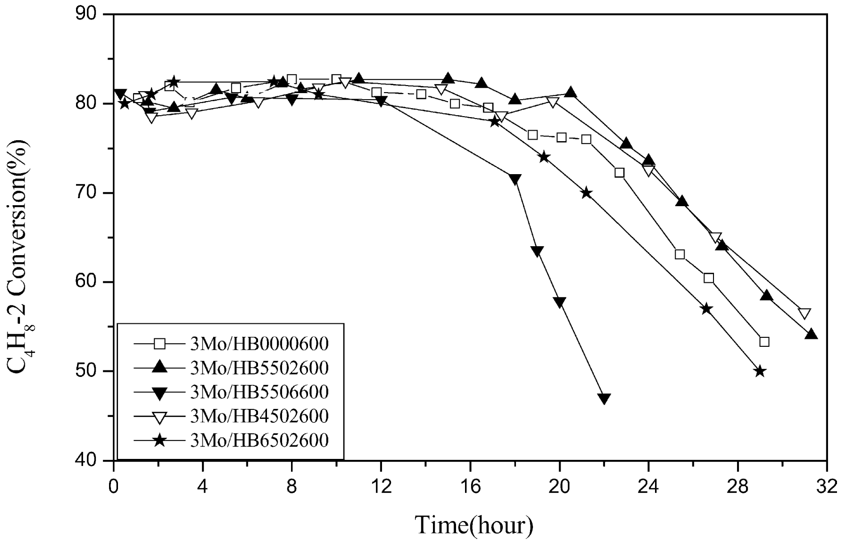

Fig. 3. Reaction performance under different hydrothermal treatment conditions (HB in the figure refers to Hβ-A) $N_2/C_2H_4 = 1.5$, $C_2H_4/C_4H_8\text{-}2 = 3/1$, $\text{WHSV}(C_2H_4 + C_4H_8\text{-}2) = 1\,h^{-1}$, $T = 120\,°C$, $P = 1.0\,MPa$.

peratures of the 3Mo/Hβ5502 catalyst are 450, 550, 600 and 700 °C, respectively. However, almost no stable time could be recorded when too high a calcination temperature, such as 850 °C, is employed.

Commereuc et al. have proposed that the relation between the stabilities of Re based catalysts with time is governed at least in part by the Lewis acidity of the active rhenium centers [10]. Hsu has claimed that both Bronsted acid and Lewis acid influence the activity [11]. In this work, we used the NH_3-TPD method to measure the catalyst acidity. Figs. 5 and 6 show the NH_3-TPD profiles of the 3Mo/Hβ-A catalyst under different hydrothermal treatment conditions and calcination temperatures. A main desorption peak centering at about 250 °C, as well as a tail-like peak, could be observed for each sample. When increasing the hydrothermal treatment temperature or the calcination temperature, both acid amount and strength of the sample decrease, besides the main desorption peak position shifts to a lower temperature. By correlating the catalyst stability with the catalyst acidity, it suggests that a suitable amount of acidity is beneficial to the catalyst stability, but not the initial activity. It was found that the 3Mo/Hβ5502700 catalyst is an optimum one, which has suitable amount of acid sites, keeping a conversion of C_4H_8-2 at about 82% during the 22 h of reaction time-on-stream.

3.3. Influence of reaction condition on reaction performance of the 3Mo/Hβ-A catalyst for metathesis of ethylene and butylene-2 to propylene

The effects of reaction temperature and space velocity on the activity of the 3Mo/Hβ-A catalyst (3Mo/Hβ5502700

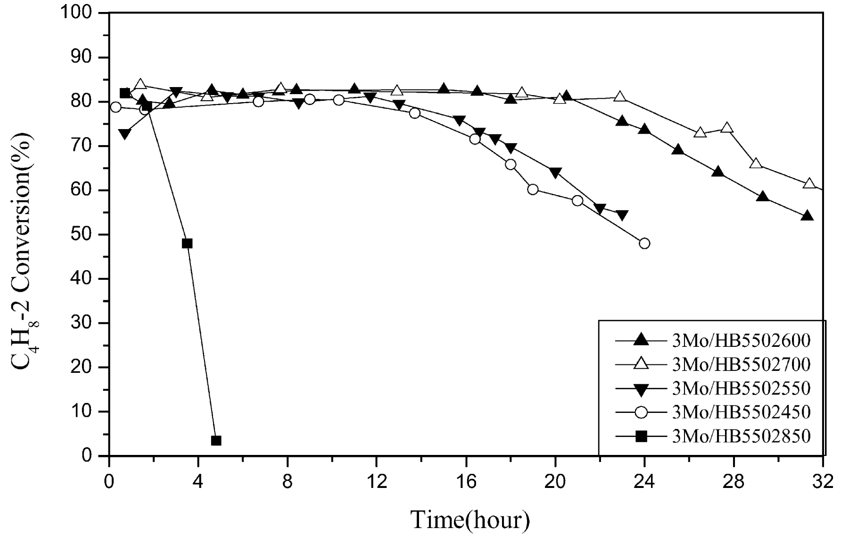

Fig. 4. Reaction performance of the 3Mo/Hβ-A catalyst as a function of calcination temperature $N_2/C_2H_4 = 1.5$, $C_2H_4/C_4H_8\text{-}2 = 3/1$, $\text{WHSV}(C_2H_4 + C_4H_8\text{-}2) = 1\,h^{-1}$, $T = 120\,°C$, $P = 1.0\,MPa$.

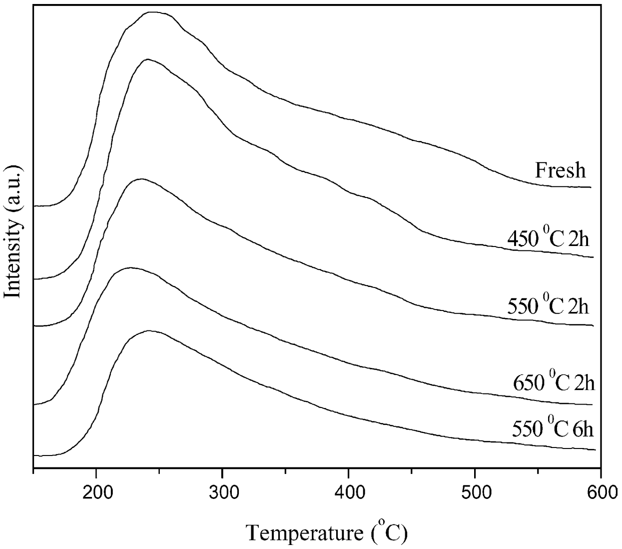

Fig. 5. NH_3-TPD profiles of the 3Mo/Hβ-A catalyst under different hydrothermal treatment conditions (catalyst calcination temperature = 600 °C, $t = 2$ h).

in Fig. 6) for the metathesis of ethylene and butylene-2 to propylene at 1.0 MPa were investigated. Although the reaction temperatures are different, the initial C_4H_8-2 conversions are similar (about 82%), but the catalyst stability decreases with the rising of the reaction temperature, owing to the increase of byproducts such as polymers. On the other hand, it is reasonable that the catalyst stability increases with the lowering of the space velocity. It is quite interesting that the pressure also affects the catalyst stability (Fig. 7). From the process of ($CH_2{=}CH_2 + CH_3{-}CH{=}CH{-}CH_3{=}2CH_3{-}CH{=}CH_2$), it seems that the reaction pressure should not have an impact on the stability of the catalyst. However, the stability of the catalyst decreases when the pressure is changed from 0.5 to 3.0 MPa, which maybe due to the fact that the increase in pressure enhanced the polymerization reaction such as $2C_4H_8 = C_8H_{16}$, etc. In the present work, it was found that the C_3H_6 selectivity actually decreases with increasing reaction pressure. In spite the initial C_4H_8-2 conversions are similar, the stability of the catalyst at 0.1 MPa is the worst among the pressures investigated, implying that other factors might also influence the reaction stability. Detailed studies are in progress. At present, it is clear that a suitable pressure such as 0.5–1.0 MPa is beneficial to the catalyst stability.

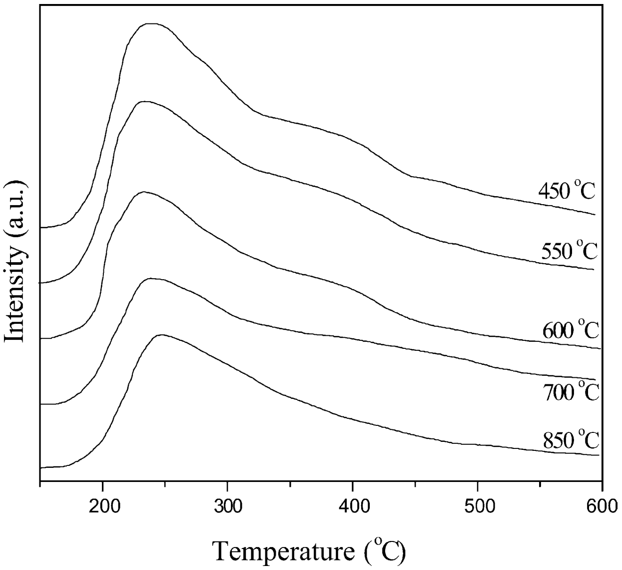

Fig. 6. NH_3-TPD profiles of the 3Mo/Hβ-A catalyst under different calcination temperatures (catalyst hydrothermal treatment condition: temperature = 500 °C, pressure of water = 290 mmHg, time = 2 h).

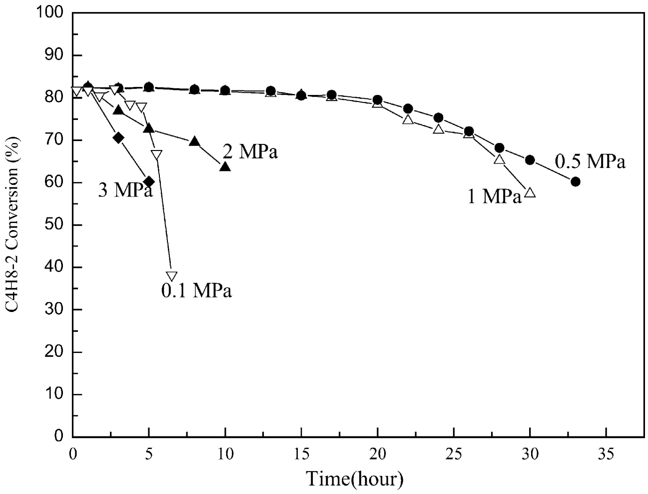

Fig. 7. Reaction performance of the 3Mo/Hβ-A catalyst as a function of pressure $N_2/C_2H_4 = 1.5$, $C_2H_4/C_4H_8\text{-}2 = 3/1$, WHSV($C_2H_4 + C_4H_8$-2) $= 1\,h^{-1}$, $T = 120\,°C$.

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