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Simultaneous dehydrogenation and isomerization of n-butane to isobutene over Cr/WO_3–ZrO_2 catalysts

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A series of WO_3-promoted Cr_2O_3-based catalysts were prepared and tested for the simultaneous dehydrogenation and isomerization of n-butane to isobutene. It is found that a Cr_2O_3/WO_3–ZrO_2 system is an effective catalyst for this reaction; however, the catalytic behavior is dependent on Cr_2O_3 and WO_3 contents, space velocity and temperature. 10 wt% Cr_2O_3/20 wt% WO_3–ZrO_2 can give high initial conversion and isobutene selectivity, but it deactivates rapidly due to the variation of surface properties and pore structure caused by carbon deposition.

Keywords: butane, dehydroisomerization, isobutene, Cr_2O_3/WO_3–ZrO_2 catalysts

1. Introduction

Isobutene is an important intermediate for many common petrochemicals and plastics. Its most widely usage is the synthesis of a fuel additive, MTBE. However, the direct supply of isobutene is limited. Large amounts of isobutane are readily available from natural gas and refinery. Therefore, production of isobutene from isobutane has caused an intensive interest in petrochemical industry. At present, most of researchers concentrate their efforts on the development of effective catalysts for the conversion of isobutane by either dehydrogenation or oxidative dehydrogenation [1].

Recently, a new process to produce isobutene from n-butane has been proposed and tested, which adopts a two-bed reactor where an isomerization step is followed by a dehydrogenation step or *vice versa*. Byggningsbacka et al. [2] have reported the combination of Zn/K-ZSM5 with a ZSM-22 system for this reaction and achieved 5% isobutene yield. Direct conversion of n-butane to isobutene is an interesting process, which can replace the above twin-reactor system. For this process, a new catalyst system, which possesses bifunctional properties for both dehydrogenation and isomerization, should be developed. It has been known that isomerization reactions generally take place on acid catalysts. High activity and selectivity of 1-butene isomerization can be achieved over the catalysts with large amount of Brønsted sites such as tungsten-oxide-promoted alumina and various types of zeolites [3]. Meanwhile, superacid solid catalysts such as sulfated zirconia or tungstated zirconia oxide are also effective for n-butane isomerization [4]. Cr_2O_3-based catalysts are believed to be effective for hydrogenation, isomerization of olefins and dehydrogenation of alkanes [5,6]. Several researchers have reported investigations on the oxidative dehydrogenation of butane over supported Cr_2O_3 catalysts [1,7]. Therefore, it is assumed that Cr_2O_3-based catalysts supported on a superacid solid could be effective for dehydroisomerization of n-butane to isobutene. In this paper, we reported a preliminary investigation on the application of tungsten-oxide-promoted Cr_2O_3/ZrO_2 catalysts for butane dehydroisomerization, focusing on the influence of catalyst variables and reaction parameters on the catalytic behavior in this reaction.

2. Experimental

Two catalyst supports, Al_2O_3 and SiO_2, were obtained as commercial products from Wako Chemicals. ZrO_2 samples were prepared by precipitation of $ZrO(NO_3)_2$ (Wako Chemicals) via dropwise addition of $NH_3\cdot H_2O$ at $pH = 10$, filtration and drying overnight at 105 °C. The resultant $Zr(OH)_4$ was then calcined at 300 °C for 3 h to obtain the amorphous ZrO_2. All tungsten-oxide-promoted supports were prepared by wetness impregnation on the supports with ammonium tungstate hydrate (Wako Chemicals), followed by calcination at 600 °C for 3 h. Cr_2O_3-based catalysts were then prepared by impregnation of $Cr(NO_3)_3$ on those promoted oxide samples and calcination at 600 °C for 3 h again.

BET surface areas of the catalysts were determined by N_2 adsorption at -196 °C using a Micromeritics volumetric instrument provided by Shimadzu. The adsorption and temperature-programmed desorption (TPD) of NH_3 experiments were carried out on a special NH_3-TPD apparatus (Ohkura Riken) interfaced to a personal computer. TPD profiles were obtained under vacuum conditions. The desorption temperature varied from 100 to 600 °C at 10 °C/min in the TPD process.

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Table 1
Catalytic performance of the various Cr-based catalysts at 500 °C.

Catalyst	Conversion (%)	Selectivity (%)							
		1-C_4H_8	Iso-C_4H_8	*trans*-2-C_4H_8	*cis*-2-C_4H_8	1,3-C_4H_6	C_1	C_2	C_3
Cr/WO_3–SiO_2	7.8	28.4	0.08	37.4	26.9	4.5	0.4	1.1	1.2
Cr/WO_3–Al_2O_3	12.8	23.2	0.1	33.6	24.3	8.2	5.9	2.7	1.6
Cr/WO_3–ZrO_2	45.0	26.4	0.4	34.7	24.9	3.8	6.0	2.3	1.3

The catalytic reactions were carried out in a high-purity alumina reactor under atmospheric pressure at 500 °C. The reactor was loaded with 1 g catalysts in most cases, unless otherwise indicated. The gas mixture consisted of n-butane and argon at a ratio of $10:90$ with a flow rate of 60 ml/min. The reactant and product concentrations were analyzed by two on-line gas chromatographs (Shimadzu GC-8A) equipped with a FID and a TCD, respectively. The TCD was used to detect n-butane, CO, CO_2 and H_2 while the FID was employed to determine all hydrocarbons.

3. Results and discussion

Table 1 presents the catalytic performance of chromium-based catalysts with 5 wt% Cr_2O_3 and 6 wt% WO_3 on the different supports in dehydroisomerization of n-butane at 500 °C. The three catalysts show a different butane conversion but similar butene selectivity around 80–90%, indicating that they are effective for dehydrogenation. The selectivity to isobutene is lower than 1% over all catalysts, which is indicative of a low amount of acidic sites for isomerization. Cr/WO_3–ZrO_2 shows the highest conversion and isobutene selectivity. Although Cr/WO_3–SiO_2 exhibits the lowest butane conversion, it produces the highest butene selectivity and the lowest cracking products C_1–C_3. Cr/WO_3–Al_2O_3 exhibits a medium butane conversion but the highest selectivity to butadiene. Therefore, in terms of catalytic conversion and isobutene selectivity, Cr/WO_3–ZrO_2 is the best catalyst.

The catalytic properties of the supported chromium catalysts are strongly affected by the redox and acid/base properties of the oxide-supported catalysts. Rossi et al. [8] have investigated isobutane dehydrogenation over Al_2O_3-, SiO_2- and ZrO_2-supported Cr_2O_3 catalysts. They found that zirconia-supported Cr_2O_3 catalysts could give higher activity than that over Cr_2O_3/Al_2O_3 and Cr_2O_3/SiO_2, which is similar to the observations in this investigation. The activation of hydrocarbons by a catalyst required the existence of an affinity between the alkane and the surface of the catalyst. The acid–base interaction between the hydrocarbon molecule and the surface of the oxide promotes the approach of the former to the active site. Larger hydrocarbons have a negative charge and should show a stronger interaction with acid catalysts [9]. It has been known that WO_3–ZrO_2 is an acid catalyst and thus Cr/WO_3–ZrO_2 will have higher acidity than that of the Cr/WO_3–Al_2O_3 and Cr/WO_3–SiO_2. Therefore, a higher conversion will be achieved on the Cr/WO_3–ZrO_2 catalyst. In addition, the higher isobutene selectivity over it is probably due to the high acidity.

It is generally assumed that the dehydrogenation over a bifunctional catalyst occurs firstly and is then followed by an isomerization. Therefore, active sites for dehydrogenation and acidic sites for isomerization are both needed so as to obtain a better yield of isobutene. In order to obtain catalysts with higher acidity and selectivity to isobutene, we prepared a series of Cr/WO_3–ZrO_2 catalysts at high WO_3 loading. Figure 1 shows the effect of WO_3 loading on catalytic behavior of Cr/WO_3–ZrO_2. The data were obtained after 1 h reaction. As shown, butane conversion and butene selectivity decrease with the increasing WO_3 loading while isobutene selectivity increases with the increasing WO_3 loading. When the WO_3 content is at 6 wt%, isobutene selectivity does not show a remarkable improvement, which suggests that lower amount of WO_3 on the catalyst may not be sufficient enough to increase the acidity and acid active sites. However, when the WO_3 loading is increased to a certain degree, ca. over 9 wt%, the isobutene selectivity will be significantly enhanced and will reach a plateau of 30% at 20 wt% WO_3. From the results shown above, it is deduced that the increase in the active sites for isomerization results in the loss of the active sites for de-

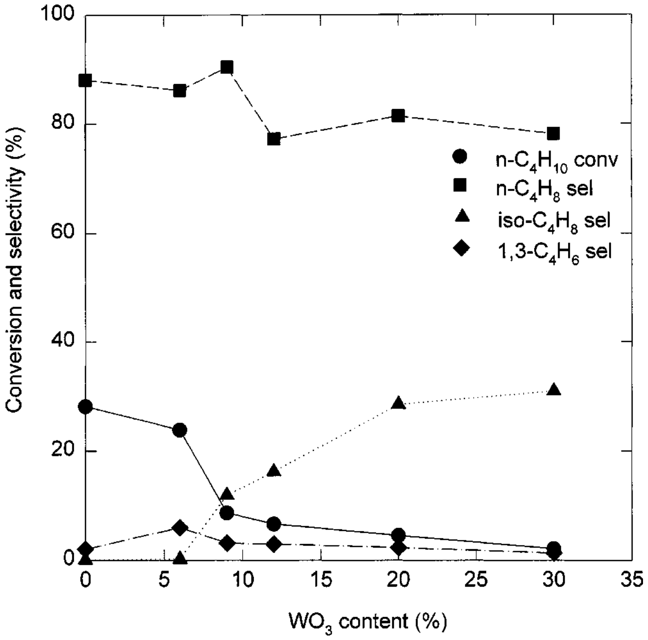


Figure 1. Effect of WO_3 loading on catalytic activity of the Cr/WO_3–ZrO_2 catalyst.

Table 2
Physico-chemical properties of Cr/WO_3–ZrO_2 catalysts.

Catalyst	S_{BET} (m^2/g)	NH_3 adsorption ($\mu mol/g_{cat}$)
Cr/ZrO_2	111.3	20.7
Cr/6 wt% WO_3–ZrO_2	64.7	8.4
Cr/20 wt% WO_3–ZrO_2	52.7	18.0

hydrogenation. Gielgens et al. [10] studied the skeletal isomerization of 1-butene over several WO_3/Al_2O_3 catalysts and observed a remarkable relation between the loading and both the selectivity and the stability. Increasing the WO_3 loading resulted in increasing selectivity to isobutene and there was an increase in the initial selectivity at a loading of about 7 wt%. Their finding is similar to the observation in this investigation. As for the stability of the catalyst, the high-loaded catalysts had a high initial selectivity but exhibited a strong deactivation.

The BET surface areas and ammonia adsorption on Cr/WO_3–ZrO_2 catalysts with different WO_3 loadings are presented in table 2. It is seen that the surface area will be reduced when WO_3 is loaded. NH_3 adsorption on Cr/WO_3–ZrO_2 catalysts is also lower than that on Cr/ZrO_2; however, NH_3 adsorption will increase when WO_3 loading increases. This suggests that the activity of n-butene isomerization is not dependent on the total acidity of the catalysts. Houzvicka et al. [11] studied the role of acid strength in skeletal isomerization of n-butene to isobutene and found that activity of the catalysts at lower acidity is not sufficient while oligomerization and by-products will form when the acidity is too high. Several researchers have reported that supported W and Mo oxide catalysts show activity in n-butene isomerization, but the reason has not been clearly understood [12,13]. Further work should be done to explore the reason for n-butene isomerization. Carniti et al. [14] suggested that WO_3 exceeds other oxides in the number of weakly and moderately acidic sites exposed on its surface. Therefore, a NH_3 TPD over the above Cr/WO_3–ZrO_2 catalysts was determined to explore the acid site distribution and their NH_3 TPD profiles are given in figure 2. As seen, the distributions of acid sites on these catalysts show different patterns. One strong and broad peak appears at 100–300 °C on the TPD profile of the unpromoted Cr/ZrO_2. For Cr/6 wt% WO_3–ZrO_2, there are three peaks, one broad peak at 100–300 °C, same temperature range as that occurring on the Cr/ZrO_2, while two more weak peaks appearing at 400–450 and 480–520 °C, respectively. For Cr/20 wt% WO_3–ZrO_2, two strong desorption peaks centered at 180 and 420 °C can be observed. As compared to the peaks occurring at Cr/6 wt% WO_3–ZrO_2, the intensities of the two peaks on Cr/20 wt% WO_3–ZrO_2 are all increased, especially for the peak at high temperature. From the variation of isobutene selectivity over the three catalysts, it is deduced that the acid sites producing the NH_3 desorption peak at high temperature are responsible for the isobutene production.

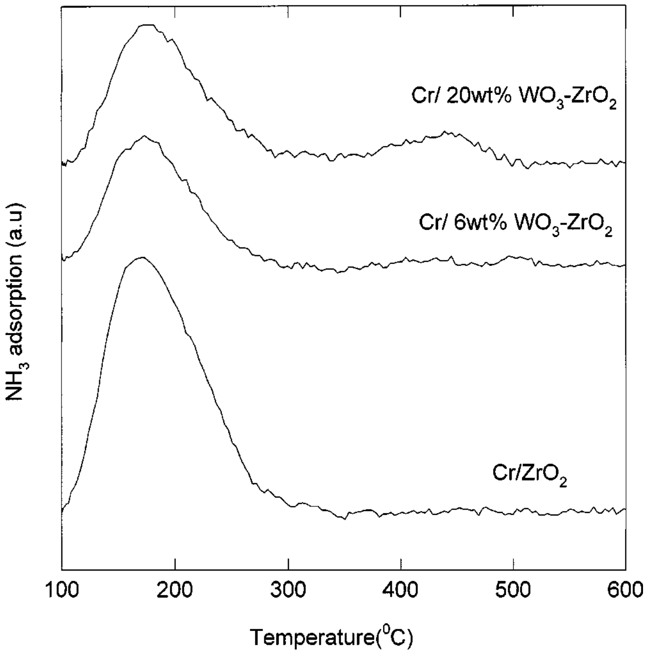


Figure 2. NH_3 TPD profiles over several Cr/WO_3–ZrO_2 catalysts.

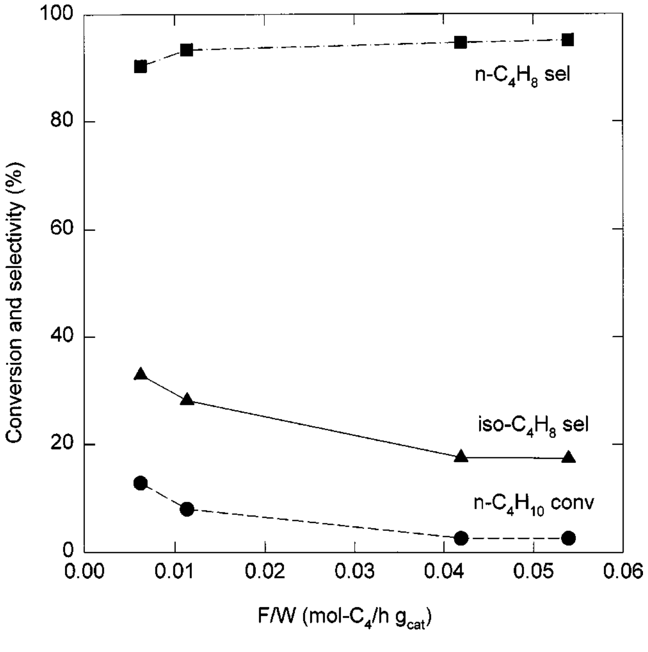


Figure 3. Effect of space velocity (F/W) on catalytic activity of the Cr/WO_3–ZrO_2 catalyst.

The effect of space velocity (F/W) is conducted over a 5 wt% Cr_2O_3/9 wt% WO_3–ZrO_2 catalyst and the results are illustrated in figure 3. One can see that butane conversion and isobutene selectivity decrease as F/W increases while butene selectivity increases with the increasing F/W. This is reasonable because the activity of dehydrogenation will be less at short contact time, resulting in less cracking and oxidation products. It is noted that isobutene selectivity shows an increasing trend as butane conversion increases.

Figure 4 presents the catalytic performance of the Cr_2O_3/20 wt% WO_3–ZrO_2 catalysts at various Cr_2O_3 loadings.

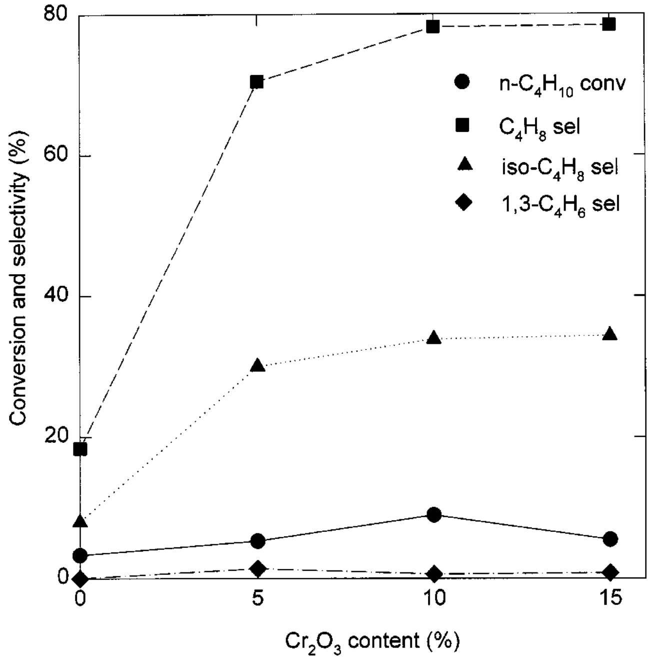


Figure 4. Effect of Cr_2O_3 loading on catalytic activity of Cr/WO_3–ZrO_2 catalyst.

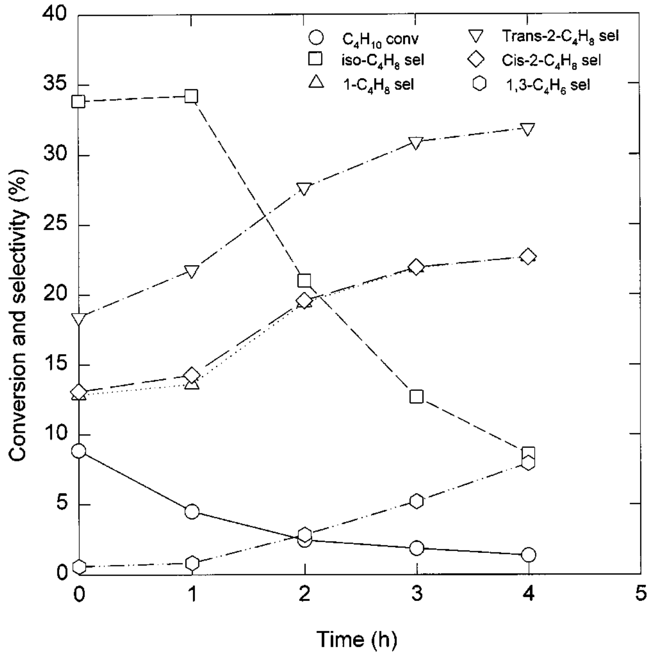


Figure 5. Stability performance of 10 wt% Cr_2O_3/20 wt% WO_3–ZrO_2 in dehydroisomerization of n-butane at 500 °C.

One can see that impregnation of Cr_2O_3 significantly improves the catalytic activity of dehydrogenation by increasing butane conversion, butene selectivity, and isobutene selectivity. The conversion reaches the highest value at 10 wt% Cr_2O_3. Butene selectivity and isobutene selectivity firstly increase with the increasing Cr_2O_3 loading and then maintain their values at the same level of 80 and 30%, respectively, after the Cr_2O_3 loading reaches 10 wt%. This seems to suggest that Cr_2O_3 is responsible for the dehydrogenation while it has little effect on isobutene selectivity.

The variation of catalytic activity over the 10 wt% Cr_2O_3/20 wt% WO_3–ZrO_2 as a function of time is presented in figure 5. It is shown that butane conversion and isobutene selectivity show decreasing trends while n-butene selectivities and butadiene selectivity increase with the reaction time. This suggests a transformation of isobutene to n-butene occurring during the reaction. It was found that a large amount of carbon deposited on the catalysts, which is believed to cause the catalyst deactivation. Carbon deposition may change the pore structure and surface acidity/basicity of the catalyst, resulting in the variation of product selectivity. BET surface area measurements indicate S_{BET} of the reacted catalyst was greatly reduced from 83 to 27 m^2/g. The pore size distributions of the fresh and used 10 wt% Cr_2O_3/20 wt% WO_3–ZrO_2 catalyst are shown in figure 6. The fresh catalyst shows a narrow pore size between 2 and 10 nm while the reacted catalyst exhibits two broad peaks in the pore size distribution profile, suggesting the variation of pore structure during the reaction. This could be attributed to carbon deposition. It has been found that the pore structure is one of the important factors influencing the activity of isomerization. For some catalysts, for example the ten-membered zeolites, the pore structure has been considered more important than the acidity. Therefore, we believe that the pore structure of the Cr/WO_3–ZrO_2 catalyst will play an important role in the shift of butene selectivity.

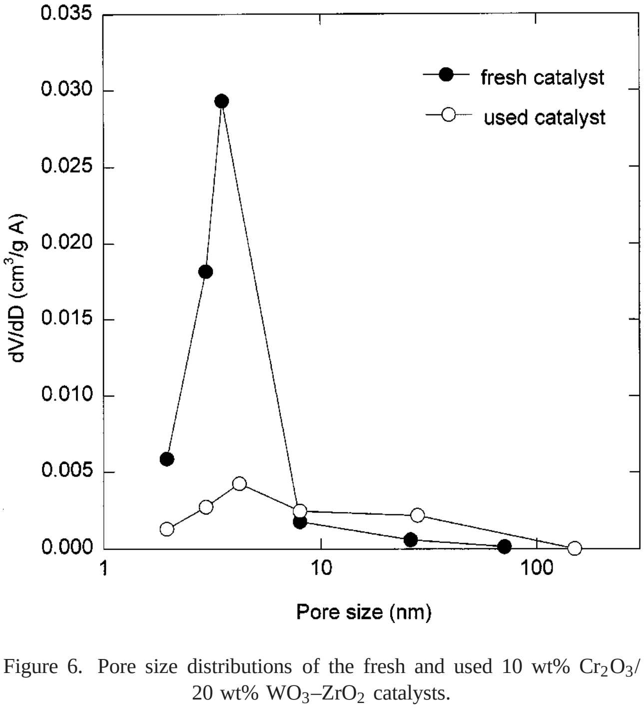
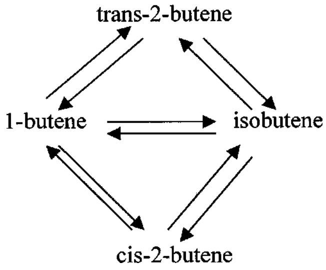


Figure 6. Pore size distributions of the fresh and used 10 wt% Cr_2O_3/20 wt% WO_3–ZrO_2 catalysts.

In the isomerization process, several transformation reactions between n-butene and isobutene could occur, as shown in the diagram below. Houzvicka and Ponec [3] reviewed the previous work on n-butene isomerization and concluded that the prevailing mechanism of skeletal isomerization of n-butene is monomolecular and requires

Brønsted acid active sites. Seo et al. [15] investigated the reversibility of skeletal isomerization between n-butene and isobutene over various catalysts and proposed that the reversibility of skeletal isomerization may contribute more evidence for a monomolecular reaction path of 1-butene to isobutene. The high tendency of reversibility of isobutene to n-butene observed in this investigation suggests that isomerization proceeds via the monomolecular reaction. In addition, no detection of C_5 compounds in products is also indicative of the monomolecular mechanism prevailing in this reaction.



4. Conclusion

The dehydroisomerization of n-butane to isobutene was investigated over a series of Cr_2O_3-based catalysts. The effects of support, WO_3 and Cr_2O_3 contents, and reaction conditions such as temperature and space velocity were studied. The Cr/WO_3–ZrO_2 system shows better activity than other supported catalysts. The catalytic activity increases with increasing temperature and Cr_2O_3 loading, but decreases as the space velocity and WO_3 loading increase. The selectivity to isobutene is dependent on the weak acid sites, which are produced by impregnation of tungsten oxide. 10 wt% Cr_2O_3/20 wt% WO_3/ZrO_2 can give high initial conversion and isobutene selectivity but it shows rapid deactivation due to carbon deposition.

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