Dehydrogenation and aromatization of propane over rhenium-modified HZSM-5 catalyst

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Abstract

The dehydrogenation and aromatization of propane over Re/HZSM-5 and Ga/HZSM-5 was investigated at temperatures ranging from 623 to 923 K under atmosphere pressure. The strong acid sites declined upon introduction of rhenium to HZSM-5, and were not influenced by gallium. Compared with Ga/HZSM-5, Re/HZSM-5 exhibited remarkable enhancement of propane dehydrogenation while the decomposition slowed down with time on stream. Addition of CO_2 (30%) to the feed obviously inhibited the transformation of propane and the selectivity to aromatics. In contrast, addition of methane enhanced the selectivity to aromatic products. Meanwhile, formation of methane from propane was inhibited and the methane from the starting mixture was transformed.
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1. Introduction

Light alkanes, such as propane and butane, are becoming attractive feeds for the production of propene and aromatics. Zn- or Ga-loaded ZSM-5 materials are proven good catalysts for the production of aromatics from light alkanes [1–3]. Zinc catalyst suffers from vaporization from zeolites due to the reduction of the zinc oxide into metals that have a low melting point and boiling point. Compared to zinc-promoted zeolites, gallium-promoted catalysts are more effective for propane transformation. The high alkane transformation activity is attributed to the presence of bi-functional sites of non-framework gallium oxide species (which have a dehydrogenation function) and zeolitic protons (which have acid function).

A great deal of work has been done for improving the catalytic activity, selectivity and stability of the aromatization catalysts. Carbon dioxide addition, in dilute concentrations, has been reported to suppress the accumulation of coke during the aromatization of propane and methane [4,5]. Stable

catalytic activity was obtained when CO_2 was added into the feed due to its effectiveness in removal of coke from the catalyst surface by the reforming type of reaction between CO_2 and CH_x. Recently, rhenium-impregnated HZSM-5 zeolites have been tested in the catalytic aromatization of methane and ethane. In the aromatization of ethane, Krogh et al. [6] found that the Re/HZSM-5 catalyst deactivates significantly slower than the well-known aromatization Zn/HZSM-5 catalyst. At the same time, the spent Re/HZSM-5 catalyst contains less coke than that on Zn/HZSM-5. Different effects observed when Re/HZSM-5 was used for the aromatization of methane. Su et al. [7] found that the original performance of Re/HZSM-5 is much better than Mo/HZSM-5 for methane aromatization. But its lifetime is much shorter than the latter due to the increase of acid sites and a larger amount of coke accumulation after reacting at 973 K.

Recently, Solymosi et al. [8] gave a preliminary study of Re/ZSM catalyst on the transformation of propane and *n*-butane. In the present study, the dehydrogenation and aromatization of propane over a Re/HZSM-5 catalyst was further investigated. First, the catalytic performance of Re/HZSM-5 for the transformation of propane was compared with that of a gallium-promoted HZSM-5 catalyst,

a well-studied aromatization catalyst. Then, the effects of reaction conditions on the catalytic performance were investigated. Furthermore, the effects of CO_2 and methane addition towards the transformation of propane were discussed on the basis of the experimental findings.

2. Experimental

Re/HZSM-5 and Ga/HZSM-5 were prepared by incipient wetness impregnation of HZSM-5 ($SiO_2/Al_2O_3 = 45$, Nankai University, PR China) with an aqueous solution of gallium nitrate and ammonium perrhenate, respectively. The resulting materials were subsequently dried and calcined in air at 823 K for 5 h. The Re and Ga loadings were 6 wt.%.

The reaction was performed in a continuous-flow microreactor made of quartz (6 mm i.d.) at atmospheric pressure. The propane content in feed was 30% in N_2 with a total flowing rate of 4 ml/min. All the gases were UHP grade and used without further purification. Generally 200 mg of loosely compressed catalyst sample was used. The products in the transformation of propane were H_2, methane, ethane, ethene, propene, benzene, toluene, xylene, and trace amount of other hydrocarbons, such as C4+ hydrocarbons, naphthalene, and CO. The hydrocarbons were analyzed by online GC with FID using a PLOT-Al_2O_3/S column, and H_2, N_2, CO and CH_4 with TCD using carbon molecular sieve column. All reaction results were expressed in propane conversion, while the yield and selectivity to various products were calculated based on the consumed propane molecules.

The structures of the catalysts were characterized by their X-ray powder diffraction (XRD) pattern using Cu Kα radiation. Temperature-programmed desorption (TPD) measurements were carried out to determine the acid properties of zeolites by using ammonia as an adsorbate. The catalyst was first treated with Ar at 773 K, and then cooled to 373 K. The adsorption was conducted at this temperature by exposing the samples to an ammonia flow. After purging the sample with an Ar stream flowing for 120 min to completely remove the physically adsorbed ammonia, the catalyst was heated up to 973 K with a heating rate of 10 K/min. The desorbed ammonium was analyzed with the mass spectrometer.

3. Results and discussion

3.1. Characterization of the as-prepared catalysts

The XRD spectrums of the Re/HZSM-5 and Ga/HZSM-5 were not significantly different from those of HZSM-5. Presumably, the gallium oxide and rhenium oxide were highly dispersed throughout the zeolites matrix.

The NH$_3$-TPD spectra of the samples were shown in Fig. 1. Two desorption peaks were observed for all the catalysts, around 500 and 700 K, indicating desorption of ammonia from the weak and strong acid sites, respectively.
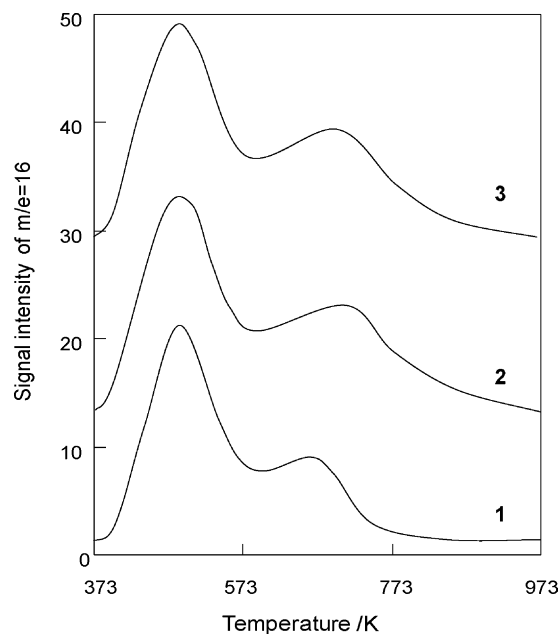

Fig. 1. NH$_3$-TPD from various catalysts: (1) Re/HZSM-5; (2) Ga/HZSM-5; (3) HZSM-5.

Su et al. [7] found that after impregnation of Re, the metal species interacts with the framework aluminum intensively and causes the dealumination of the catalyst. In the present work, introduction of gallium did not significantly change the temperature of desorption and the amount of ammonia desorbed. This indicated that incorporation of gallium into the zeolites matrix did not significantly influence the acidity, as reported previously [9]. While the Re/HZSM-5 catalyst showed a distinct decrease of ammonia desorption at high temperature, indicating the dealumination of the catalyst and exchanging of protons of Brønsted acid sites by rhenium ions since Brønsted acid sites are the main strong acid sites [10].

3.2. Steady transformation of propane over modified HZSM-5

The transformation of propane was conducted at 823 K and the conversion of propane and yield of various products versus time on stream were presented in Fig. 2. It was found that the conversion and product yield sensitively depends on the composition of the catalyst. Unmodified ZSM-5 exhibited a lower activity (77.7% conversion) toward the transformation of propane. It should be noted that there was no induction period over the unmodified ZSM-5 during the transformation of propane, while this was observed over rhenium and gallium modified HZSM-5 catalyst (about 30 min). After induction period the catalyst suffers from continuous deactivation due to the accumulation of cokes. Maggiore et al. [11] found a similar activity of Re/HZSM-5 and HZSM-5 during the aromatization of propane, while it was found in this work that the total conversion of propane increased extensively when Re
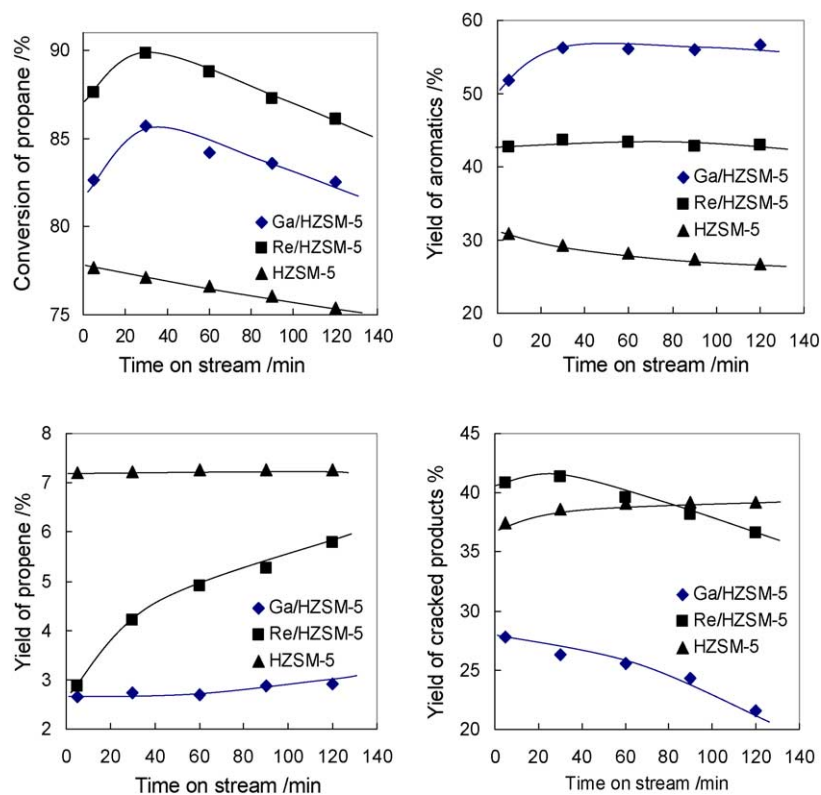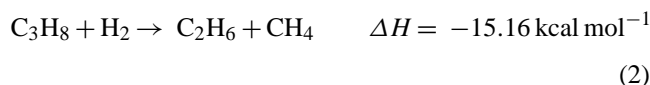
Fig. 2. Propane transformation over HZSm-5, Re/HZSM-5 and Ga/HZSM-5 catalysts.

and Ga was introduced to HZSM-5. This could be attributed to the lower loading of rhenium in their experiments as had also been reported by Krogh et al. [6].
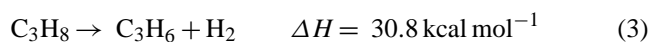
It could be found that Re/HZSM-5 (90% conversion, Fig. 2) was more effective than Ga/HZSM-5 (85% conversion) for propane transformation. Meanwhile, the yield of aromatic products over Re/HZSM-5 was somewhat lower than that over Ga/HZSM-5. Over Ga/HZSM-5, the yield of aromatics was around 56% at the steady state and they mainly consisted of benzene (24%) and toluene (23%) followed by xylene (8%). As for Re/HZSM-5, the yield of aromatics decreased to 43% compared with Ga/HZSM-5 and the main aromatic products were toluene (20%) followed by benzene (16%) and xylene (7%). It should be noted that the yield to C9+ products over Re/HZSM-5 was lower than that over Ga/HZSM-5. In a recent work, Song et al. [12] found that strong acid sites were indispensable for the conversion of olefin to aromatics. The lower selectivity of aromatic products over Re/HZSM-5 could be attributed to the exchange of protons of Brønsted acid sites by rhenium ion and dealumination of the catalyst as observed by NH$_3$-TPD experiments.

As shown in Fig. 2, the yield of cracked products reached 36–42% when gallium and rhenium was introduced. The main components in light hydrocarbons were ethane (25% yields over Ga/HZSM-5 and 28% yields over Re/HZSM-5 at 30 min) and methane (11% yields both over Ga/HZSM-5 and Re/HZSM-5 at 30 min) probably through decomposition

(reaction 1) and hydrogenolysis of propane (reaction 2):

$$C_3H_8 \rightarrow C_2H_4 + CH_4 \qquad \Delta H = 19.0 \, kcal \, mol^{-1} \qquad (1)$$

$$C_3H_8 + H_2 \rightarrow C_2H_6 + CH_4 \qquad \Delta H = -15.16 \, kcal \, mol^{-1} \qquad (2)$$

The selectivity of other light hydrocarbons, such as ethene and propene, was lower than 6% during the time on stream. The selectivity of aromatics and propene increases slightly with time on stream at the expense of other products, such as methane, butane and butene. Although the aromatics comprised over 50% in the products, Re/HZSM-5 catalyst produced much more cracked products than HZSM-5 and Ga/HZSM-5 during the induction period. After which, the yield of the cracked products over Re/HZSM-5 decreased with time on stream, while the yield of dehydrogenated product (i.e. propene) increased simultaneously. These results implied that rhenium oxide over HZSM-5 was reduced with propane (or produced hydrogen) to highly dispersed metallic Re, which was responsible for the propane dehydrogenation (reaction 3) and aromatization (reaction 4) toward propene and benzene on Re/HZSM-5. This was identical to the results of dehydro-aromatization of methane over Re/HZSM-5 reported by Wang et al. [13], who acquired similar results with TG/DTA/mass and EXAFS studies:
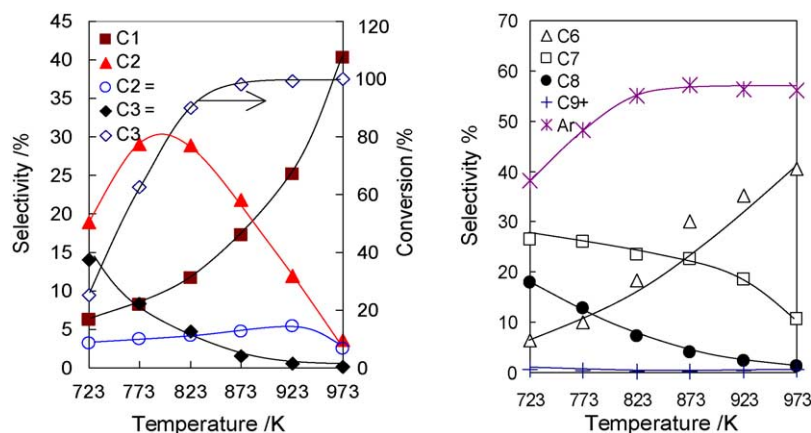
$$C_3H_8 \rightarrow C_3H_6 + H_2 \qquad \Delta H = 30.8 \, kcal \, mol^{-1} \qquad (3)$$

Fig. 3. Propane transformation over Re/HZSM-5.

$$2C_3H_8 \rightarrow C_6H_6 + 5H_2 \qquad \Delta H = 75.6\,\text{kcal mol}^{-1} \qquad (4)$$

3.3. Effect of reaction temperature on the conversion of propane over the Re/HZSM-5 catalyst

The propane conversion and product selectivity were found to be strongly influenced by the reaction temperature as illustrated in Fig. 3. The propane conversion over Re/HZSM-5 increased almost linearly at temperatures lower than 823 K as had been observed over H-GaAlMFI zeolites [14]. Over 823 K, the increase of propane conversion slowed down and reached 100%. Similar results were observed for aromatics selectivity which reached its highest value of 57% above 873 K. The selectivity for methane, ethene and benzene also increases with the increasing of temperature, while the selectivity of ethene changed gradually with temperature and passed through a maximum (30%) at 800 K. The selectivity to propene at 723 K (14%) was higher than that at 973 K (0.09%). These findings suggest that lower reaction temperatures would be favorable for the production of propene (reaction 3) and high temperature for the oligomerizing and aromatizing of propene (reaction 4). Decomposition of propane over Re/HZSM-5 becomes prominent at high temperature since CH$_4$ selectivity elevated upon increasing of the reaction temperature. The thermodynamic data for various reactions (viz. dehydrogenation, cracking, hydrogenolysis and aromatization) suggest that the propane dehydro-aromatization is highly favored at high temperature and the temperature has a little influence on hydrogenolysis of propane [15]. This is consistent with our results.

3.4. Effect of space velocity on the product selectivity over Re/HZSM-5

Effect of space velocity on selectivity of various products over Re/HZSM-5 was studied. The experiments were carried out at 823 K and different W/Fs. The Data shown in Fig. 4 were taken at 60 min after the beginning of the propane reaction with a GHSV between 480 and 4000 h^{-1}. As had

already been observed over HZSM-5 and Ga (or Zn) modified HZSM-5 catalyst [2], the conversion of propane (not shown) decreased with the increasing of the space velocity. At the same time, the selectivity for aromatics was decreased, but that for propene, and also for ethene, was increased with increasing the space velocity. In general, the formation of methane was quite small and decreased with the increasing of space velocity. Kitagawa et al. [16] had been studied the product yields as a function of propane conversion over Ga/ZSM-5, and found that the yield of ethane was small even at high propane conversion. In contrast to that over Ga/HZSM-5, the selectivity of ethane was always larger than methane over the entire GHSV tested. Since the selectivity for ethene decreased with the decrease of GHSV (and hence the increase of propane conversion), ethane would result mainly from the rapid hydrogenation of ethylene on the rhenium sites as has been observed over platinum sites [17,18]. This implies that apart from hydrogenolysis of propane (reaction 2), the decomposition of intermediate alkenes to ethane is also prominent and more effective over Re/HZSM-5 than over Ga/HZSM-5. In other words, the activity of hydrogenolysis is prevailing on rhenium sites than on gallium sites.
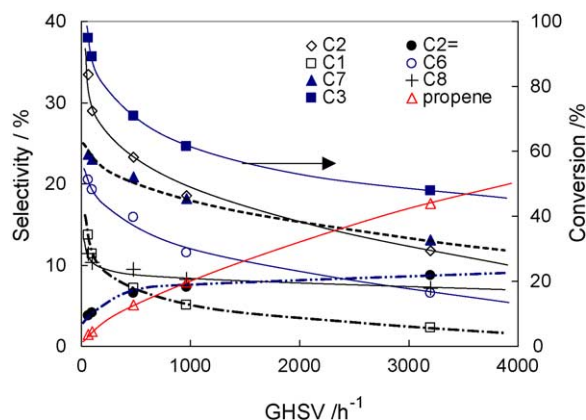

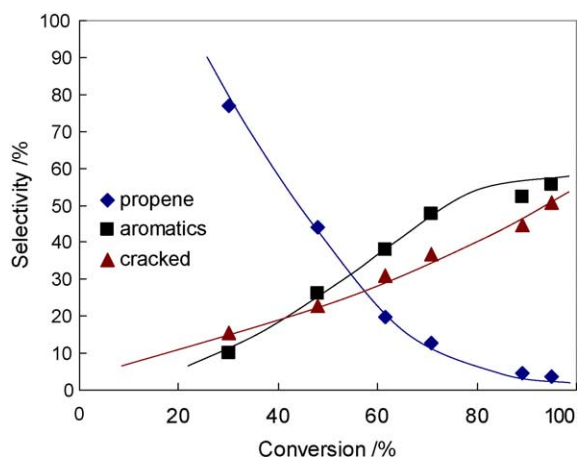Fig. 4. Propane transformation over Re/HZSM-5.

Fig. 5. The selectivity to propene, to aromatics and to cracked products as a function of propane conversion in the reaction of propane over Re/HZSM-5 catalyst. Reaction conditions: 823 K; atmospheric pressure.

Results showing the dependence on the propane conversion of various product selectivities were presented in Fig. 5. Similar to the results of HZSM-5 and modified HZSM-5 catalysts reported previously [9], the selectivity to propene decreased with increasing propane conversion, whereas the selectivity to aromatics and cracked products (C1 + C2) increased. That is to say, at low conversion of propane, the main products were propene (Fig. 5) and ethene (Fig. 4) over Re/HZSM-5. Two primary reactions, dehydrogenation and cracking, might occurred during the initial stage of propane activation. This finding strongly suggested that the reaction of propane over Re/HZSM-5 was identical to that over HZSM-5 and other modified HZSM-5 catalysts.

3.5. Influence of CO_2 and CH_4 additive on the catalytic activity of Re/HZSM-5

The effect of CO_2 and CH_4 additive on the conversion and product selectivity was studied and presented in Table 1. For

Table 1
Effects of co-reactants on the catalyst transformation of propane over Re/HZSM-5 catalyst

Additive in the feed	N_2	CO_2	CH_4
Conversion (%)			
C_3H_8	88.77	57.60	86.86
Selectivity (%)			
C1	11.41	24.92	−25.51
C2	29.01	9.64	18.97
C2=	4.18	5.79	5.05
C3=	5.53	5.65	4.25
C4+	0.97	0.86	0.62
Aromatic			
C6	18.09	9.33	25.91
C7	22.64	10.39	33.82
C8	7.26	3.41	11.30
C9+	0.21	0.00	0.07

Reaction conditions: 823 K, atmospheric pressure, propane content was 30%. Data were acquired as referred to the conversion of propane.

comparison, the conversion of propane mixed with nitrogen was studied in the same condition. Contrary to the results of Ihm et al. [5], who found that carbon dioxide introduction ($C_3H_8/CO_2 = 2.25$) slightly increased the conversion of propane, the conversion of propane in our experiments decreased from 88.8 to 57.6%. Wang et al. [19] found that during the transformation of methane over Mo/HZSM-5, adding a few percent of CO_2 to the CH_4 feed resulted in the promotion of catalyst stability in forming CO, while excessive addition of CO_2 largely inhibited the formation of aromatics. They thought that this took place in a manner similar to the complete poisoning by the addition of a few percent of O_2. It was reasonable to deduce that similar effect of CO_2 existed during the propane transformation over Re/HZSM-5 since a large amount ($C_3H_8/CO_2 = 0.43$) of CO_2 was introduced.

In contrast, addition of methane to the propane stream had no influence on the conversion of propane, while the selectivity to aromatic products was significantly enhanced. Compared to that mixed with N_2, the selectivity to ethane and C9+ was remarkably inhibited. It is interesting to find that when methane was introduced into propane instead of nitrogen, the selectivity of methane over Re/HZSM-5 decreased from 11.4 to −25.5% based on the transformation of propane. In accordance with present results, Chu and Qiu [20] had reported a higher formation rate of benzene for a methane/ethane co-feed system. This indicated that the formation of methane was inhibited and the methane from the starting mixture is transformed. It seems that the alkanes (propane or ethane) could be more easily activated to give surface intermediate species, and then more methane could be activated to produce aromatics. Indeed, Echevsky et al. [21] had reported similar results for the reaction of methane with isobutane over a 2% Ga/HZSM-5 catalyst. Nevertheless, the present results contradict with the work of Brandford et al. [22]. The possible explanation is presently unavailable and needs further investigation.

4. Conclusion

The dehydrogenation and aromatization of propane over Re/HZSM-5 catalyst were studied and compared with HZSM-5 and Ga/HZSM-5 catalyst. Re/HZSM-5 showed higher activity toward dehydrogenation and aromatization. The temperature and space velocity had a pronounced influence on the product distribution. Different impacts were observed by using CO_2 and methane as co-reactants. The former largely inhibited the propane transformation, while the latter improved the selectivity of aromatic products and inhibited the decomposition of propane.

Acknowledgement

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