ELSEVIER

Applied Catalysis A: General 238 (2003) 99–107

APPLIED CATALYSIS A: GENERAL

www.elsevier.com/locate/apcata

Synthesis of linear alkylbenzene catalyzed by Hβ-zeolite

Minghan Han*, Zhe Cui, Cong Xu, Wei Chen, Yong Jin

Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

Received 8 January 2002; received in revised form 18 April 2002; accepted 24 May 2002

Abstract

For the alkylation of benzene with long-chain olefins, Hβ-zeolite catalyst not only has the advantages of high selectivity to 2-phenyl isomers with no corrosive or environmental problems, but it also can be regenerated repeatedly. The characterization of the coke shows that the deactivation of catalysts is caused by a jam of bulkier molecules, such as naphthalene, indane and linear alkylbenzenes, which are too big to move quickly in the intracrystalline pores of the catalysts. These bulkier molecules deposit in intracrystalline pores and then in larger pores. The aromatic compounds in raw olefins must be removed because they can deactivate the catalyst quickly; the moisture in the reactants should be 20–30 ppm. The deactivated catalyst can be regenerated by benzene washing at higher temperature. New species, such as alkylbenzene with short chains, naphthalene, indane, biphenyl, condensed ring compounds and unsaturated compounds, are formed by cracking and cyclization in the regeneration process.

Keywords: β-Zeolite; Linear alkylbenzene; Alkylation; Deactivation; Regeneration

1. Introduction

Linear alkylbenzenes (LAB) with long-chains (typically 10–14 carbon) are commonly used commercial products which have some conceivable positional isomers, i.e. 2-, 3-, 4-, 5-, 6-phenyl, etc. A high percentage of 2-phenyl isomer is desired because it has the highest biodegradability, solubility and detergent properties among the related isomers.

Typically, the alkylated aromatics are manufactured commercially using Friedal-Crafts method. Such methods produce high conversions, but the selectivity to 2-phenyl isomers is only about 20%, so selectively catalyzed alkylations are considered widely in the world. In addition, these acidic catalysts in commercial processes are extremely corrosive in nature, thus requiring special handling and equipment. Furthermore, the use of these acids might also induce some environment problems. With increasing environmental concern, it is more and more important to find substitutes equal or superior to these acid catalysts in all respects. Therefore, it would be desirable to utilize a safer and simpler catalyst, preferentially in solid state, to produce the desired products.

Zeolite catalysts, because of their high selectivity, absence of corrosion and environmentally safe properties, are widely studied to replace anhydrous HF or $AlCl_3$ catalyst. In addition, due to their narrow pore dimensions, the selectivity to 2-phenyl isomer is higher than that of HF catalyst. Many kinds of zeolites have been studied in recent years [1–11], but they are easily deactivated and it is difficult to industrialize them.

In this paper, the alkylation, deactivation and regeneration for the synthesis of LAB catalyzed by a catalyst made of Hβ-zeolite are studied comprehensively, and a promising process [12] is reported.

---

* Corresponding author. Tel.: +86-10-62781469; fax: +86-10-62772051.
E-mail address: hanmh@flotu.org (M. Han).

0926-860X/02/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S0926-860X(02)00334-4

2. Experimental

2.1. Material

The catalyst pellet, 2.5 mm in diameter, used for alkylation of benzene with olefins, is made of β-zeolite, of which the crystal diameter is roughly 0.2 μm.

Benzene, with at least 99.0% purity, was obtained from Beijing Yanshan Petrochemical Corporation. The C_{10}–C_{14} olefin/paraffin mixture (Table 1) were provided by Fushun Petrochemical Ltd.

2.2. Apparatus, procedure, analysis and characterization

The experiments for LAB synthesis were carried out in a stainless steel fixed bed reactor (SS316; 12 mm i.d.), down-flow type. The catalysts were always dried at 500 °C for 6 h in a drying oven, then cooled to the reaction temperature in a flow of dry N_2. To evaluate the lifetimes of the catalysts used for the alkylation of benzene with long-chain olefins, we define that the catalysts have deactivated when the conversion of dodecene is $<95\%$.

The analysis of the reactants and products is carried out in a quartz capillary column (SE30, 50 m) in a gas chromatograph (FID, Shimadzu GC-14B) or GC–MS (Agilent 6890-5973N).

A technique [13] is used to characterize the compounds responsible for the zeolite deactivation. This technique consists of treating the coked zeolites at room temperature with a solution of hydrofluoric acid at 40% in order to dissolve the zeolite and to liberate the inner “coke”. The components of “coke” extracted by methylene chloride are analyzed by GC–MS.

Specific surface areas and pore volumes of sample catalysts are obtained by nitrogen physisorption using an automated BET apparatus (Coulter 100CX) under 140 °C, 10^{-4} Pa vaccum level.

IR measurements are performed with a Nicolet Nexus 670 model FT-IR spectrometer. The zeolite sample is compacted into an IR transparent wafer and activated in a conventional vacuum cell under 10^{-3} Pa, 450 °C for 6 h. Pyridine vapor is adsorbed at room temperature for 0.5 h and then desorbed at a pressure of 10^{-3} Pa at 200 °C for 3 h.

Table 1
Composition of raw olefins

	Component (wt.%)	Total
Olefins		
C_{10}	0.69	8.16
C_{11}	2.83	
C_{12}	3.15	
C_{13}	1.47	
C_{14}	0.02	
Paraffins		
C_{10}	9.12	86.67
C_{11}	32.8	
C_{12}	32.4	
C_{13}	13.3	
C_{14}	0.11	
LABs with the chain of C_4–C_7	4.17	4.17

3. Results and discussion

3.1. Phenylalkane isomer distribution

Table 2 shows the comparison of the phenylalkane isomer distribution for different processes in which different catalysts are used. Obviously, these processes exhibit a great difference in the selectivity of 2-phenyl isomers. If one compares it with the conventional catalysts, HF or $AlCl_3$, Hβ catalyst has the highest selectivity to 2-phenyl isomers. Among the different isomers, the 2-phenyl isomer has the highest biodegradability, solubility and detergent properties. Therefore, using Hβ-zeolite catalyst as replacement of HF or $AlCl_3$ has the advantages of high selectivity, no corrosion and fewer environmental problems.

However, as with other solid acid catalysts, Hβ-zeolite is easily deactivated, the lifetime is <20 h. To industrialize a Hβ-zeolite process, one must study the

Table 2
Comparison of the phenylalkane isomer distribution for different processes

Catalyst	Phenylalkane isomer distribution (%)				
	2-Isomer	3-Isomer	4-Isomer	5-Isomer	6-Isomer
HF	16.7	16.4	17.5	24.1	25.3
$AlCl_3$	32	22	16	15	15
Hβ	50.1	27.0	13.5	6.49	2.97

Table 3
Comparison of surface area and volume of different catalysts

Catalyst	Micropore volume (ml/g)	Meso/macropore volume (ml/g)	Micropore surface area (m^2/g)	Meso/macropore surface area (m^2/g)
Fresh	0.1386	0.1650	346.80	94.35
Deactivated at 80 °C	0.1215	0.1642	317.9	92.8
Deactivated at 120 °C	0.1143	0.1507	286.7	89.9
Deactivated at 180 °C	0.1072	0.1238	258.2	85.46

Reaction conditions: 2.0 MPa, 2.5 h^{-1}, mole ratio of benzene to olefins is 15.

deactivation mechanism systematically, and a convenient regeneration method is needed.

3.2. Surface area and pore volume

The evolution of the surface area and pore volume of different catalysts is presented in Table 3. It can be seen that surface area and pore volume decrease when catalysts are deactivated. At 80 °C, only volume and specific surface area for micropores decrease with the deactivation, and the deactivation has no effect on the macropores and mesopores. But, at 180 °C, volume and specific surface area for all pores vary remarkably. This is because the activity of the catalyst and the diffusion rate of the compounds in the pores vary at different temperatures. At lower temperature, a few bulkier molecules can block the channels and decrease the conversion of olefins remarkably, but, at higher temperature, the catalyst will not be deactivated until many bulkier molecules have deposited in the pores. Obviously, the coke deposits in intracrystalline pores at first and then in the larger pores gradually.

3.3. Compounds responsible for the zeolite deactivation

To study the mechanism of the deactivation, it is helpful to characterize the coke composition clearly. The deactivated catalysts were prepared in the fixed bed reactor under the conditions of 150 °C and 2.0 MPa; mole ratio of benzene to olefins is 15 and weight hourly space velocity is 2.5 h^{-1}. When the conversion of olefins decreases to 60%, the input of olefins is shut down, while the benzene is still introduced for an additional 4 h to remove the species that have no influence on the catalyst deactivation.

After treating the coked catalysts at room temperature with a solution of hydrofluoric acid, one finds that the coke can be extracted by methylene chloride completely. The components of the organic compounds deposited in the undeactivated and deactivated catalysts analyzed by GC–MS are shown in Fig. 1. For the undeactivated catalyst, there are only paraffins and LAB product in the extractive solution. If one compares the isomer distribution of the products in Table 2, more 5-isomer LAB and 6-isomer LAB are found in deactivated catalyst. Such results prove that the diffusion of 5-isomer LAB and 6-isomer LAB in the zeolite catalyst is much slower than that of 2-isomer LAB, so they are easier to detain in the catalyst. The shape-selective catalysis benefits product distribution, but the bulkier molecules will block the pores of the catalyst and deactivate the catalyst.

For the deactivated catalyst, the deposited compounds are more complicated than those from undeactivated catalyst, some new species, such as naphthalene, 1-methyl-3-nonyl-indan, 1,4-dibutyl-1,2,3,4-tetrahydro-naphthalene and 5-hexyl-2,3-dihydro-1H-indene are formed. Steric hindrances of these compounds are more significant than those of the reactants, so the deactivation of catalyst may be due to channel blocking by these bulkier molecules.

By analyzing the reactants, one can see that the olefin/paraffin mixture contains olefins, paraffins and alkylbenzenes with the chain of C_4–C_7 (Table 1, Fig. 2). The paraffins are inert components, so alkylbenzenes with the chain of C_4–C_7 in raw material may cause catalyst deactivation. Fig. 3 shows that the lifetime of the catalyst increases remarkably with the removal of C_4–C_7 alkylbenzenes in reactants by some adsorbent. Therefore, the new species in the coke may come from the impurities of the material or may be formed by the cyclization and dehydrogenation of alkylbenzenes with the chain of C_4–C_7.

In addition, the sizes of alkylbenzenes are bigger than those of the reactants, especially 5- and

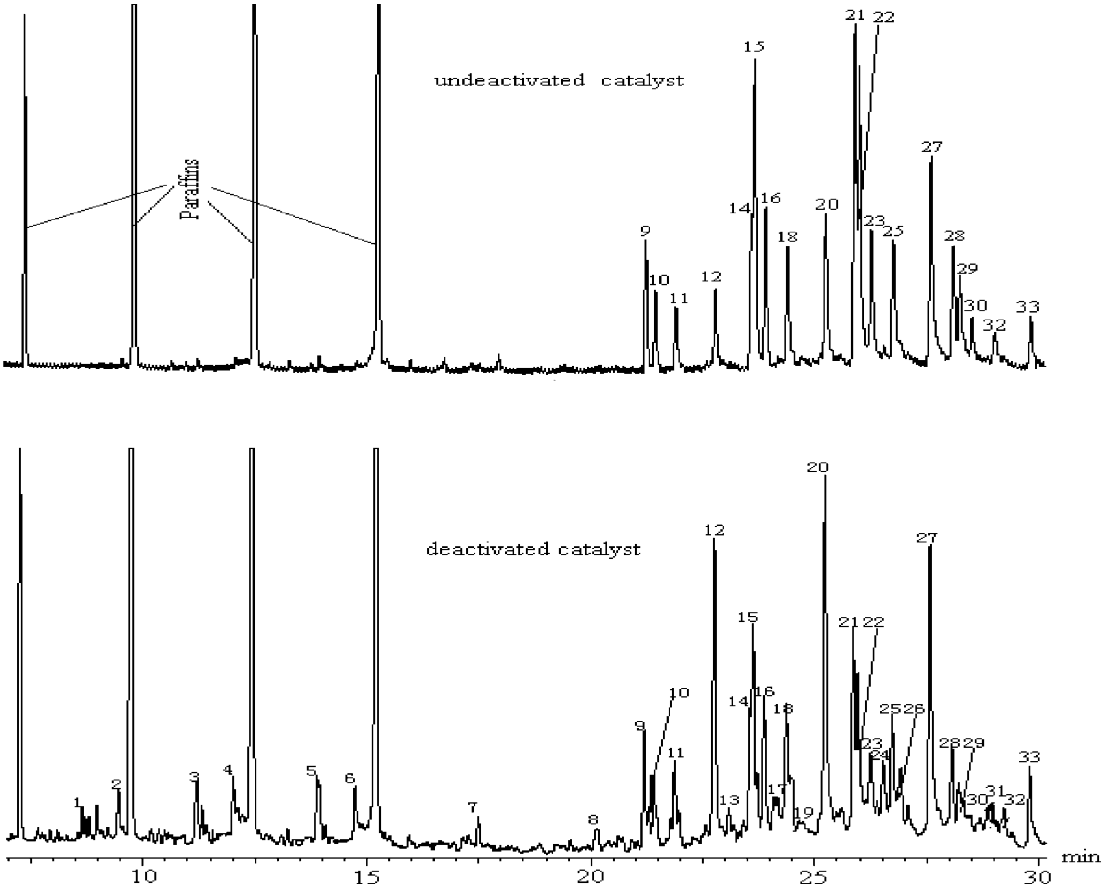


Fig. 1. Components of the organic compounds deposited in the catalyst: (1) 3-butyl-benzene; (2) 3-undecene; (3) 3-pentyl-benzene; (4) 2-pentyl-benzene; (5) 3-hexyl-benzene; (6) 2-hexyl-benzene; (7) tetradecane; (8) 2-nonyl-benzene; (9) 5-decyl-benzene; (10) 4-decyl-benzene; (11) 3-decyl-benzene; (12) 2-decyl-benzene; (13) 1-methyl-4-isohexyl-benzene; (14) 6-undecyl-benzene; (15) 5-undecyl-benzene; (16) 4-undecyl-benzene; (17) 1,1-dimethylnonyl-benzene; (18) 3-undecyl-benzene; (19) 1,4-dibutyl-1,2,3,4-tetralin; (20) 2-undecyl-benzene; (21) 6-dodecyl-benzene; (22) 5-dodecyl-benzene; (23) 4-dodecyl-benzene; (24) 5-hexyl-2,3-dihydro-1H-indene; (25) 3-dodecyl-benzene; (26) naphthalene; (27) 2-dodecyl-benzene; (28) 6-tridecyl-benzene; (29) 5-tridecyl-benzene; (30) 4-tridecyl-benzene; (31) 1-methyl-3-nonyl-indane; (32) 3-tridecyl-benzene; (33) 2-tridecyl-benzene.

6-isomers, which will slow down the diffusion of compounds in catalyst channels. During the reaction, the 5- and 6-isomers accumulate gradually, so the activity of the catalyst will decrease slowly until the catalysts are finally deactivated. This conclusion can be proved by the reaction of benzene with dodecene, in which the catalyst lifetime does not increase remarkably in spite of the absence of impurities in dodecene. Because 5- and 6-isomers will form definitely in the alkylation of benzene with olefins, the deactivation of the catalyst is unavoidable.

It is worth noting that no oligomer and no dialkyl benzene have been detected in the coke, so olefins neither polymerize nor react with LABs in the process.

3.4. Effect of the moisture on the lifetime of the catalyst

For the alkylation reaction with HF catalyst, there must be a sufficient amount of water in the reactants (0.5–1.0%); by this, the undesired product coming from secondary reactions can be decreased to the

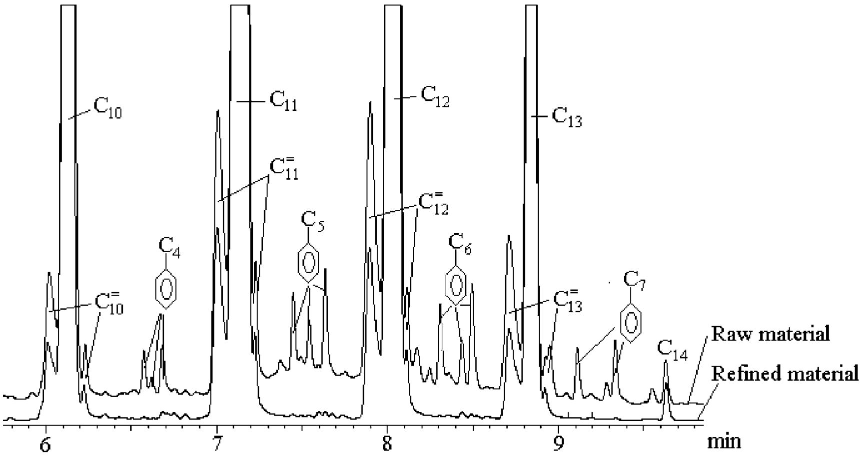


Fig. 2. GC graphs of raw and refined olefins/paraffins.

minimum level. But for the zeolite catalyst, the moisture in reactants greatly influences the reaction. Fig. 4 shows the effect of moisture in the reactants on the lifetime of the catalyst. It can be seen that the moisture has a significant effect on the lifetime of the catalyst and that the optimal water content is about 20–30 ppm. When the water content is smaller, the amount of Bronsted acid in the catalyst is not large enough; on the other hand, when the water content is too large, acidic hydroxyl groups on the surface of the catalyst also decrease [14]. Namely, when a proper amount of water is in the reactants, a proper amount of water is adsorbed on the surface of the catalyst, when the Bronsted acid in the catalyst is large enough and the catalyst has its longest lifetime. Obviously, the moisture has a similar effect on the activity of the catalyst.

3.5. *Effect of temperature*

Fig. 5 shows the effects of reaction temperature on the distribution of products, lifetime of catalyst and the selectivity to linear alkylbenzenes. Temperature

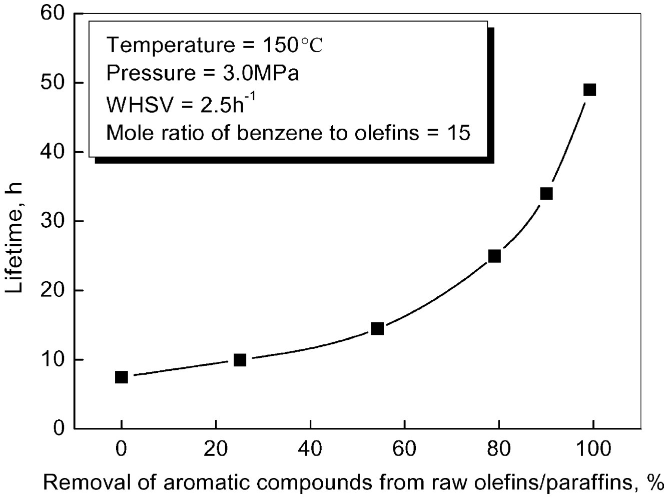


Fig. 3. Effect of the removal of aromatic compounds from raw olefins and paraffins on the lifetime of the catalyst.

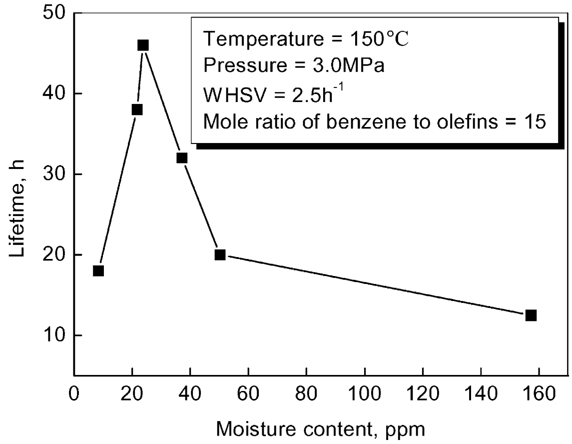


Fig. 4. Effect of moisture content in the reactants on the lifetime of the catalyst.

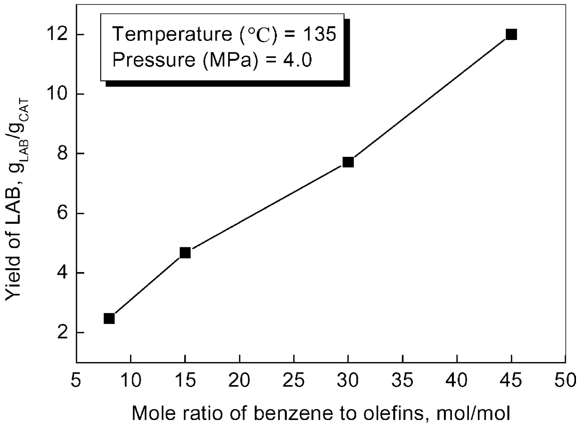


Fig. 6. Effect of the mole ratio of benzene to olefins on the yield of LAB.

has almost no effect on the distribution of products, however, with the increase of temperature, the lifetime increases but the selectivity of linear alkylbenzenes decreases. Therefore, the temperature can not be too high; the suitable temperature is about 135 °C.

3.6. *Effect of mole ratio of benzene to olefins*

Fig. 6 shows the yield of LAB at different mole ratios of benzene olefins for a certain amount of catalyst before it begins to deactivate. It can be seen that a higher mole ratio of benzene to olefins can prolong the lifetime of the catalyst. However, a high mole ratio of benzene to olefins will cause a large amount of benzene to be separated from the product and recycled. For this reason, a low mole ratio of benzene to olefins is desirable.

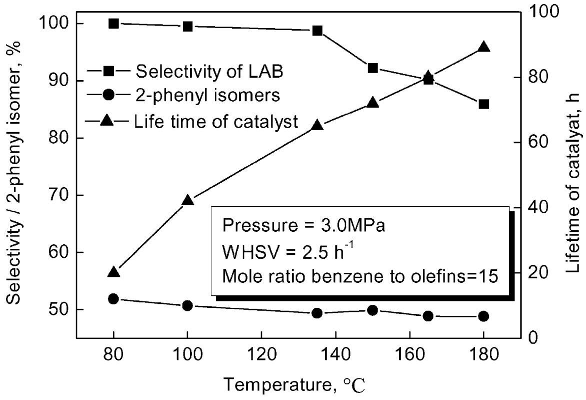


Fig. 5. Effect of temperature on selectivity, 2-phenyl isomer and lifetime.

3.7. *Effect of WHSV of reactants*

The effect of WHSV on the conversion of olefins is shown in Fig. 7. At low reaction temperature, the conversion of olefins decreases with the increase of WHSV. At high reaction temperature, WHSV has only a little influence on the conversion of olefins because the activity of catalyst and mass transfer rate is high enough. The WHSV should be $<3\,h^{-1}$ because a low temperature is feasible.

3.8. *Catalyst regeneration*

The above research shows that the deactivation of catalysts is unavoidable, so the regeneration of catalysts is very important.

Fig. 8 gives the variation of the liquid composition from the outlet of reactor at different regeneration times. When the deactivated catalysts are regenerated by benzene washing at high temperature, some new species, such as alkylbenzenes with short chains (carbon number ≤ 6), naphthalene, indane, biphenyl, condensed ring compounds and unsaturated compounds, are found. In order to verify if the new species are formed in the regeneration, a mixture of benzene and

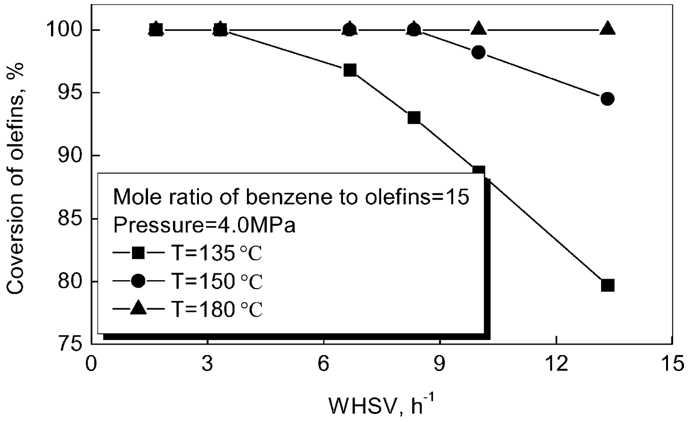


Fig. 7. Effect of WHSV on the conversion of olefins.

linear alkylbenzenes with long-chains of 9–14 carbons is fed into the catalyst bed under the same regeneration condition as those given in Fig. 8, and a similar liquid composition is obtained. Therefore, it can be concluded that, during the regeneration, the alkylbenzenes with long-chains are cracked into alkylbenzenes with short chains and olefins, and then form naphthalene, indane, biphenyl, condensed ring compounds and unsaturated compounds by alkylation and cyclization.

To get a optimal regeneration condition, the effects of temperature, WHSV of benzene, and time on the deactivated catalyst regeneration are studied; the orthogonal experimental design method is applied to design the experiments: three levels to each factor (Table 4). The results are presented in Table 5. After regeneration, the lifetime of the regenerated catalysts is evaluated under 160 °C, 3.0 MPa, 15 mol ratio of benzene to olefins and 2 h^{-1} WHSV. Comparing with fresh catalyst of which the lifetime is 60 h, one finds that temperature has the most significant effect on lifetime, then WHSV and finally time. When the temperature is 280 °C, the activity of deactivated catalysts recovers almost 100%. This can be verified by the acidity characterization of the catalysts in Table 6; the acidity of deactivated catalyst can recover completely after regeneration by hot benzene washing. However, with the increase of regeneration temperature, benzene saturated vapor pressure will increase greatly. If one wants to reduce equipment investment, high pressure is unsuitable and the suitable regeneration temperature should be $\leq$280 °C.

Table 4
Levels of orthogonal experiment factors

Factor	Temperature (°C)	Time (h)	WHSV (h^{-1})
Level 1	220	16	0.5
Level 2	250	24	1
Level 3	280	32	2

Table 5
Result of orthogonal experiments

Number	Temperature (°C)	Time (h)	WHSV (h^{-1})	Lifetime (h)
1	220	16	2.0	45
2	250	16	0.5	54
3	280	16	1.0	56
4	220	24	1.0	42
5	250	24	2.0	48
6	280	24	0.5	60
7	220	32	0.5	40
8	250	32	1.0	46
9	280	32	2.0	61

Table 6
Comparison of acid sites between fresh, deactivated and regenerated catalysts

Acid sites ($\times 10^{23}$ sites g^{-1})	Total acid sites	B acid sites	L acid sites
Fresh catalysts	3.70	3.50	0.20
Deactivated catalysts	1.81	1.67	0.14
Regenerated catalysts	3.69	3.49	0.20

Regeneration conditions: 280 °C, 5.5 MPa, 1 h^{-1}, 24 h.

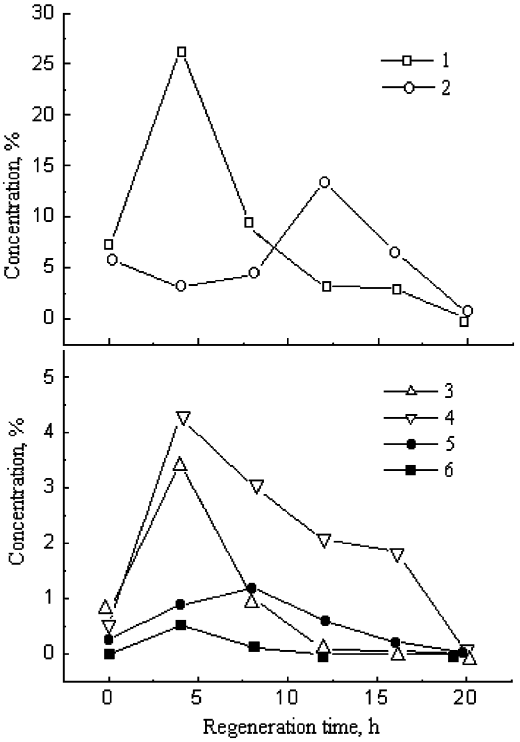
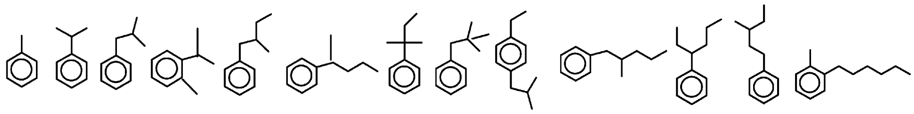


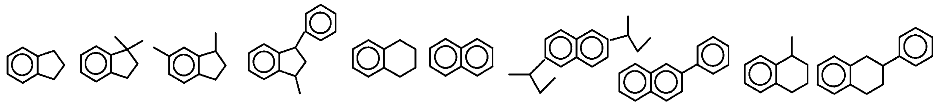
Fig. 8. Variation of the composition at reactor outlet with regeneration time. Regeneration condition: temperature 280 °C, pressure 5.5 MPa and WHSV $1\,h^{-1}$.

1.

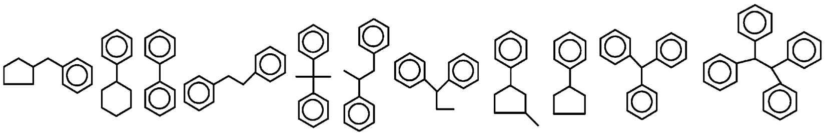


2. LAB

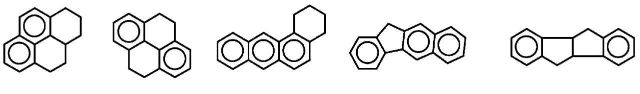
3.



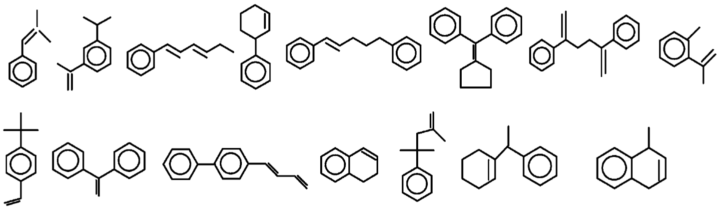
4.



5.



6.



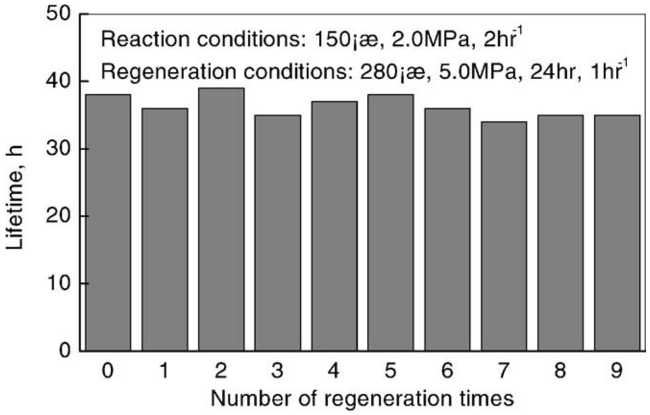


Fig. 9. Reactivity of the catalyst.

Even though the deactivated catalyst can be regenerated by benzene washing, its lifetime for one period is not long enough. For industrial application, the catalyst must be regenerated repeatedly. Fig. 9 illustrates that the reactivity valves of the catalyst are very good after repeat regeneration. Therefore, Hβ is a very promising catalyst for the synthesis of LAB in industry.

4. Conclusion

For the alkylation of benzene with long-chain olefins, Hβ-zeolite catalyst not only has the advantages of high selectivity to 2-phenyl isomers and no corrosive and environmental problems, but it also can be regenerated repeatedly, so it is a very promising catalyst for the industrial applications.

To prolong the lifetime of the catalyst, the aromatic compounds in raw olefins must be removed because they can make the catalyst deactivated, and the moisture in the reactants should be 20–30 ppm. The suitable reaction conditions are 135 °C, 2 MPa, $\leq 3\,h^{-1}$ WHSV.

The deactivation of catalysts is caused by a jam of bulkier molecules, such as naphthalene, indane and linear alkylbenzenes, which are too big to move quickly in the intracrystalline pores of catalysts, so they deposit first in intracrystalline pores and then gradually in the larger pores.

The deactivated catalyst can be regenerated by benzene washing at higher temperature. New species, such as alkylbenzene with short chains, naphthalene, indane, biphenyl, condensed ring compounds and unsaturated compounds, are formed by cracking and cyclization in the regeneration process. The suitable regeneration condition is ≤280 °C and WHSV of benzene is about $1\,h^{-1}$.

Acknowledgements

We acknowledge gratefully the financial support of SINOPEC.

References

[1] G.E. Stridde, US Patent 3,965,043 (1976).
[2] G.E. Stridde, US Patent 4,075,126 (1978).
[3] L.B. Young, US Patent 4,301,317 (1981).
[4] B.V. Vora, P.R. Pujado, T. Imai, Chem. Ind. 19 (1990) 187.
[5] B.V. Vora, P.R. Pujado, T. Imai, T.R. Fritsch, Tenside Surf. Det. 28 (1991) 287.
[6] S. Sivasnaker, A. Thangaraj, R. Abdulla, P. Ratnasamy, in: Proceedings of the 10th International Congress on Catalysis, Budapest, Hungary, 1992, p. 19.
[7] S. Sivasnaker, A. Thangaraj, J. Catal. 138 (1992) 386.
[8] J.A. Kocal, US Patent 5,196,574 (1993).
[9] R.T. Sebulsky, A.M. Henke, Ind. Eng. Chem. Process Des. Dev. 10 (1997) 272.
[10] X. Wang, L. Xu, Q. Wang, Petrochem. Technol. 7 (1997) 58–61.
[11] W. Chen, Dissertation, Tsinghua University, Beijing, 1998.
[12] M. Han, J. Wang, Y. Jin, Chin. Patent, Applied Number 01110139.3.
[13] M. Guisnet, P. Magnoux, Appl. Catal. 54 (1989) 1.
[14] B. Feng, S. Chen, K. Chang, J. East China Univ. Sci. Technol. 13 (1987) 327.