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KF/Al_2O_3 as Solid Base for the Synthesis of Polycarbonate Diols (PCDLs)

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Abstract Polycarbonate diols (PCDLs) are known as important intermediate for the manufacture of novel polyurethanes. In this work, a series of KF loaded oxides and alumina doped with potassium halides were prepared and employed as the catalysts for the PCDL synthesis via the reaction of hextane-1, 6-diols (HD) and dimethyl carbonate (DMC) followed by vacuum oligomerization. Experimental results indicated that among the catalysts tested, KF/Al_2O_3 exhibited the best catalytic activity. Moreover, the catalyst could be reused for three times with acceptable catalytic activity. The basic centres with medium and strong strength generated through the interaction between KF and Al_2O_3 were catalytically active for the reaction.

Keywords Polycarbonate diols · Alumina-supported potassium fluoride · Solid base catalyst · Recyclable catalyst

1 Introduction

Polycarbonate diols (PCDLs) can be used as the precursor for the preparation of novel polyurethanes. The polyurethanes obtained show better hydrolytic stability, mechanical properties and anti-oxidation ability than the conventional ones base on polyether or polyester diols [1–3].

PCDLs may be synthesized via many routes. Among them, transesterification of dimethyl carbonate (DMC) with aliphatic diols, as illustrated in scheme 1, is a more promising one [4].

Compared with other methods, the transesterification process has many advantages such as flexibility for synthesizing PCDLs with multiple structures, use of limited quantities of catalysts and controlled programming of the molecular weight of the target products [4]. Moreover, the realization of commercial production of DMC via oxidative carbonylation of methanol renders the route better prospect [5].

Though various homogeneous catalysts are commonly adopted for this reaction, the disadvantages of these catalysts are evident. For example, they are hardly separated from the reaction mixtures by means of simple filtration and can not be reused [6, 7]. Recently, great advance has been made in catalyst recycling for polymer synthesis [8–10]. However, the report with respect to the present reaction has not yet appeared as far as we know. Therefore, development of recyclable solid catalysts with higher efficiency for the PCDL synthesis through transesterification reaction is highly desirable.

Solid base has enjoyed growing attention due to its environmentally friendly nature and unique properties. Of a variety of solid bases, KF/Al_2O_3 is a typical example. It has been employed as an effective catalyst in a variety of organic reactions including Michael, Knoevenagel and related addition reactions, aldol condensations, hydration of amides, alcoholysis of esters and epoxides, and the Darzens reaction [11–18]. In the present work, feasibility of KF/Al_2O_3 as a catalyst for the synthesis of PCDLs was investigated. Elemental analysis, XRD and CO_2-TPD techniques were used to characterize the catalysts.

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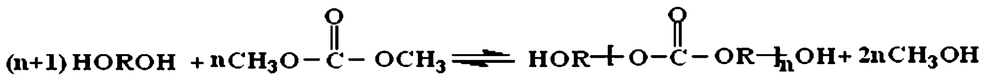

$$(n+1)\,HOROH + nCH_3O-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_3 \rightleftharpoons HOR{+}O-\overset{\overset{\displaystyle O}{\|}}{C}-OR{+}_nOH + 2nCH_3OH$$

Scheme 1

2 Experimental

2.1 Preparation of Catalyst

The reagents used in this work were all commercially available without further treatment prior to utilization. The Al_2O_3 was referred to commercial γ-Al_2O_3 having BET surface area of 140 $m^2 \cdot g^{-1}$. All catalysts employed in this work were prepared by impregnating the supports with an aqueous solution of corresponding potassium salts for 24 h. The slurries made were heated in an oven at 393 K overnight and then calcined in air at 473 K for 5 h. The loading amount of potassium compounds was 30 wt.% based on the weight of the supports.

2.2 Catalyst Characterizations

The XRD measurement was performed on a Bruker AXS's D8 ADVANCE powder X-ray diffractometer using Cu Kα radiation, over a 2θ range of 5–80° with a step size of 0.017° at a scanning speed of 5°/min.

The temperature-programmed desorption of CO_2 (CO_2-TPD) was used to determine the basic properties of the catalysts. The desorption of CO_2 was monitored on-line by a thermal conductivity detector (TCD) during heating the sample from 298 K to the desired temperature at a ramp rate of 10 K/min.

The contents of K and F were determined by atomic absorption spectrometry (Hitachi 18080) after dissolution of the solid, and by potentiometry using a specific electrode at PHS-3C, respectively.

2.3 Synthesis of PCDLs

The reaction was performed in a 500 mL four-necked flask equipped with a mechanical stirrer, reflux condenser, thermometer and feeding funnel. In a typical test, HD (68.73 g, 0.58 mol) and the catalyst (in weight percent of the HD) were added into the flask. After purging with nitrogen, the temperature of the flask was gradually raised to certain value under atmospheric pressure and then DMC (57.82 g, 0.64 mol) was slowly added through the feeding funnel to the reaction mixture within a time-span of 1.5 h. The volatile by-products were removed through the reflux condenser over a period of 1.5 h. Subsequently, the reaction temperature was raised to 453 K and the pressure was reduced to about 5.07×10^4 Pa. Finally, the pressure was reduced to 5.00×10^3 Pa and kept on for several hours.

The distillate was analyzed by a gas chromatograph (Shimadzu GC-14B) equipped with a flame ionization detector (FID). PEG 20M was used as stationary phase. Column temperature was 393 K and injection temperature was 473 K. The yield was expressed in percentage of the theoretical value that was calculated based on 100% conversion of HD to PCDLs.

The molecular structures and molecular weights of PCDLs were analyzed by FT-IR spectroscopy (Nicolet 380 FT-IR spectrometer), ^{1}H-NMR ($CDCl_3$) (Bruker's drx-300) and Gel-permeation chromatography (GPC) at 308 K in *N,N*-dimethylformamide solution (Shimadzu LC-20AD Chromatograph). The calibration curve was made using standard sample of monodispersed polystyrene.

The spectral data of the product except small peaks ascribed to the end groups were shown as follows.

IR (KBr): 2,939, 2,870 and 1,483(CH2), 1,740(carbonate C=O), 1,263 and 1,071 cm^{-1} (ester C–O–C).

^{1}H-NMR ($CDCl_3$): δ = 1.42(t, 2H, c), 1.65(t, 2H, b), 3.50(t, 2H, d) and 4.08(t, 2H, a) (see Scheme 2).

3 Results and Discussion

3.1 Screening of the Catalysts

The catalyst evaluation for the present reaction was performed and the results are shown in Fig. 1. When KF was loaded on different supports such as SiO_2, TiO_2, ZrO_2, ZnO and Al_2O_3, disparate catalytic performances were observed. The KF/SiO_2 and KF/TiO_2 showed low catalytic activity. Both KF/ZrO_2 and KF/ZnO exhibited higher activity. Especially, KF/Al_2O_3 exhibited the highest activity of 85% HD conversion. This suggested that the support played a vital role in deciding catalytic activity of the catalysts, and Al_2O_3 was the most suitable support. Because pure Al_2O_3 was little active and KF itself showed lower activity than KF/Al_2O_3, it might be reasonable to deduce that the interaction of KF and Al_2O_3 might create unique active sites which endowed KF/Al_2O_3 with high catalytic ability for this reaction.

$$HO\overset{d}{CH_2}(CH_2)_5{+}O\overset{\overset{\displaystyle O}{\|}}{C}O\overset{a}{CH_2}\overset{b}{CH_2}\overset{c}{CH_2}CH_2CH_2CH_2{+}_n OH$$

Scheme 2

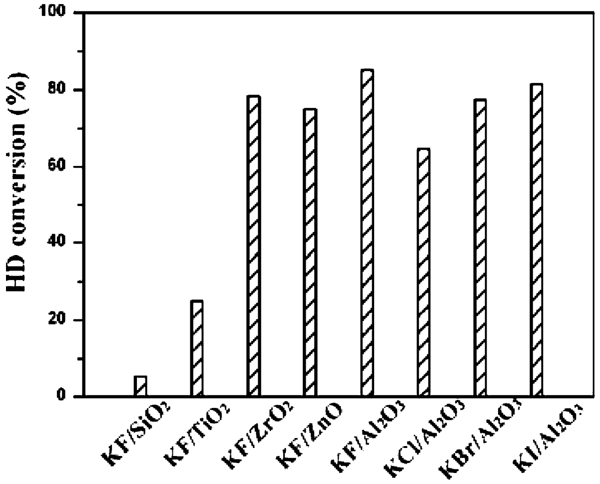

Fig. 1 Catalytic activities of various catalysts. Transesterification reaction conditions, HD:DMC = 0.58 mol:0.64 mol; reaction temperature, 433 K; reaction time, 3 h; catalyst amount, 0.5 wt.%; pressure, atmospheric pressure

In order to examine the effect of anion type of the halide, Al_2O_3 doped with KCl, KBr and KI were used as the catalysts and the reaction results were compared with that of KF/Al_2O_3 as shown in Fig. 1. It was found that the types of anions of halide had certain impact on the activity of the catalysts and KF showed the best performance in the cases studied.

Taking into account the basicity dependence of the PCDL synthesis via transesterification, the basicity of the catalysts was characterized using CO_2-TPD.

Figure 2 shows the CO_2-TPD profiles of KF loaded oxides calcined at 473 K for 5 h. The desorption peaks with maxima at about 363 K, 410 K and 465 K indicated the presence of three types of basic centres having different strength. They denoted in turn weak, medium and strong basic ones, respectively. It seemed that certain correlation between the activity and total basicity of the catalysts existed, namely, the more basic the catalysts were, the higher activity they had. However, more attention was paid to medium and strong basic centres in terms of practical reaction temperature employed. A better consistency between the activity of the catalysts and the amount of these two kinds of centres was observed. For example, KF/Al_2O_3 having maximum medium and strong basic centres possessed the highest activity, while the rest could be deduced by analogy. Thus, we could appreciate that these two types of centres in the catalysts were responsible for the HD conversion.

Figure 3 shows CO_2-TPD profiles of Al_2O_3 doped with various potassium halides. For comparison, the curve of KF/Al_2O_3 in Fig. 2 was also included. Similar to Fig. 2, three kinds of basic centres with different peak temperatures were observed. Besides total basicity, the amount of medium and strong basic centres was closely related to the activity of the catalysts. This also indicated that these centres catalyzed HD conversion.

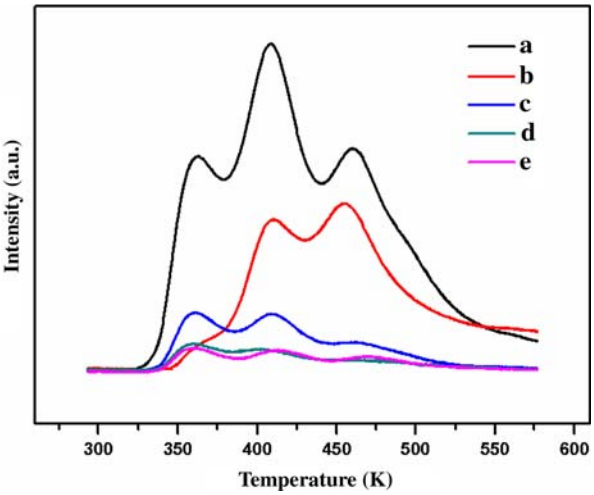

Fig. 2 CO_2-TPD profiles of catalysts: (**a**) KF/Al_2O_3; (**b**) KF/ZrO_2; (**c**) KF/ZnO; (**d**) KF/TiO_2 and (**e**) KF/SiO_2

3.2 Reuse of Catalyst

In order to examine the catalytic efficiency of recycled KF/Al_2O_3, it was reused by filtrating out the catalyst, washing it with methanol and heating in an oven for 5 h at 393 K prior to use for the next experiment. It was found that at the end of first reuse, KF/Al_2O_3 sustained a better activity with 80% HD conversion. After third run, KF/Al_2O_3 still gave HD conversion of 68%. Meaningfully, subjected to calcination at 473 K for 5 h in air, used catalyst could restore almost all of its original activity and conversion of 84% was attained. This was not difficult to be understood in view of the CO_2-TPD profiles given in Fig. 4.

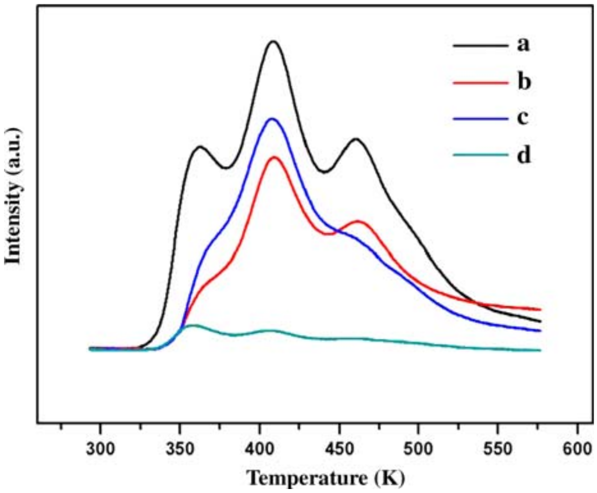

Fig. 3 CO_2-TPD profiles of catalysts: (**a**) KF/Al_2O_3; (**b**) KI/Al_2O_3; (**c**) KBr/Al_2O_3 and (**d**) KCl/Al_2O_3

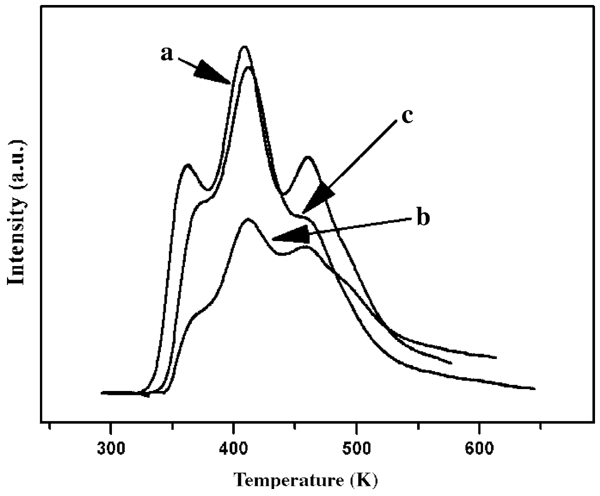

Fig. 4 CO_2-TPD profiles of samples: (**a**) fresh KF/Al_2O_3; (**b**) third reused KF/Al_2O_3 and (**c**) regenerated KF/Al_2O_3

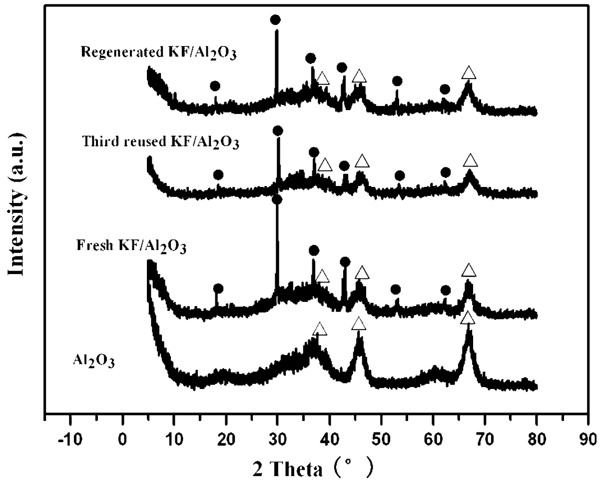

Fig. 5 XRD patterns for Al_2O_3, fresh, third reused and regenerated KF/Al_2O_3. •: K_3AlF_6, △: Al_2O_3

For the third reused catalyst, basicity of strong and medium basic centres declined to certain extent. However, for the regenerated one, these basic characteristics almost restored to the original level of the fresh catalyst. These facts demonstrated that the basicity of strong and medium basic centres determined the catalytic activity of KF/Al_2O_3 regardless of fresh, used or regenerated catalyst.

Two reasons may account for the reduction of catalyst basicity after use. One is the leaching of active ingredient, and the other is the coverage of basic sites by organics. However, the results of elemental analysis showed that compared with the fresh catalyst, no obvious change in K and F contents for the third reused one was found, indicating that decline of basicity was not caused by leaching of active ingredient. Actually, as the reaction proceeds, molecular weight of the product gradually grows and some products are inclined to stay on the catalyst surface leading to the partial coverage of the basic sites. The organics could not be removed completely by simple washing with methanol, and resulted in successive accumulation over the sites and the drop of the catalyst basicity. It appeared that this was the most likely reason for the decline of catalyst basicity after use.

XRD patterns of the fresh, the third reused and the regenerated KF/Al_2O_3 are depicted in Fig. 5, respectively. Three diffraction peaks around 2θ value 37.5°, 46°, 67° ascribable to γ-alumina were observed for all the catalysts, indicating that the matrix of the catalysts retained. In addition, spectral characteristics belonging to K_3AlF_6 phase appeared for the catalysts [19]. Note that the intensities of the lines changed with the catalysts and decreased in following order: fresh $KF/Al_2O_3 >$ regenerated $KF/Al_2O_3 >$ third reused KF/Al_2O_3. This accorded with their catalytic activities and their basicity characteristics shown in Figs. 4 and 6. Therefore, it was reasonable to infer that K_3AlF_6, derived from the interaction of KF and Al_2O_3, induced basic centres, in particular, medium and strong basic centres and constituted active phase for this reaction.

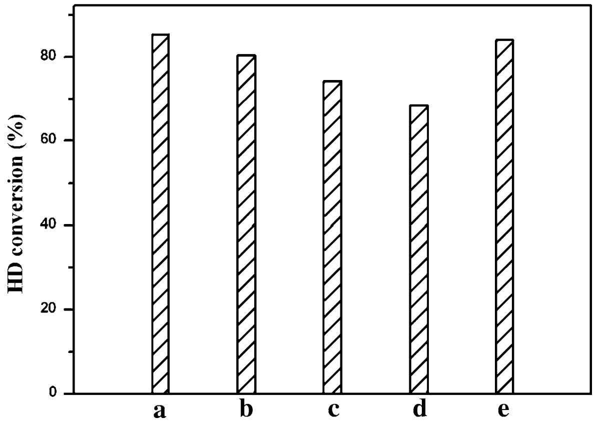

Fig. 6 Recycle study of KF/Al_2O_3: (**a**) fresh KF/Al_2O_3; (**b**) first reuse; (**c**) second reuse; (**d**) third reuse and (**e**) ◆ regenerated KF/Al_2O_3. Reaction conditions were identical with that of Fig. 1. ◆: Regeneration was conducted by calcining the used catalyst at 473 K for 5 h in air

The inconsistent conclusions whether K_3AlF_6 was active sites for KF/Al_2O_3 catalyzed reactions had been reported by different researches. For example, Baba et al. demonstrated that K_3AlF_6 was not active species for self-condensation of benzaldehyde and methathesis of trimethylsilylethylene [20, 21]. However, the possibility of K_3AlF_6 acting as active species for Michael addition of nitromethane to butane-2-one could not be excluded. In our opinion, this depended on the idiographic reaction and the reaction conditions. In our work, K_3AlF_6 being active sites was more reasonable based on the results above.

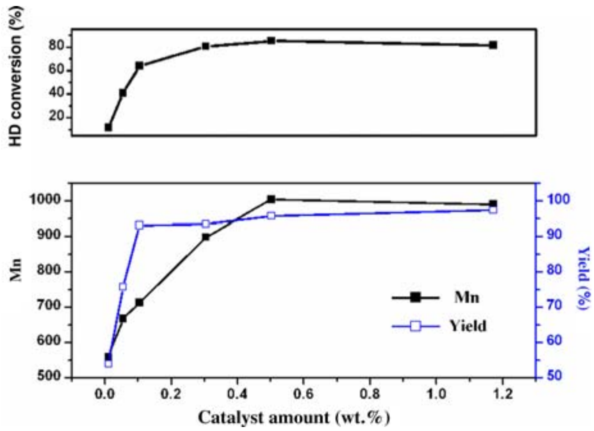

Fig. 7 Influence of catalyst amount on the HD conversion, Mn and yield of PCDL. Transesterification reaction conditions: HD:DMC = 0.58 mol:0.64 mol, reaction temperature: 433 K, reaction time: 3 h, pressure: atmospheric pressure. Vacuum oligomerization conditions: reaction temperature: 453 K, reaction time: 8 h

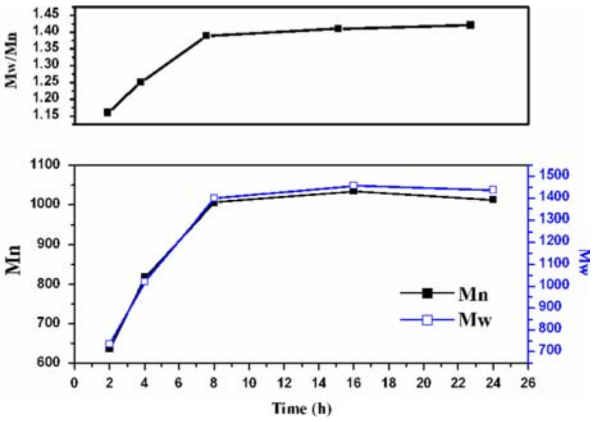

Fig. 9 Influence of time of the vacuum oligomerization on the Mw/Mn, Mn and Mw of PCDL. Transesterification reaction conditions: HD:DMC = 0.58 mol:0.64 mol, reaction temperature: 433 K, catalyst amount: 0.5 wt.%, reaction time: 3 h, pressure: atmospheric pressure. Vacuum oligomerization conditions: reaction temperature: 453 K

3.3 Catalytic Performance of KF/Al_2O_3 for the Synthesis of PCDL with Molecular Weight 1,000

In the following parts, we studied the influence of various reaction conditions on the process using KF/Al_2O_3 as a catalyst. Stoichiometrically, 0.58 mol HD and 0.64 mol DMC were taken to obtain target PCDL whose numeric average molecular weight was designed as 1,000. Whole PCDL synthesis involved transesterification between DMC and HD, and subsequent vacuum oligomerization.

Fig. 7 shows the HD conversion, Mn and yield of PCDL as the function of catalyst amount. It was found that the HD conversion and Mn increased rapidly with increasing catalyst amount from 0.01 wt.% to 0.5 wt.%, and then decreased a little. However, the yield of PCDL still grew weakly above 0.5 wt.%. With 0.5 wt.% of catalyst, the yield of PCDL up to 96% was obtained with the Mn of 1,006.

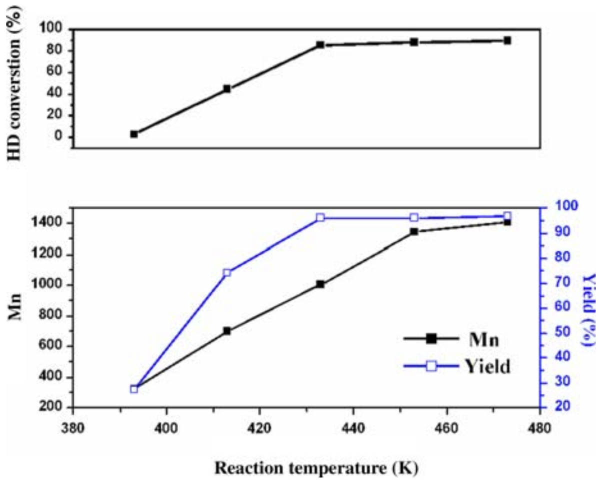

Fig. 8 Influence of reaction temperature on the HD conversion, Mn and yield of PCDL. Transesterification reaction conditions: HD:DMC = 0.58 mol:0.64 mol, catalyst amount: 0.5 wt.%, reaction time: 3 h, pressure: atmospheric pressure. Vacuum oligomerization conditions: reaction temperature: 453 K, reaction time: 8 h

Figure 8 shows the effect of reaction temperature. Different from the uninterrupted increase of Mn, the HD conversion and yield first increased when the temperature went up from 393 K to 433 K and kept constant with further raising the temperature. Therefore, 433 K was chosen as the suitable temperature for the process. Higher temperature turned the final product coloured.

It is well known that vacuum operation is essential for this reaction to obtain desired product. Figure 9 shows the effect of vacuum time course on the Mn, Mw and Mw/Mn of PCDL. These values all increased quickly during the initial 8 h, and then the Mw/Mn changed lightly while the other two remained almost constant. It appeared that 8 h was suitable for attaining the preconcerted goal.

4 Conclusions

In conclusion, KF/Al_2O_3, as a solid base catalyst, exhibited good performance for the synthesis of PCDLs through transesterification of DMC with HD, followed by vacuum oligomerization. The catalyst also showed reasonable activity with three times of recycle. The characterization of KF/Al_2O_3 using elemental analysis, CO_2-TPD and XRD revealed that the catalytic activity was closely related with the basicity of medium and strong basic centres existing in the catalyst. K_3AlF_6 phase generated via the interaction of KF with Al_2O_3 during the catalyst preparation was proposed as the active site of the catalyst for the reaction.

Under the optimum reaction conditions, HD conversion of 85% and PCDL yield of 96% were obtained.

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