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## OXIDATIVE DEHYDROGENATION OF PROPANE TO PROPENE OVER BARIUM PROMOTED Ni-Mo-O CATALYST

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### Abstract

Oxidative dehydrogenation of propane to propene was investigated over Ba-promoted Ni<sub>0.9</sub>MoO<sub>4</sub> catalysts (molar ratio of Ba/Mo: 1%, 3%, 6%, 9%, 12%, 15%). The selectivity for propene increases with the increasing number of basic sites on the catalyst, and molybdenum ions play an important role in propane activation. No significant deactivation of the 6% Ba- Ni<sub>0.9</sub>MoO<sub>4</sub> and Ni<sub>0.9</sub>MoO<sub>4</sub> at 773 K for 80 h and for 40 h, respectively, appeared, indicating that the 6%Ba-Ni<sub>0.9</sub>MoO<sub>4</sub> has great advantage over the Ni<sub>0.9</sub>MoO<sub>4</sub>.

*Keywords:* Propene, oxidative dehydrogenation of propane, Ni-Mo-O catalyst, barium promoter

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## INTRODUCTION

The direct conversion of light alkanes into various products is one of the most challenging problems in catalytic chemical industry since it can enable natural gas to be used as the feedstock for producing, in large scale, chemicals conventionally obtained from oil [1,2]. At the moment some dehydrogenation catalysts are available. Although many types of catalysts containing vanadium, palladium, zinc and gallium have been reported to be active in dehydrogenation, none of them shows good properties both in activity and selectivity. In recent years, alkali promoters have been used to improve the catalytic properties of molybdate systems in selective oxidation [3,4,5] and some of them have even been mentioned as promoters for industrial catalysts.

Catalysts based on transition metal molybdates, such as bismuth, cobalt and nickel molybdates, have recently received extensive attention. Among them, the nickel molybdates, and in particular, stoichiometric NiMoO<sub>4</sub>-like catalysts have attracted the greatest interest. Generally, NiMoO<sub>4</sub> possesses two main polymorphic phases under atmospheric pressure:  $\alpha$  phase at a low temperature and  $\beta$ -phase at a high temperature. Both phases are monoclinic with space group C2/m [6].

Lezla *et al.* found [7] that the alkali promoted  $\alpha$  and  $\beta$  phase of NiMoO<sub>4</sub> behaved similarly, decreasing the catalytic activity of *n*-butane conversion and increasing the selectivity to butene and butadiene in ODH of butane; the addition of molybdenum oxide enhanced the catalytic performance of nickel molybdate for the oxidative dehydrogenation of propane to propene significantly.

In this paper, the catalytic behavior of barium promoted  $\alpha$ -Ni-Mo-O catalysts (Ni/Mo molar ratio =0.9) was investigated. The Ni<sub>0.9</sub>MoO<sub>4</sub> with 9% barium (Ba/Mo molar ratio) is the most active catalyst for the selective oxidation of propane.

## EXPERIMENTAL

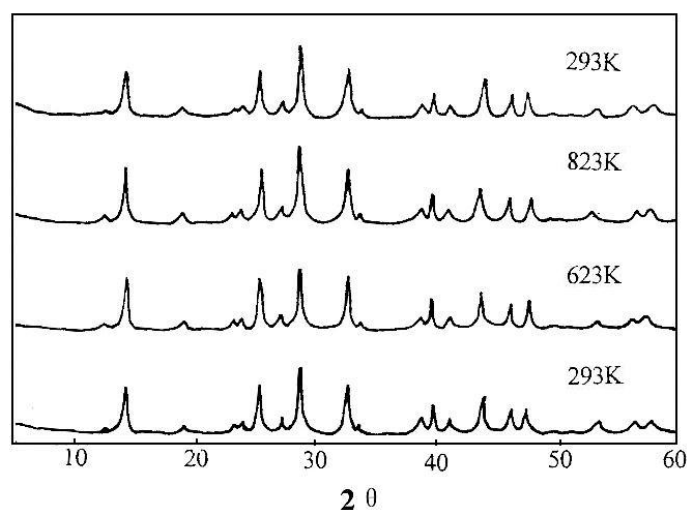
The precursors of catalysts were prepared by a precipitation method. Detailed procedures are described elsewhere [6]. The resulting solid was ground and heated at 320°C for 2 h, followed by grinding and heating at 550°C for 2 h. Barium promoted samples were prepared by adding 3 g of nickel molybdate to 30 mL of deionized water containing a suitable amount of barium nitrate (1%~15%). Crystal structure of the samples was determined by X-ray diffraction (XRD) (Shimadzu XD-3A diffractometer) using CuK $\alpha$  radiation, at 30 kV and 20 mA. Experiments on identification of  $\alpha$  and  $\beta$  phases of the molybdates were carried out using a HTXRD diffractometer (Philips PW1050) equipped with a high temperature chamber. The infrared spectra (IR) were recorded using a Nicolet Impact 410 spectrometer. The acidic properties of the catalysts were determined by temperature-programmed desorption (TPD) of ammonia: 0.03 g catalyst was embedded in a fixed-bed quartz tube with an i.d. of 4 mm. First, the sample was treated at 500°C for 1 h in Ar stream, followed by cooling to room temperature in Ar. Then, the adsorption of ammonia was conducted at 50°C for 30 min. The sample was heated from room temperature to 500°C at a linear heating rate of 10°C/min in a 3%H<sub>2</sub>/Ar flow at a rate of 30 mL/min. The oxidative dehydrogenation of propane was carried out in a conventional fixed-bed quartz reactor (40 cm long, and i.d. of 8 mm), contacted an on-line Shimadzu GC-8A gas chromatograph equipped with a 3 m Paropak Q column for analyzing the products, detected by a FID detector. A

thermocouple was placed in the middle part of the catalyst bed to monitor the reaction temperature. 0.2 g catalyst was embedded for each run. The reactant mixture consisted of  $C_3H_8/O_2/N_2$  with a molar ratio of 1/1/5 and flowed at a total rate of 70 mL/min. The blank tests showed no  $C_3H_8$  conversion under the conditions studied.

## RESULTS AND DISCUSSION

### Structure of catalyst

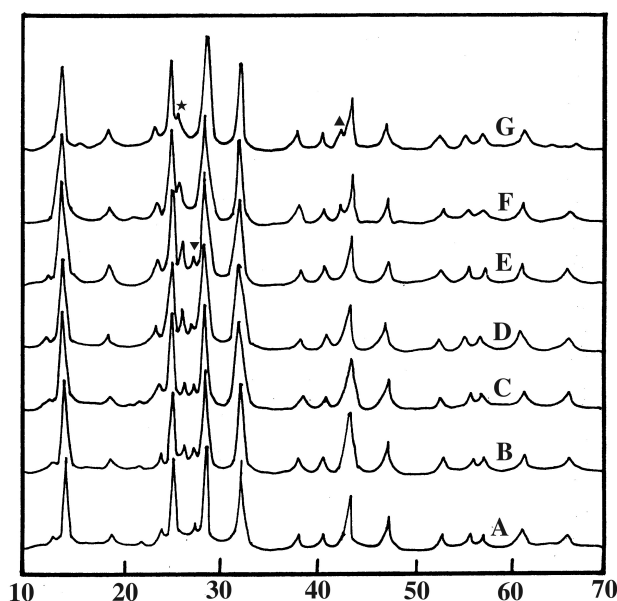
Transition metal molybdates may crystallize into two phases  $\alpha$  type and  $\beta$  type. In the former the molybdenum ions are in octahedral coordination and in the latter the molybdenum ions are in distorted tetrahedral coordination [6]. Although a few papers concerning the existence conditions of these two phases have been published, the transformation between the  $\alpha$  and  $\beta$  type is still not completely elucidated. In addition, the stabilities of both  $\alpha$  and  $\beta$  phases strongly depend on the preparation and treatment conditions and their physico-chemical properties vary essentially and are complicated [10,11]. Based upon the experimental results of different authors, it is difficult to make a clear conclusion on the conditions under which  $\alpha$  or  $\beta$  phase can be constructed and their transformation occurs.



**Fig. 1.** High temperature XRD patterns of  $Ni_{0.9}MoO_4$  at different temperatures in air

On the other hand,  $\alpha$  and  $\beta$  phases of  $\text{NiMoO}_4$  show different activity and selectivity for the oxidative dehydrogenation of alkanes. The authors of the present work have verified if both phases of  $\text{NiMoO}_4$  coexisted during the ODH of propane to propene.

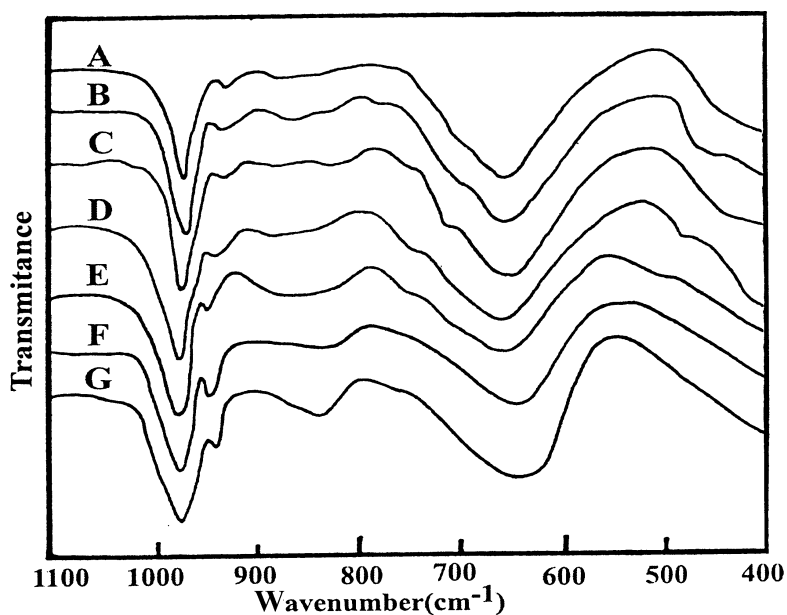
As is shown in Fig. 1, the stability of  $\alpha$   $\text{NiMoO}_4$  is indicated by the high temperature XRD measurements under dynamic conditions. At different temperatures (293, 623, 823, 293 K; heated up and cooled down) the  $\text{Ni}_{0.9}\text{MoO}_4$  catalyst exhibited the same  $\alpha$  phase crystalline structure. Its characteristic diffraction peaks are at 14.0, 18.9, 23.9, 25.2, 28.7 (100), 32.6, 38.5, 41.3, 43.7 and 47.3°, respectively, which are consistent with ASTM-card 33-948. These data indicate that the  $\text{Ni}_{0.9}\text{MoO}_4$  sample keeps its  $\alpha$ -phase structure within a wide temperature range (293~823 K). Thus, under the above conditions only  $\alpha$ - $\text{NiMoO}_4$  was obtained. In other words, the  $\beta$  phase nickel molybdate was not detected throughout the temperature range of the reaction. Comparing with others' [10,11], one can find that some conclusions about the properties of these two phases, to a certain extent, are contradictory. Thus, the present authors think it is worthy to provide more information on the phase transformation of nickel molybdate. Moreover, there also exists orthorhombic  $\text{MoO}_3$  in this catalyst, and the peaks of  $\alpha$  phase were not changed any more in the temperature range.



**Fig. 2.** XRD patterns of different barium promoted  $\text{Ni}_{0.9}\text{MoO}_4$  (A) unpromoted, (B) 1%, (C) 3%, (D) 6%, (E) 9%, (F) 12%, (G) 15%.  
\* :  $\text{BaO}_2$ , ▼:  $\text{MoO}_3$ , ▲:  $\text{BaMoO}_4$

The XRD patterns of barium doped  $\text{Ni}_{0.9}\text{MoO}_4$  exhibit the same a phase structure and orthorhombic  $\text{MoO}_3$  as shown in Fig. 2. A peak at  $26.7^\circ$  for  $\text{BaO}_2$  (ASTM 7-233) appears for the samples doped with 1~15% of Ba, the peak intensities of which increase with increasing barium content below 9% and decrease with barium over 9%. Meanwhile, the characteristic diffraction peaks of  $\text{MoO}_3$  appear in 0~9% Ba-promoted samples and disappear in 12~15% ones, in which two small new peaks of  $\text{BaMoO}_4$  appear at  $26.5$  and  $42.5^\circ$  (ASTM29-193), accompanying the decrease in the intensity of the  $\text{BaO}_2$  peak. It is believed that the existence of  $\text{BaMoO}_4$  is the main reason for poor catalytic activity in this reaction. Otherwise,  $\text{MoO}_3$  is thought to be stabilized in the presence of  $\alpha\text{-NiMoO}_4$ . In the latter case, there may be some synergic effects as reported in the literature [13-16]. So it may be difficult to form crystalline  $\text{BaMoO}_4$  in the samples with low barium concentration.

The XRD patterns of the samples (the corresponding figure omitted) obtained after 4 h of reaction demonstrated that the structure of catalysts was preserved after the reaction. However, the 6%Ba- $\text{Ni}_{0.9}\text{MoO}_4$  and  $\text{Ni}_{0.9}\text{MoO}_4$  did not show characteristic diffraction peaks of  $\text{MoO}_3$  after life-time test reaction.



**Fig. 3.** IR spectra of different barium promoted  $\text{Ni}_{0.9}\text{MoO}_4$   
(A)unpromoted, (B)1%, (C)3%, (D)6%, (E)9%, (F)12%, (G)15%

## IR spectra

The IR spectrum of the unpromoted  $\text{Ni}_{0.9}\text{MoO}_4$  agrees well with the data shown in the literature [6]. As is shown in Fig. 3, two new bands located near  $820\text{ cm}^{-1}$  and  $870\text{ cm}^{-1}$  appear for the nickel molybdate doped with Ba. These two bands may be attributed to  $\text{O}_2^{2-}$  ions, which usually display  $\nu$  O-O vibrations between  $800$  and  $900\text{ cm}^{-1}$  [17], respectively. Moreover, they are influenced by the promoter contents. It can be seen that an increase of Ba concentration leads to an increase of the intensity of both bands. One can find two typical stretching vibration modes of Mo=O at around  $990\text{ cm}^{-1}$  and of a Mo-O-Mo at  $860\text{ cm}^{-1}$  of  $\text{MoO}_3$ , respectively, which is partially overlapped by the vibrational bands of  $\text{BaO}_2$  ( $870\text{ cm}^{-1}$ ). With the increase of Ba content, the band at  $860\text{ cm}^{-1}$  disappears. This result coincides with the conclusion obtained from the X-ray diffraction patterns of the samples, namely, excessive  $\text{BaO}_2$  is combined with  $\text{MoO}_3$  to form  $\text{BaMoO}_4$ .

IR spectra of unpromoted catalysts after life-time test reaction show apparent changes. There is no band at  $860\text{ cm}^{-1}$  attributed to  $\text{MoO}_3$ , while in the Ba-promoted catalyst the vibrational band of  $\text{BaO}_2$  at  $820\text{ cm}^{-1}$  still exists.

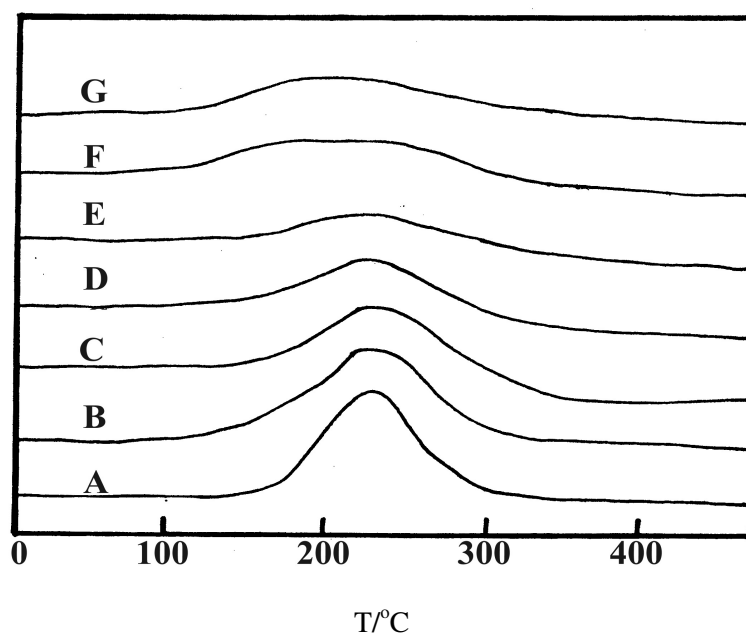
The results of IR and XRD measurements of Ba-doped  $\text{Ni}_{0.9}\text{MoO}_4$  catalysts provide evidence for the existence of new oxygen species related to barium peroxides. It is deduced that the propene selectivity in this reaction may be related to such oxygen species over doped nickel molybdate catalysts. Among the elements of group II A, the observation of peroxide compounds in the barium containing catalysts is due to that only barium yields the most stable peroxide. The IR and XRD characterization of 6%Ba promoted and unpromoted catalyst before and after the life-time test verified that a part of  $\text{MoO}_3$  sublimed in the steady-state reaction, implying that molybdate ions were active for ODH of propane. As usual, molybdenum ions existing as molybdate salts show better catalytic activity for the conversion of hydrocarbons than does the single phase of molybdenum oxide. In addition, nonstoichiometric molybdate possesses high selectivity for ODH of low paraffins to produce olefins. There are many types of molybdate salts, particularly of divalent transition metals, such as  $\text{FeMoO}_4$ ,  $\text{CoMoO}_4$ ,  $\text{NiMoO}_4$  and  $\text{MnMoO}_4$  in which the divalent metal ions act as balance ions.

## Steady-state experiments

Catalytic performance of  $\text{Ni}_{0.9}\text{MoO}_4$  doped with 0~15% barium for ODH of propane was tested at 773 K and the results are shown in Table 1. Propene, methane and carbon oxides were found in the reaction products, while no other oxygenated organic compounds were detected.

**Table 1**  
Catalytic activities of barium promoted  $\text{Ni}_{0.9}\text{MoO}_4$

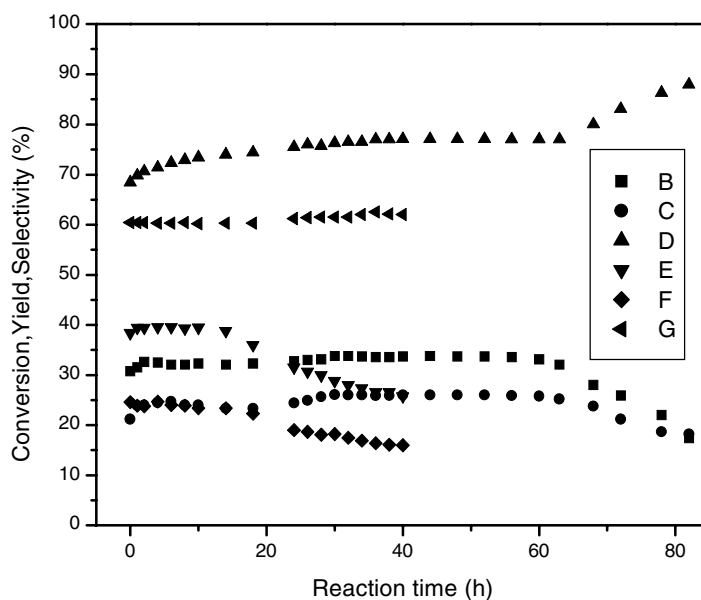
Catalyst	Conversion (%)		Selectivity (%)			Yield (%)
	$\text{C}_3\text{H}_8$	$\text{C}_3\text{H}_6$	CO	$\text{CO}_2$	$\text{CH}_4$	
1%Ba- $\text{Ni}_{0.9}\text{MoO}_4$	40.4	64.0	18.6	16.4	0.8	25.9
3%Ba- $\text{Ni}_{0.9}\text{MoO}_4$	40.0	64.9	18.2	16.0	0.9	26.0
6%Ba- $\text{Ni}_{0.9}\text{MoO}_4$	39.8	72.9	14.0	12.1	1.0	29.0
9%Ba- $\text{Ni}_{0.9}\text{MoO}_4$	40.9	74.6	13.2	11.2	1.0	30.5
12%Ba- $\text{Ni}_{0.9}\text{MoO}_4$	38.4	65.3	17.8	16.1	0.8	25.1
15%Ba- $\text{Ni}_{0.9}\text{MoO}_4$	35.2	65.0	17.9	16.3	0.8	22.9



**Fig. 4.**  $\text{NH}_3$ -TPD profiles of different barium promoted  $\text{Ni}_{0.9}\text{MoO}_4$  (A) unpromoted, (B) 1%, (C) 3%, (D) 6%, (E) 9%, (F) 12%, (G) 15%

As listed in Table 1, the added barium improved the selectivity of propene, which increased with the increase of barium content from 1 to 9%, but decreased with the increase of its content from 12 to 15%. In the meantime, the

conversion of propane changed from 40.4 to 35.2%. The authors assume that the reason for this fact could be related to the adsorption bond strength between hydrocarbon and the catalyst surface as well as its acid-base character in the ODH reaction [9]. The activity of the barium doped catalysts varies in parallel with the increase of their basicity, as shown by  $\text{NH}_3$ -TPD profiles (Fig.4). The stronger the catalyst basicity the higher the selectivity to propene. This fact may be due to the surface basicity which prevents them from further oxidation to carbon oxides, because it favors the desorption of dehydrogenation products [8,9].



**Fig. 5.** The stability of activity of 6% barium doped and undoped  $\text{Ni}_{0.9}\text{MoO}_4$  (B) Conv.  $\text{C}_3\text{H}_8$ , (C) Yield.  $\text{C}_3\text{H}_6$ , (D) Selec.  $\text{C}_3\text{H}_6$  over 6%  $\text{Ba-Ni}_{0.9}\text{MoO}_4$  and (E) Conv.  $\text{C}_3\text{H}_8$ , (F) Yield.  $\text{C}_3\text{H}_6$ , (G) Selec.  $\text{C}_3\text{H}_6$  over  $\text{Ni}_{0.9}\text{MoO}_4$

A very broad peak of desorbed  $\text{NH}_3$  for the barium free catalyst and barium doped nickel molybdate in the temperature range of 200–300°C evidenced the existence of active sites with different acidities. It is found that the total acidity of the catalysts increases until the Ba content increases to 9%. Along with the further increase of Ba loading, the number of acid sites decreases and the



basicity of the samples increases, indicating that such acid sites become gradually weaker. For the 15% Ba-  $\text{Ni}_{0.9}\text{MoO}_4$ , the total basicity became weaker compared with the 12% Ba doped catalyst. These results suggest that some of the formed barium peroxide is probably wrapped by crystals of the catalysts or that some compound was formed with high Ba content. Thus the surface concentration of barium peroxide on the catalyst decreased. As verified and reported by other authors [12,13,14], the higher basicity of alkaline metals makes the interaction between hydrocarbons and the catalyst surface difficult. Thus a suitable range of basicity of the alkaline earth metal promoted  $\text{Ni}_{0.9}\text{MoO}_4$  catalysts is in favor of the desorption of olefins. The  $\pi$ -bonds are considered to be nucleophilic because of their high electron density. Thus propene interacts much more strongly with the unpromoted  $\text{Ni}_{0.9}\text{MoO}_4$  than with the barium promoted ones.

The activity stability of the 6% barium doped  $\text{Ni}_{0.9}\text{MoO}_4$  and unpromoted  $\text{Ni}_{0.9}\text{MoO}_4$  for the ODH of propane at 773 K is shown in Fig.5. It can be seen that the unpromoted catalyst provides a 38% conversion of propane, which remained unchanged for 7 h, then decreased to 32% after 30 h; the propene selectivity increased similarly as reported in reference [15]. In contrast, the barium doped catalyst was extremely stable; it preserved a conversion of 32% and a selectivity of 75% for 30 h. In particular, its selectivity to propene strongly increased during the next 30 h of time on stream reaching around 90%, and no tendency of deactivation was detected until 82 h of reaction.

## CONCLUSION

The redox, acid-basic properties and catalytic performance for ODH of propane were improved by addition of barium to nickel molybdate. However, more barium leads to the formation of  $\text{BaMoO}_4$ . The selectivity to propene keeps unchanged because the acid-base properties of catalysts facilitate desorption of propene, preventing its further oxidation to  $\text{CO}_x$ .  $\text{MoO}_3$  plays an important role in the activation of propane. The improvement of catalytic performance is attributed to the biphasic synergy of  $\text{BaO}_2$  and molybdenum ions. The selectivity to propene from propane over 6% Ba doped  $\text{Ni}_{0.9}\text{MoO}_4$  catalyst was 74% for 60 h and further increased to 90% within another 20 h; the selectivity did not decrease.

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