

Research Article

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Synthesis of *tert*-amylbenzene for side-chain alkylation of cumene catalyzed by a solid superbase

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Abstract: The side-chain alkylation of cumene and ethylene over a solid superbase catalyst K/KOH/ γ -Al₂O₃ is investigated. The effects of the reaction temperature, pressure, and time on the conversion of cumene and selectivity of *tert*-amylbenzene (TAB) are discussed. The experimental results show that the conversion of cumene to *tert*-pentylbenzene increases with the increase in reaction temperature and ethylene pressure. The catalytic reaction has certain operational flexibility in terms of the reaction temperature, pressure, and time. In addition, the catalytic reaction can achieve directional conversion. The optimum operating conditions are obtained using a single factor test. The conversion of cumene is 99.8% and the selectivity toward TAB is 97.9% under catalyst concentration of 4 wt%, reaction temperature of 55°C, reaction pressure of 0.45 MPa, and reaction time of 30 min. The deactivation of catalyst is mainly caused by oxygen and water in the raw material.

Keywords: cumene, *tert*-amylbenzene, ethylene, side-chain alkylation, solid superbase

1 Introduction

The concept of solid superbase was proposed by Tanabe [1], who defined the solid superbase as a solid whose

basicity function $H_- \geq 26$. Solid superbase is mostly prepared by dispersing alkaline earth metal oxides or composite oxides of alkali metal and alkaline earth metal oxides on a corresponding carrier [2]. It exhibits excellent catalytic ability in reactions such as olefin double bond isomerization, addition, and condensation reactions.

Most researchers explored the catalytic characteristics of solid superbase. Suzukamo et al. [3] prepared a solid superbase by continuously treating γ -alumina with sodium hydroxide and sodium at 280–350°C under the nitrogen atmosphere. The base exhibited an outstanding performance in catalyzing the isomerization of 5-vinylbicyclo [2.2.1] hept-2-ene to 5-ethylidenebicyclo [2.2.1] hept-2-ene. Meyer et al. [4] studied the catalytic behavior of the superbases Na/NaOH/ γ -Al₂O₃ and Cs_xO/ γ -Al₂O₃ as well as the basic zeolites Na/NaX and Cs_xO/CsX in the Michael addition of ethyl acrylate and acetone, and they found that the solid superbase showed high catalytic activity at a lower catalyst loading. Borah et al. [5] employed the solid superbase K/ γ -Al₂O₃ as a highly efficient catalyst to perform direct 1,4-addition reactions of simple amides with α , β -unsaturated carbonyls. High yield of the desired compound 1, 5-dicarbonyl was obtained with excellent anti-diastereoselectivities. Ma et al. [6] found that when the solid superbase catalyst K/KOH/ γ -Al₂O₃ was used in the transesterification reaction of rapeseed oil and methanol to produce biodiesel, high production efficiency was obtained under mild reaction conditions, the yield of biodiesel can reach as high as 84.52% after 1 h at 60°C, with a 9:1 molar ratio of methanol to oil, a catalyst amount of 4 wt%, and a rotating speed of 270 g.

TAB is an important organic synthesis intermediate and chemical raw material. It is mainly used during the production of *tert*-amyl anthraquinone, an important carrier of hydrogen peroxide. The catalytic process of TAB synthesis mainly includes acid catalysis and base catalysis [7–10]. The acid catalysis method involves the Friedel-Crafts alkylation [11–16] of benzene using *tert*-amyl alcohol [12–14], isoprene, and *tert*-pentane chloride catalyzed by an acid catalyst, such as sulfuric acid and aluminum

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trichloride. The alkali catalysis process is mainly side-chain alkylation, with alkali metal or alkali metal hydride used as its catalyst.

Cowley et al. [17] have used solid phosphoric acid to catalyze the Friedel-Crafts alkylation of benzene and isoprene to produce TAB. The alkylation process was investigated in the range of temperature 160–220°C, pressure of 3.8 MPa, and olefin-benzene ratio of 1/6–6. It was found that control over the isomerization of the carbon chain skeleton could be achieved by adjusting the olefin-benzene ratio. Furthermore, the main and side reactions can be controlled to reflect the progress. Under mild conditions, Sumitomo Chemical Co., Ltd has developed a solid superbase of sodium supported by alumina [18–22], and it was used for the reaction of cumene and ethylene. In the end, a high selectivity of more than 99% was obtained. In addition, some studies have also used molecular sieve catalysts to catalyze the synthesis of TAB from benzene and isoprene [7], but they have problems such as catalyst deactivation and large amounts of by-products. In contrast, the side-chain alkylation of cumene and ethylene has the advantages of fewer by-products, high reaction efficiency, and great development potential.

In this article, cumene and ethylene were used as raw materials, and the alkylated reaction of cumene with ethylene on a solid superbase K/KOH/ γ - Al_2O_3 and the effect of operating conditions on the synthesis of TAB were studied in detail.

2 Experimental methods

2.1 Reagents and chemicals

Pseudoboehmite powder: P-DF-07-LSi, Shandong Aluminum Industry Company; potassium hydroxide: AR, Beijing Chemical Plant; metal potassium: purity >99%, Aladdin reagent; sodium hydroxide: AR, Beijing Chemical Plant; metal sodium: purity >99%, Beijing Chemical Plant; nitrogen: purity >99.999%, Beijing Sanhe Magnificent Gas Co., Ltd; propylene: AR, Beijing Chemical Plant, refluxed by sodium metal for 5 h after refining; ethylene: purity >99.9%, Beijing Sanhe Grand Gas Co., Ltd.

2.2 Catalyst preparation

Pseudoboehmite (2.5 g) was calcined at 550°C for 10 h and stirred in a four-necked flask under 360°C with the

protection of high purity N_2 gas atmosphere. Then, KOH (0.50 g) was added and stirred for 3 h at a constant temperature and all the H_2O generated during the reaction was removed. When the system was cooled to 290°C, 0.25 g of potassium was added to the system with uniform stirring. After 0.5 h of reacting, N_2 atmosphere was cooled to room temperature and the product was taken out and then sealed for reserve.

2.3 Synthesis of *tert*-pentyl

A 160 mL stainless steel autoclave produced by Parr Instrument Company was used. The catalyst was washed in the stainless-steel reactor with 64.4 g of cumene in high purity nitrogen atmosphere. The nitrogen atmosphere was then replaced by ethylene for five times, then stirred, heated to a certain temperature, and continuously filled with ethylene under a certain pressure. After a certain reaction time, the temperature of the reactor was reduced to room temperature and the product was emptied out of the reactor. The liquid phase composition was analyzed by gas chromatography. The conversion of the raw materials was calculated as $C\%$ and the selectivity of the standard products was $S\%$. The experiment was repeated twice, and the average value was taken as the evaluation result.

2.4 Analysis method and data treatment

A Shimadzu GC-14C gas chromatograph with a hydrogen flame ionization detector was used for the quantitative analysis of the products. Column temperature: initial temperature: 150°C, holding for 3 min; final temperature: 240°C, heating rate $5^\circ\text{C}\cdot\text{min}^{-1}$, holding for 5 min; the shunt ratio was 50:1, gasification chamber temperature was 280°C and detector temperature was 280°C.

In addition to the main product (TAB), a small amount of by-products (the total concentration of by-products was 2–3%) was detected, as shown in Table 1.

Table 1 shows that in addition to the main reaction, there are other side reactions, such as excessive reaction of side chain alkylation products and disproportionation of raw materials. According to the qualitative results, the by-products are all benzene derivatives. From the conservation of the number of benzene rings, the conversion of cumene can be used as an index to evaluate the effect of the reaction conditions.

One-way conversion of cumene:

$$C\% = \frac{\text{Total amount cumene involved in the reaction}}{\text{Total amount of cumene}} \times 100\% \\ = \sum_{i=2}^5 \frac{\omega_i\%}{M_i} \times 100\% \quad (1)$$

Selectivity of TAB formation:

$$S_{\text{TAB}}\% = \frac{\text{Amount of cumene converted to TAB}}{\text{Total amount of cumene involved in the reaction}} \times 100\% \\ = \frac{\frac{\omega_2\%}{M_2}}{\sum_{i=2}^5 \frac{\omega_i\%}{M_i}} \times 100\% \quad (2)$$



Since all the substances tested are alkyl aromatics, that is, they are homologue with each other, the analysis results can be corrected by the area normalization method to obtain the mass concentration of each component ($\omega\%$), which can be used to calculate the reaction conversion rate, selectivity, and other parameters.

3 Results and discussion

3.1 Catalyst characterization

Details of the catalyst preparation process, conditions, and characterization can be found in literature. It only describes the characterization results of the catalysts used in this experiment.

Table 1: Qualitative analysis of the reaction products

Serial number	Name of the product	Structure
1	Cumene	$\text{C}_6\text{H}_5\text{CH}(\text{CH}_3)_2$
2	<i>Tert</i> -pentylbenzene	$\text{C}_6\text{H}_5\text{C}(\text{CH}_3)\text{C}_2\text{H}_5$
3	Benzene	C_6H_6
4	1,1-Dimethyl-2,3-dihydro-1 <i>H</i> -indene	
5	1,1,2,3,3-Pentamethyl-2,3-dihydro-1 <i>H</i> -indene	

3.1.1 Indicator method

There are indicator methods and CO_2 -TPD methods for the determination of basic and alkali content of catalysts. The indicator method is cumbersome to operate, and the $\text{K/KOH}/\gamma\text{-Al}_2\text{O}_3$ is not used to determine basic and alkali content because of its active characteristics. However, it is worth pointing out that cumene as the raw material itself is an indicator of Hammett function $H_- = 37$, all the potassium metals were stored in purified cumene. During the preparation of the catalyst, when the metal K coated with cumene is added to the flask, the catalyst shows red. And the catalyst showed reddish brown because of the high temperature which kept the attached cumene volatile. When the catalyst preparation was completed and the catalyst was sealed and protected by cumene, the catalyst still showed red, indicating that the Hammett function of the prepared $\text{K/KOH}/\gamma\text{-Al}_2\text{O}_3$ basic strength was at least 37 as shown in Figure 1.

3.1.2 The analysis of CO_2 -TPD-MS

The CO_2 -TPD curve of loaded KOH and K shows that the incorporation of active components and additives has a great increase in the alkali strength and alkali content of the catalyst as shown in Figure 2. It can be seen from the figure that the above catalysts have three obvious CO_2 desorption peaks at 180°C , 650°C , and 780°C . It can be seen that the loading of metal K has a great influence on the amount of alkali and strength of the catalyst, so that the catalyst carrier generates a large amount of weak base positions and super strong base positions and leads to the strong adsorption-desorption peak of CO_2 to shift to



Figure 1: $\text{K/KOH}/\gamma\text{-Al}_2\text{O}_3$ catalyst with cumene as an indicator.

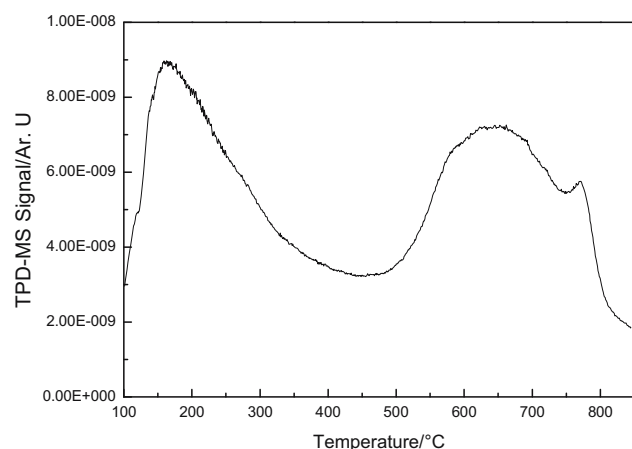


Figure 2: CO₂-TPD of the catalyst.

the right. Therefore, the generation of these basic sites plays a key role in the catalytic ability.

3.1.3 FTIR analysis of CO₂ adsorption

Figure 3 shows the peaks observed at 2,362, 2,388, and 669 cm⁻¹ correspond to the vibration peaks of vibration reduced rotation (P branch), vibration plus rotation (R branch), and vibration transition (Q branch) of CO₂, respectively. The catalyst exhibits a strong binding capacity for CO₂ and surface alkaline strength. The catalyst sample shows a weak absorption peak at 1,446 cm⁻¹, which was attributed to the asymmetric stretching vibration of potassium bicarbonate (O–C–O). The catalyst exhibits infrared absorption bands at 1,397 and 1,518 cm⁻¹, which belong to the symmetrical and asymmetrical

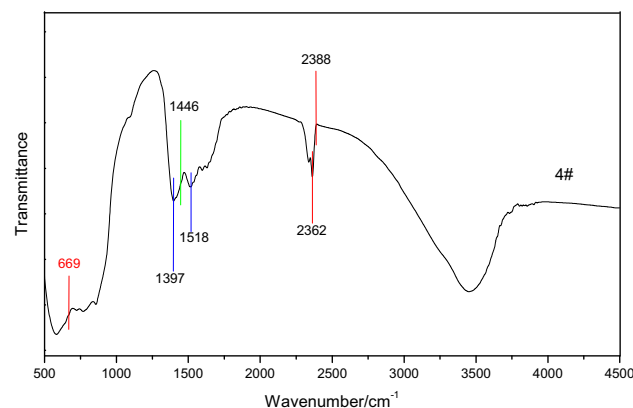


Figure 3: Infrared spectrum of the CO₂ adsorption state of the K/KOH/γ-Al₂O₃ catalyst.

stretching vibrations of monodentate carbonate (O–C–O), respectively, indicating that there is monodentate potassium carbonate coordinated with the carrier on the surface of Al₂O₃ after CO₂ adsorption, which means that there is a strong alkaline potassium species tightly bound to the surface of the fresh catalyst Al₂O₃ before adsorption.

3.1.4 X-ray diffraction (XRD) result analysis

Because K/KOH/γ-Al₂O₃ and KOH/γ-Al₂O₃ have poor resistance to air, the samples were prepared by covering with *n*-octane purified by refluxing and re-evaporating with metal Na. The samples prepared by this method were analyzed by XRD. As a result, a broad peak appeared only at a relatively small angle, which had no effect on the qualitative analysis of the crystal form of the catalyst sample. Diffraction peaks such as 2θ = 37.4°, 39.5°, 45.9°, and 67.0° appear in the above spectrum, which were attributed to γ-Al₂O₃; diffraction peaks such as 2θ = 32.7°, 38.6°, 46.8°, 58.1°, 68.6°, and 78.4° appear in the K/KOH/γ-Al₂O₃ and KOH/γ-Al₂O₃ spectra (Figure 4), which were attributed to β-KAlO₂ and it can be seen that the KAlO₂ appeared during the preparation of the solid superbase is produced by the interaction of γ-Al₂O₃ and KOH. The reaction equation is as follows:



The effect of metal K on catalyst preparation is not limited to the formation of component KAlO₂. When the loading of the metal K is 20 wt%, the presence of metal K in the catalyst is not detected, and the K species on the surface of K/KOH/γ-Al₂O₃ are all ionized, which is consistent with relevant scholars' research on Na/NaOH/γ-Al₂O₃ superbase.

3.2 Reaction conditions

3.2.1 Effect of the reaction temperature

The side-chain alkylation reaction of cumene was carried out under an ethylene pressure of 0.45 MPa. The effect of the reaction temperature on the reaction results was investigated, as shown in Figure 5.

Figure 5 shows that the reaction temperature has an obvious effect on the side-chain alkylation activity. The conversion of cumene increases first and then decreases with the increase in temperature when the reaction went on for 10 min. The conversion reaches the maximum when the temperature is 115°C. From a thermodynamic point of view, since the side-chain alkylation of cumene

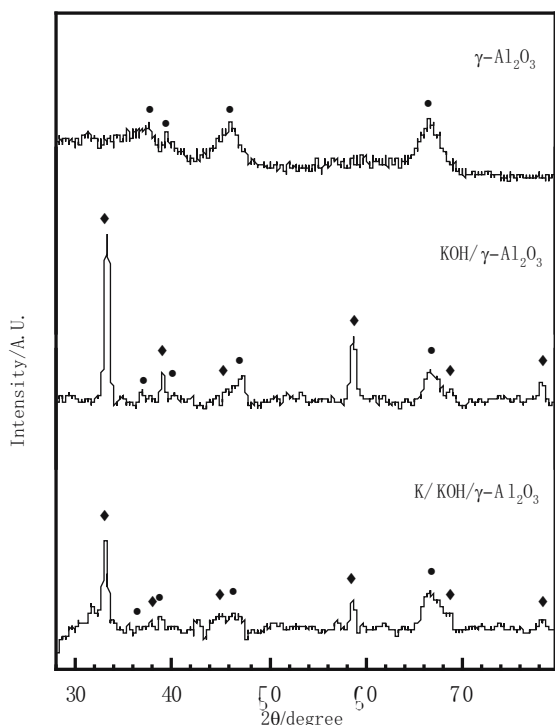


Figure 4: XRD patterns of samples: • $\gamma\text{-Al}_2\text{O}_3$, ◆ $\beta\text{-KAlO}_2$.

and ethylene is an exothermic reaction, when the reaction temperature is lower, the temperature has a greater influence on the reaction rate constant, and the reaction rate constant varies with temperature. However, when the temperature rises to a certain level, the equilibrium conversion rate will decrease with the increasing of reaction temperature. When the reaction went on for 30 min, the conversion of cumene was more than 98% in the range of 55–205°C, and the selectivity of TAB in both

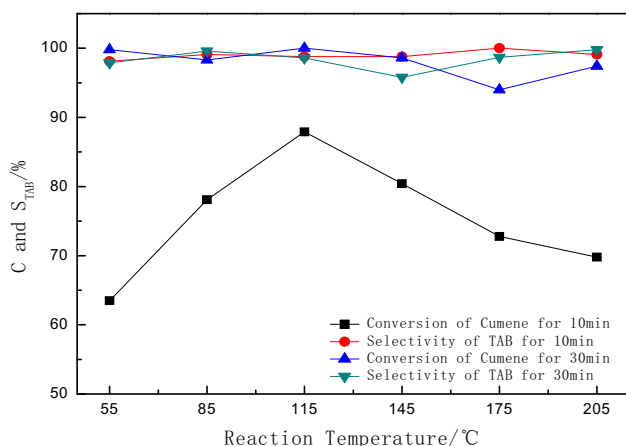


Figure 5: The effect of reaction temperature on the conversion of cumene and selectivity toward TAB.

groups remained at a high level. Figure 5 shows that the side-chain alkylation of cumene can be carried out at 115°C.

3.2.2 Effect of reaction pressure

Figure 6 shows the effect of the reaction pressure on the reaction results on investigation at 55°C. It shows that the effect of the ethylene pressure on the reaction system was obvious. When the reaction time is 10 min, the conversion of cumene was 63.6% at 0.45 MPa and when the reaction time was 30 min, cumene was completely converted at 0.45 MPa. Figure 6 also shows that with the increase in reaction pressure, side reactions will hardly be induced, and the selectivity of the reaction to TAB is more than 98%. However, it was also found that the conversion of cumene was 13.1% and 30.6% at 0.1 MPa over 10 and 30 min, respectively. Under atmospheric pressure, the conversion rate of cumene is low. This is because under atmospheric pressure, ethylene is still in the gaseous phase, and its contact with cumene is insufficient, which leads to an incomplete reaction. Therefore, it is necessary to increase the pressure appropriately.

3.2.3 Effect of the reaction time

The effects of the reaction time on the reaction results were investigated under the condition of reaction temperature of 55°C and pressure of 0.45 MPa (Figure 7).

Figure 7 shows that the reaction rate of the side-chain alkylation catalyzed by K/KOH/ $\gamma\text{-Al}_2\text{O}_3$ is faster, especially

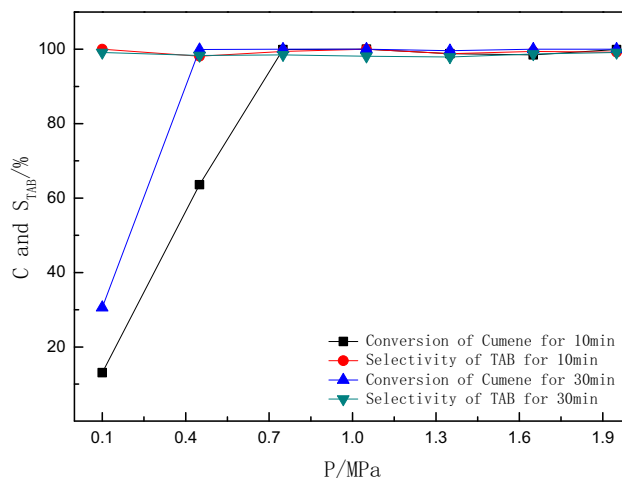


Figure 6: The effect of reaction pressure on conversion of cumene and selectivity of TAB.

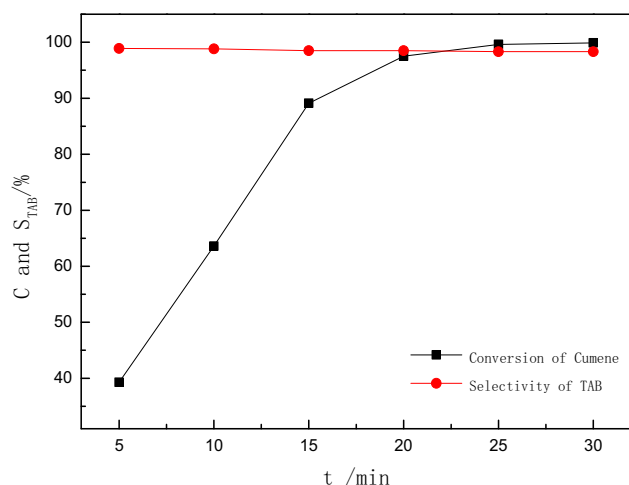


Figure 7: The effect of reaction time on the conversion of cumene and selectivity toward TAB.

within the first 15 min. It can be observed in the experiment that the exothermic reaction is intense in the early stage of the reaction. To a certain extent, the selectivity of the reaction to TAB does not change with the increase in temperature, which indicates that the reaction has the following characteristics: wider temperature operating range. With the prolongation of reaction time, the reaction conversion gradually increased; when the reaction time was 30 min, the conversion of cumene reached 99.8% and the selectivity of the target product was almost not changed. Therefore, prolonging the reaction time did not cause any side effects. In order to ensure the complete reaction, 30 min was chosen as the appropriate reaction time.

3.2.4 Investigation of catalyst life

In this article, three groups of experiments were designed to study the lifetime of the catalyst. The three groups of experiments were as follows:

1# The catalyst used in this article was added to 64.4 g cumene with 0.45 MPa ethylene filled in for the side-chain alkylation, reacting at 55°C for 30 min. After the reaction, only the solution was decanted, 40 g fresh cumene was added, and the reaction was repeated four times. The reaction temperature was elevated to 115°C during the fourth reaction, the reaction pressure and time were maintained at 0.45 MPa and 30 min, respectively as a comparative experiment.

2# The reaction time of the first four repeated experiments was changed to 10 min and the other related operations were the same as the first group of experiments.

3# The first four repeated experiments were performed in the absence of ethylene, heated, and mixed for 10 min, and other related operations were the same as experiment 1#.

Since the time of 1# and 2# repeated reactions is different and it is not longitudinally comparable, the conversion rate of cumene (99.8% and 63.6%, respectively) under the reaction time of 30 min and 10 min is used for normalizing the results of 1# and 2#. The normalized result is shown in Figure 8, from which we can find that the service life of the K/KOH/ γ -Al₂O₃ catalyst is not good. Although the first two reactions have a high activity, it decreases significantly with the increase in cycle times. The conversion of cumene was only 46.1% and 46.2% of the activity of fresh catalyst when the cycle number of catalyst 1# reached the fourth time and the reaction time was 30 min, respectively. Under the reaction conditions of 115°C, 0.45 MPa, and 30 min, comparative experiments were carried out with four catalyst samples in a 1# to 3# experimental cycles with the mass of cumene being 50 g. The experimental results are shown in Figure 9.

From the data in Figure 9, it can be seen that the activities of catalysts 1# to 3# are basically the same after mixing and reacting with cumene at the same number of cycles. However, the catalytic performance of the catalyst 3# as a comparative experiment was much lower than that of the fresh catalyst, which indicates that the four blank experiments of mixing cumene with the catalyst and the transfer operation have a significant effect on the reduction in the catalyst activity. The causes of catalyst deactivation can be summarized as two points, namely, the cumulative effect of trace oxygen in the

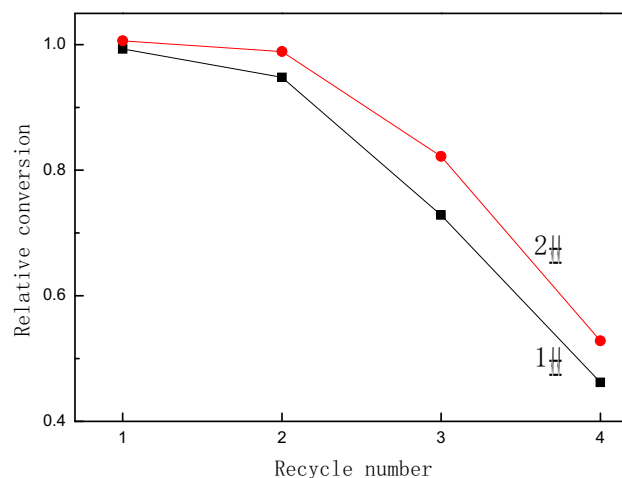


Figure 8: The activity of the catalyst.

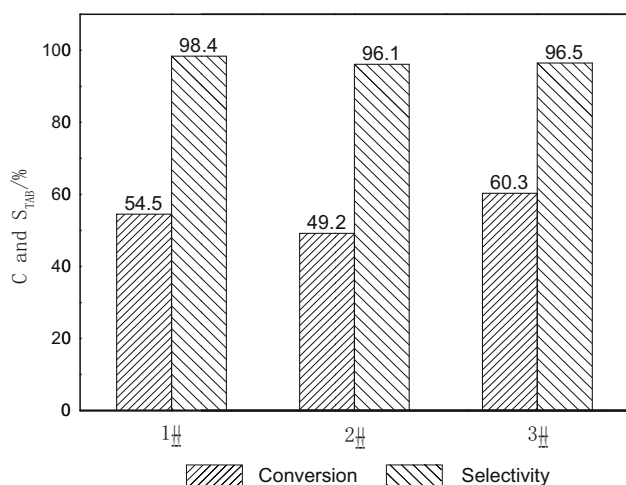


Figure 9: Contrast experiment of catalyst activity.

reaction feed on the catalyst and the mechanism deactivation effect caused by contact between the reaction feed and the catalyst [23]. Therefore, the opportunity for air contact should be avoided in the reaction, which will greatly reduce the oxygen content and water content in cumene, and thus improve the catalyst life in terms of oxygen and water poisoning. According to the above research, the service life of the K/KOH/ γ - Al_2O_3 catalyst did not reach the expected effect. The catalyst activity was only about 50% of that of the fresh catalyst after four cycles. The deactivation was related to the cumulative poisoning caused by trace oxygen and water in the raw materials.

4 Conclusion

By characterizing the catalyst, the results show that the K/KOH/ γ - Al_2O_3 catalyst has super basicity and the main active site of the catalytic reaction does not lie in the strongest basic position of the catalyst, that is, the desorption sites for CO_2 observed at 780°C in CO_2 -TPD analysis; XRD and infrared analysis of the CO_2 adsorption state show that the main component of the catalyst is β - KAlO_2 ; the morphology of the catalyst is characterized by SEM, indicating that the active component of the K/KOH/ γ - Al_2O_3 catalyst is mainly attached to the catalyst pores.

The side-chain alkylation of cumene and ethylene was studied. The results show that the reaction can be accelerated by increasing the reaction temperature and ethylene pressure, and the catalytic reaction has operational flexibility in terms of the reaction temperature,

pressure, and time, while the operating conditions are suitable for the selection of TAB. The selective effect is not sensitive, and the catalytic reaction can basically achieve a directional transformation.

The conversion rate of cumene can reach 99.8% and the selectivity of TAB can reach 97.9% under the following conditions: 4 wt% catalyst concentration, reaction temperature of 55°C , reaction pressure of 0.45 MPa, and reaction time of 30 min.

The service life of K/KOH/ γ - Al_2O_3 solid superbase catalyst has not reached its expected effect. The catalytic activity after four cycles is only about 50% of that of the fresh catalyst. The deactivation is related to the oxygen content in the raw materials.

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