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Experimental study on coking, deactivation, and regeneration of binderless 5A zeolite during 1-hexene adsorption

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Abstract Coking, deactivation, and regeneration of 5A zeolite during 1-hexene adsorption were studied on a fixed-bed adsorber and a themogravimetric analyzer. Adsorption activity measurement, scanning electron microscope (SEM) analysis, X-ray diffraction (XRD) analysis, FT-IR analysis, ^{1}H NMR analysis, and porosity measurement were used to reveal the mechanism of coking and deactivation of 5A zeolite, and evaluate the influences of binder on them. There are distinct increases in both coke content and deactivation degree with increasing the adsorption temperature. Deactivation degrees of zeolite increase as coke contents rise, however, they display smaller increasing rate at higher coke content. The rates of coke formation and deactivation of 5A zeolite are significantly enhanced by the binder mainly due to the fact that the activity sites offered by the amorphous compounds contained in the binder catalyze the formation of coke precursors. As compared to the coke formed in zeolite with binder, the coke in binderless zeolite is more aromatic. The coke which consists of inflammable part and nonflammable part can be oxidatively removed completely while the temperature approaches 787 K. No destruction in 5A zeolite crystal structure was observed in the regenerated binderless sample. The formation of coke during 1-hexene adsorption on zeolite can be explained using the carbonization-cyclization reaction mechanism. Furthermore, the kinetics models for formation and removal of coke were developed.

Keywords 5A zeolite · 1-Hexene · Coke formation · Deactivation · Regeneration

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1 Introduction

5A zeolite shows excellent adsorption performance, therefore can be used for separating selectively normal hydrocarbons from naphtha. The raffinate oil rich in non-normal hydrocarbons is a high quality feedstock of the catalytic reforming process or the excellent blending component of high-octane number gasoline. Meanwhile, the desorption oil rich in normal paraffins show a higher ethylene yield of the steam cracking process as compared to the naphtha feed. As a result, the utilization efficiency of naphtha can be improved significantly by using adsorption separation technology based on the 5A zeolite adsorbent (Shen et al. 2005; Liu and Shen 2009).

The deactivation has been considered as one key problem which can affect the performance of zeolite (Absil et al. 1984; Magnoux et al. 1993). Cyclization and polymerization reactions of hydrocarbon molecules which lead to the coke formation cannot be prevented during adsorption-separation operation. Coking deactivation, therefore, has been ascribed as the main reason that causes the decrease in adsorption activity of 5A zeolite during adsorption operation (Ruthven 1984). The studies on the formation of coke from propene over 5A zeolite indicated that the retention of the nonvolatile compounds (coke) on zeolite caused the coverage of adsorption sites or the blockage of pores, and resulted in deactivation of the zeolite (Thomazeau et al. 1996; Misk et al. 1996, 2000). As compared to paraffins or naphthenes, olefins lead to higher deactivation rate of this zeolite (Maixner et al. 1986). Additionally, the operation conditions have significant influences on the deactivation of 5A zeolite during the adsorption-desorption operation (Uguina et al. 2002). Furthermore, the properties of zeolite also show a profound impact on coking deactivation of zeolite (Guisnet et al. 1986). The effect of the binder present in an industrial adsorbent on the coking of 5A zeolite has been investigated through comparing the rate of coke formation from propene over pure zeolite with that over industrial adsorbent (Misk et al. 2000). It was indicated that coking over the zeolite without binder was faster than over the industrial adsorbent. The results were mainly attributed to the trapping of coke precursors by the binder. However, some adsorption-separation experiments performed at a fixed bed adsorber containing 5A zeolite pellets illustrated different results (Sun 2009). Although the coke depositing on deactivated zeolite can be removed by oxidative treatment (Thomazeau et al. 1996), regeneration is often incomplete owing to various secondary effects under severe oxidation conditions. As a result, the adsorption activity may still be reduced permanently due to improper conditions of coke removal.

Several industrial binderless 5A adsorbents developed by UOP and Sinopec Catalyst Company have been used in industrial Molex process (Diao 2001; Ding 2003). Binderless 5A zeolite showed higher adsorption capacity, higher adsorption rate, and lower coking trend as compared to 5A zeolite with binder (Sun et al. 2008). As a result, the economy of separation process can be improved and the valuable resource consumption can be decreased by using binderless 5A zeolite as adsorbents. While the coke formation from propene on 5A adsorbent and the influence of binder on coking of adsorbent have already been investigated, there are no studies on coking from other olefin compounds especially having carbon number of six to eight (mainly contained in naphtha), or no studies on the kinetics of coke formation from olefins on 5A zeolite. Furthermore, the proper conditions of regeneration of coked 5A adsorbent are of great importance and should be established so as to lead to industrial adsorption separation process. In previous works, we have reported the kinetic of coke removal from binderless 5A zeolite by oxidative treatment (Sun et al. 2009). In this paper, experimental studies of deactivation and regeneration of 5A zeolite during 1-hexene adsorption were carried out on a fixed-bed adsorber and a themogravimetric analyzer, respectively. The effects of operating conditions as well as binder contained in adsorbent on coke formation from 1-hexene over 5A zeolite were determined and the mechanism of coking deactivation was discussed. Also the oxidative regeneration of deactivated zeolite under different conditions was investigated. Furthermore, the kinetic models for the formation and oxidative removal of coke were established.

2 Experimental

2.1 Materials

Binderless pellets of 5A zeolite were synthesized following the procedures described previously (Sun 2009). Industrial pellets with binder were supplied by UOP (Shanghai, China). The chemical compositions of binderless 5A zeolite and binder present in industrial adsorbent are listed in Table 1. The average particle diameters of the two samples are both 4 mm, and the average diameters of crystals in binderless pellets and pellets with binder are 1.1 and 4.4 µm respectively. Prior to experiments, the zeolite samples were calcined for 4 hours in the presence of O_2 at a temperature of 723 K. *n*-Hexane (purity >97 %, methylcyclopentane impurity about 2 %) and cyclohexane (purity >99.5 %) were supplied by Feida Industrial & Commercial Co., Ltd. (Shanghai, China). Hydrofluoric acid (with HF weight content of 40 %) was obtained from Lingfeng Chemical Reagent Co. Ltd. (Shanghai, China). 1-Hexene (purity >96 %, cyclohexane impurity about 3 % and the rest belonging to isomers of hexene) was obtained from Fluka (Shanghai, China). All regents were redistilled before used as the adsorbates and the middle fractions were used only. N_2 and O_2 (purity >99.9 %) were obtained from Shanghai Wugang Co., Ltd. (Shanghai, China).

Table 1 Oxides composition of binderless 5A zeolite and Binder

Oxides	Contents (wt.%)	
	Binder	Binderless 5A zeolite
SiO_2	47.14	34.54
Al_2O_3	39.46	27.71
Fe_2O_3	3.20	/
CaO	0.52	8.37
MgO	0.08	/
Na_2O	1.01	7.18
K_2O	2.00	/
TiO_2	6.59	/

2.2 Coking deactivation of 5A zeolite

Coking deactivation of 5A zeolite was carried out on a fixed-bed adsorber, as shown in Fig. 1. Prior to the experiment, samples of 5A zeolite were dehydrated under a N_2 flow at 673 K for more than 2 h. Thereafter, the adsorbates were introduced into the adsorber using N_2 stream. Once the column temperature reached the required value, v6 was switched to connect the N_2 stream to the adsorbate vessel, meanwhile, v3 was opened to introduce the adsorbate. After certain adsorption time later, v6 was switched and v3 was closed. After that, the adsorption column was swept using N_2 flow for 2 h at the same temperature. Again, N_2 was let in and the column temperature was sustained at 673 K for 2 h. At last, zeolite samples were taken out after the column was cooled under N_2 flow. The adsorption capacities and the coke contents of zeolite samples were measured immediately. The reference sample was obtained by introducing N_2 (without any hydrocarbon adsorbates) into the column under the same conditions.

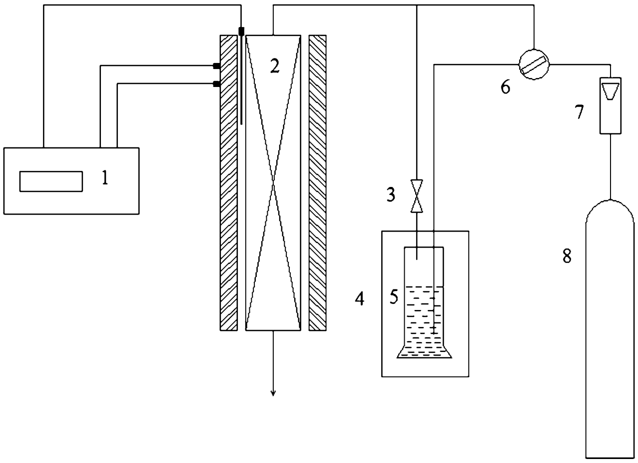


Fig. 1 Schematic drawing for deactivation experiment. *1*—Temperature control unit; *2*—Fixed bed adsorber with 5A zeolite; *3*—Needle valve; *4*—Constant-temperature bath; *5*—Vessel containing adsorbates; *6*—Three-way valve; *7*—Flow meter; *8*—N_2 cylinder

Deactivation degree (D) is calculated using Eq. (1):

$$D = (X_b - X_d)/X_b \times 100\ \% \tag{1}$$

where X_b and X_d are the n-hexane adsorption capacities (g/g) of blank zeolite sample and deactivated sample, respectively.

2.3 Oxidative regeneration and coke content measurement

Oxidative regeneration and coke content measurement for deactivated zeolite samples were carried out on a ZRY-1P integrated themogravimetric analyzer (Shanghai Precise & Scientific Instrument Co., Ltd.). The schematic drawing is shown in Fig. 2. The sample was first swept by N_2 flow under given temperature until the weight of sample reached a constant. Hereafter, the N_2 flow with certain partial pressure of O_2 was introduced into the system. Oxidation process was accomplished while the weight of sample reached another constant value. Coke content of the deactivated sample was determined according to the weight loss during the oxidation.

Coke content of deactivated zeolite sample is calculated using Eq. (2):

$$C_0 = (m_1 - m_2)/m_2 \tag{2}$$

where C_0 is coke content, g/g, m_1 is the mass of zeolites sample after desorbing in N_2 stream, g, and m_2 are the mass of zeolites after being regenerated in O_2 stream, g.

2.4 Adsorption activity measurement

Adsorption activity of the zeolite sample was characterized by the adsorption capacity of n-hexane in 293 K (Sun et al. 2009). Adsorption capacity (X, in g/g) is denoted as the amount of n-hexane adsorbed by per gram sample.

2.5 Characterization techniques

Crystal morphology of the zeolite sample was revealed by a JSM-6360LV scan electronic microscope (Jeol, Japan) at scan voltage of 15 kV.

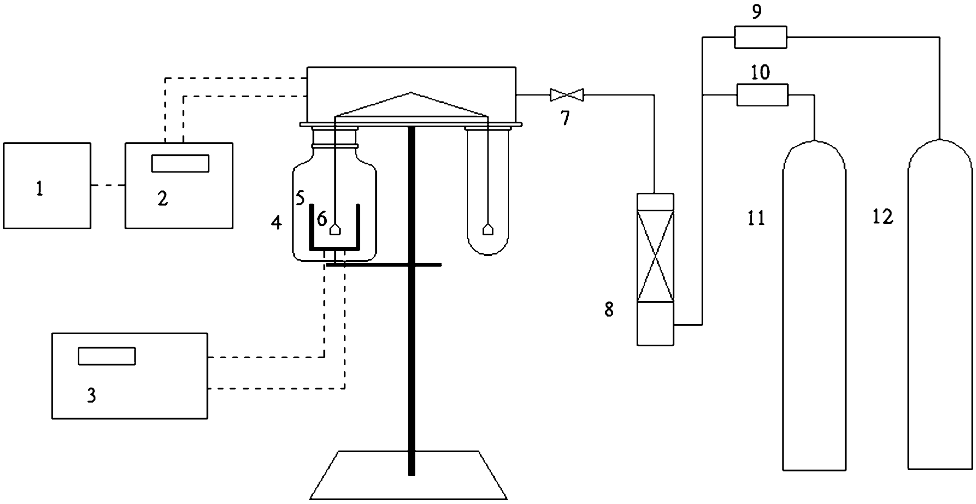
The zeolite sample was analyzed on an ASAP2010 apparatus (Micromeritics Instrument Corporation, USA) in order to obtain the specific surface area and pore structure data. Before adsorbing liquid nitrogen at a temperature of 77 K, all samples were treated at 463 K for 6 h.

FT-IR spectrometry analysis was carried out on a 5SXC apparatus (NICOLET, USA).

^{1}H NMR analysis was carried out on a DRX 500 apparatus (Bruker, Germany).

X-ray diffraction (XRD) analysis was performed on a D/Max 2550 X-ray diffractometer (Ricoh, Japan). The sample was scanned with CuK_α, 100 mA/40 kV and a rate of 0.02°/0.15 s.

Fig. 2 Schematic drawing for determining the coke content. *1*—Computer; *2*—Balance unit; *3*—Temperature control unit; *4*—Quartz cover; *5*—Furnace; *6*—Platinum cup with sample; *7*—Flow meter; *8*—Dryer; *9*, *10*—Needle valves; *11*—N_2 cylinder; *12*—O_2 cylinder



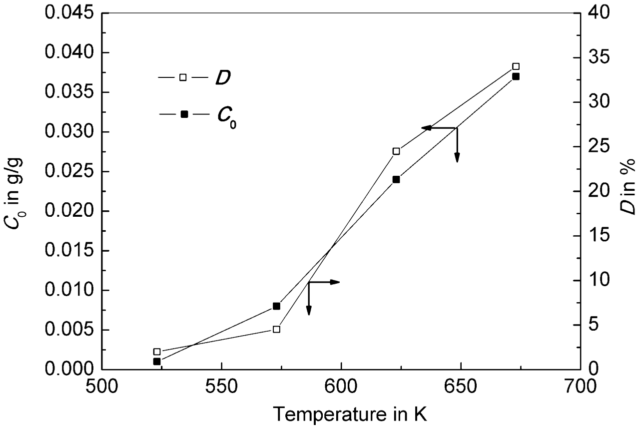


Fig. 3 Coke contents and deactivation degrees of binderless 5A zeolite at various temperatures with 1-hexene partial pressure of 30 kPa and adsorption time of 2 h

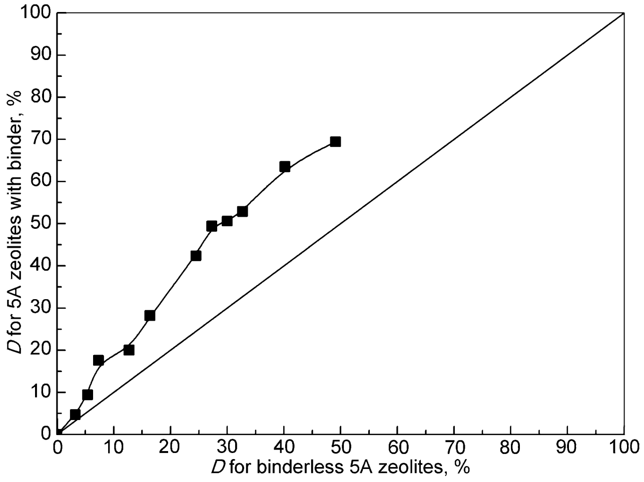


Fig. 4 Comparison of deactivation degrees between binderless 5A zeolite and zeolite with binder

3 Results and discussion

3.1 Effects of adsorption temperatures on coke contents and deactivation degrees

The effects of adsorption temperatures on coke contents and the deactivation degrees of coked samples are depicted in Fig. 3. With rising the temperature from 523 K to 673 K, coke contents increase from 0.001 g/g to 0.037 g/g while deactivation degrees increase from 2 % to 34 % respectively. There are two crossings of the two curves indicating a nonlinear decrease in adsorption activity of 5A zeolite with the coke content rising. It can be explained as the deactivation of 5A zeolite is due to different location of the coke on adsorbent. At low temperature stage, the coke content is low and the coke molecules are still small. Deactivation is mainly attributed to coverage of adsorption sites, the deactivation degree, therefore, illustrates a slower increase than the coke content while the temperature increases. However, the increasing trends of both deactivation degree and coke content change as temperature increases up to a certain value. Coke molecules which are large enough to block the apertures are formed at higher temperature. Then the deactivation is dominated by the blockage of passage in the zeolite. As a result, the deactivation degree increases faster than the coke content with temperature rising. The changes in slopes of deactivation degree-temperature and coke content-temperature curves make the two crossings. At last, the effect of coke content on the deactivation degree decreases while most of the main apertures of zeolite are blocked at the higher temperature. The profound impacts of temperatures on coke deposits are crucial in selecting proper operation temperature in order to lengthen the lifetime of 5A zeolite.

3.2 Effects of binder on coke contents and deactivation degrees

Coke contents and deactivation degrees of binderless 5A zeolite and the one with binder were compared at 623 K, 1-hexene partial pressure of 40 kPa, and adsorption time of 0.5 h. For the sample without and the one with binder, the coke contents are 0.019 g/g and 0.026 g/g, while deactivation degrees are 16.4 % and 28.2 % respectively. This means that there is a significant influence of binder on coking of 5A zeolite during 1-hexene adsorption. In order to check the results, further experiments were carried out by mixing binderless sample and the sample with binder in the adsorber column, and performing the adsorption experiments under a series of various conditions (different temperatures, times, or partial pressures of adsorbate). Deactivation degrees at each condition were compared between binderless 5A zeolite and zeolite with binder; the results are shown in Fig. 4. As can be seen, deactivation degrees of zeolite with binder are larger than those of binderless sample. The similar effect of binder has been found during isopropylation reaction of benzene over H/beta zeolite catalysts (Kasture et al. 2004). It should also be noted that the difference in the deactivation degrees of the two samples are slightly more pronounced for larger deactivation degrees.

The deactivation degrees of both 5A zeolites as functions of adsorption time are shown in Fig. 5. From this figure, the two zeolite samples illustrate the distinct evolution of deactivation degree with time. In the initial period, the binderless sample seems to undergo roughly the same deactivation as the other. The reason is that the coverage of adsorption sites with coke molecules plays a key role in the initial deactivation stage. Although the rate of coke formation on binderless sample is lower than that on the other, more activity sites certainly offer coke molecules more opportunity to occupy. The binderless zeolite therefore has a greater rate of

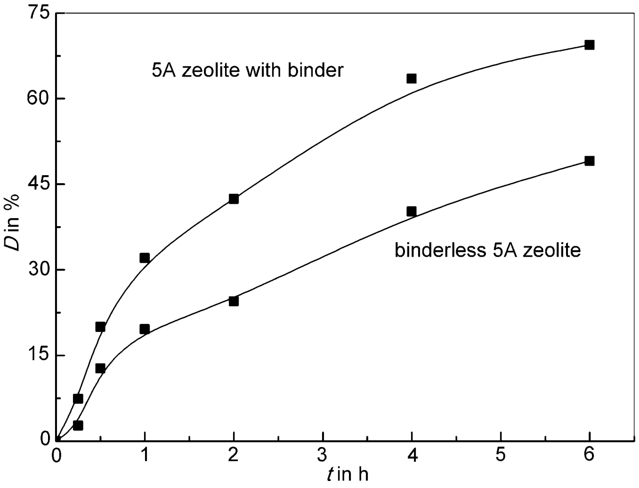


Fig. 5 Deactivation degrees of both binderless 5A zeolite and zeolite with binder as functions of adsorption time

deactivation because of the higher content of zeolite crystals and more adsorption sites in it. With the coking going on, the deactivation changes to be dominated by the blockage of main apertures. An increase in the coking rate owing to the effect of binder leads to the greater deactivation rate of the adsorbent with binder. Furthermore, the rates of coke formation on both adsorbents decline during the last two hours. This is mainly because the acid sites which catalyze the coking reaction are covered with coke. It also can be speculated that the two curves in Fig. 5 can cross at the same terminal which is of 100 % deactivation degree and a certain time. As a result, the two curves exhibit very different shapes.

One additional experiment was performed by using pellets containing only binder at 623 K, 1-hexene partial pressure of 40 kPa, and adsorption time of 0.5 h. The coke content is observed 0.003 g/g which is lower than that of either binderless zeolite (the corresponding value of 0.019 g/g) or the one with binder (the corresponding value of 0.026 g/g). Similar results have been reported in the study on propene adsorption over 5A zeolites with-and-without binder (Misk et al. 2000). Nevertheless, it cannot be deduced that the binder reduces the coke formation on the adsorbent. In contrast, the binder plays an important role in exaggerating coke formation as well as deactivation of 5A zeolite. The very low coke content on binder can be ascribed to the lacking of micro-pore in binder. Small coke molecules formed in early stage of coking can diffuse freely out of the binder even migrate into the pore of the 5A zeolite (for the sample with binder). The binder is composed of the body of amorphous silica alumina and the impurity of metal compounds. According to the results about the deactivation of beta zeolite, the binder of amorphous silica alumina present in beta zeolite enhances the deactivation during cumene synthesis (Kasture et al. 2004). The chemical composition the binder is listed in Table 1. From this table, two elements of Fe and Ti can also be observed in the binder. Ti compounds can be used as the active component in oligomeization reaction of alpha olefins owning to its high catalytic activity (Fujita et al. 2004). Meanwhile, the Fe compounds can act the acid center which is responsible for the coking reaction (Bartholomew 2001). The activity sites offered by such amorphous compounds produce more coke precursors. As a result, coke formation seems to be accelerated by the activity assay supported by the binder.

3.3 Effect of temperature on oxidative removal of coke

When deactivated zeolite samples are oxidized at 582, 685, 787, and 884 K, the corresponding coke removal efficiencies are 64 %, 93 %, 100 %, and 100 %. The increase in removal efficiency of coke with an increase in temperature suggests that only certain proportion of coke substances can be removed by oxidation at a low temperature. This means that the coke substances are heterogeneous, hence display different oxidizable performance. The TG-TPO results for the combustion of the coke deposited on the HZSM-5 catalyst also confirm that the heterogeneous coke is generally made up of components with different H/C ratios (Valle et al. 2012). The coke cannot be completely removed by vacuum treatment even if the temperature reaches to 773 K. For the coke formed from propene adsorption on 5A zeolite, the complete oxidative removal can be reached at 873 K (Thomazeau et al. 1996). According to the oxidizability, the coke can be divided into two parts: inflammable coke composed of amorphous and hydrogen-rich components, and nonflammable coke that has similar structure to graphite (Масагутов et al. 1992). At 582 K, the oxidative removal efficiency of coke formed from 1-hexene on binderless 5A zeolite is practically found 64 % and the regeneration is incomplete. The coke compounds can be completely removed when the temperature reaches 787 K. It should also be noted that higher oxidization temperature must be avoided because high temperature may cause the destruction of the crystal structure and the permanent deactivation of zeolite. We have found some shrinkage of the adsorbent pellets while the treatment temperature is higher than 873 K. So, a temperature higher than 823 K is not recommendable.

3.4 Properties of regenerated 5A zeolite

At the temperature of 293 K, experimental adsorption capacities of n-hexane on fresh 5A zeolite and a zeolite sample regenerated at 787 K are 1.34 mmol/g and 1.32 mmol/g, respectively. The similar adsorption capacities indicate that adsorption activity can be recovered completely by oxidative treatment under proper conditions.

The SEM images of fresh, deactivated, and regenerated binderless 5A zeolite samples are presented in Fig. 6. No obvious morphology difference is found from the SEM results.

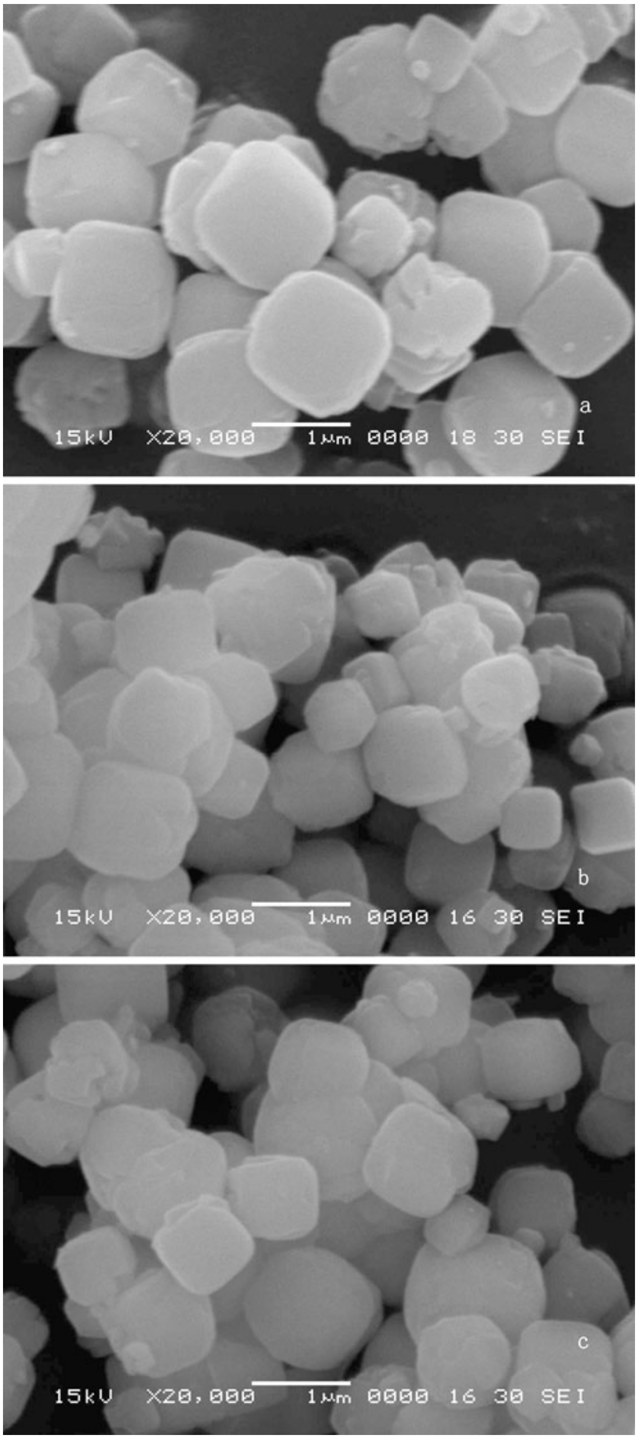


Fig. 6 SEM photographs of 5A zeolite powders. (**a**) fresh; (**b**) deactivated (with coke content around 0.05 g/g); (**c**) regenerated (regeneration under 883 K)

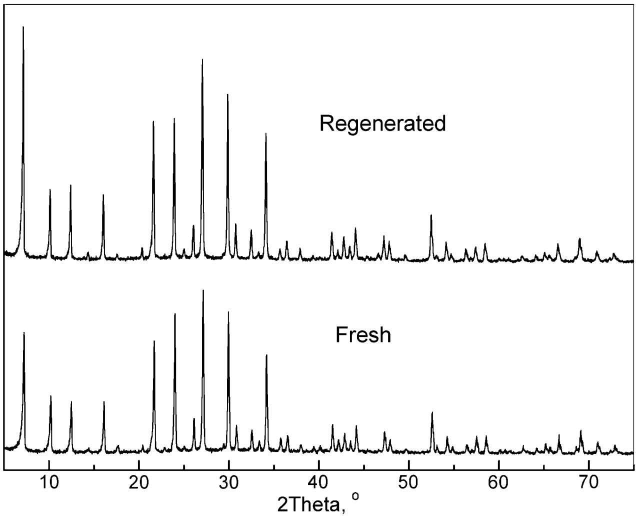


Fig. 7 XRD patterns of fresh and regenerated 5A zeolite samples

In addition, these three binderless samples were analyzed by X-ray diffraction (XRD) in order to reveal the effects of coking and regeneration on the crystal structure of 5A zeolite. The similar XRD patterns of different samples (depicted in Fig. 7) suggest that neither coking nor regeneration process causes any significant change in crystal structure. The deactivation of 5A zeolite during 1-hexene adsorption, thus, can be attributed to coke deposit but not destruction in the crystal structure. There exists only temporary coking deactivation during the adsorption process. Moreover, the regeneration conditions chosen in this paper will not cause change in the crystal structure of zeolite.

3.5 Mechanism of coking deactivation of 5A zeolite

The coking deactivation of 5A zeolite is mainly due to two aspects: the coverage of sites, and the blockage of pores. On one hand, large coke molecules formed in α-cages cover the active sites in cavities but cannot diffuse out, on the other, some of the eight-member-ring apertures linking to the α-cages are blocked by coke molecules, thus excluding adsorbate molecules.

Figure 8 shows the influence of coke contents on deactivation degrees of zeolite. With the increase of coke contents, the deactivation degrees show a continuous but damped increase. This increase is because the pores with smaller diameter are more easily blocked during the coking process. The coke formed in the early stage of coking reduces the adsorption activity of zeolite substantially because in this stage, the coke occupies adsorption sites and blocks relatively small pores. Furthermore, coke generally grows up based on the precursors; hence, the amount of coke particles mainly depends on the amount of coke precursors formed in the early stage of coking. The coke formed later will have less probability to occupy the adsorption sites or block the apertures.

The BET analysis results of zeolite samples are also listed in Table 2. S_{BET} (specific surface area) and V_{p} (pore volume) of deactivated sample are smaller than those of the fresh sample due to the blockage of some pores. Compared to the fresh sample, the coked zeolite sample displays a larger d_{p} (average pore diameter). The reason is that

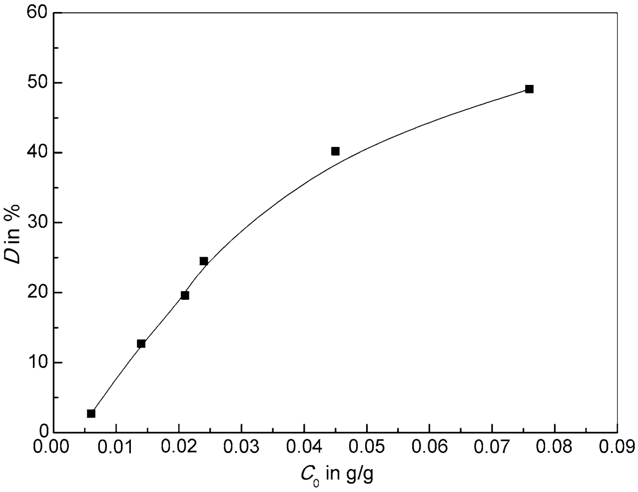


Fig. 8 Deactivation degree for deactivated zeolite samples with different coke contents

Table 2 BET analysis results of the fresh, deactivated and regenerated binderless 5A zeolite

Sample	S_{BET} (m^2/g)	V_p (cm^3/g)	d_p (1.7–300) (nm)
Fresh	551.66	0.031	4.92
Deactivated[a]	126.00	0.0078	37.88
Regenerated[b]	420.67	0.027	12.39

[a] With coke content around 0.05 g/g

[b] Regeneration under 883 K

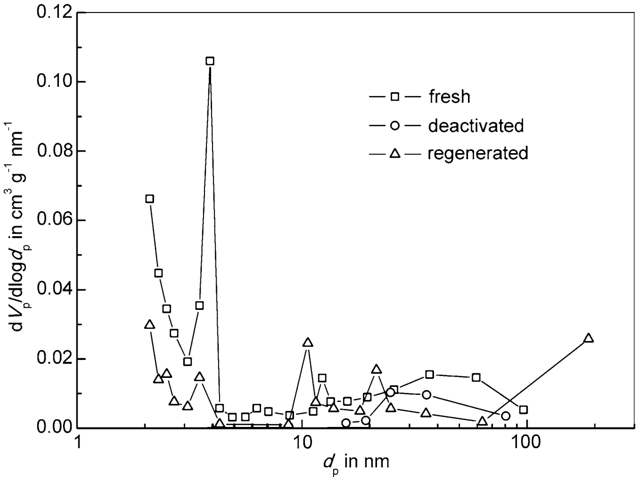


Fig. 9 Pore diameter distributions (test range for d_p of 1.7–300 nm) of fresh, deactivated (with coke content of 0.05 g/g) and regenerated (regeneration under 883 K) binderless 5A zeolite

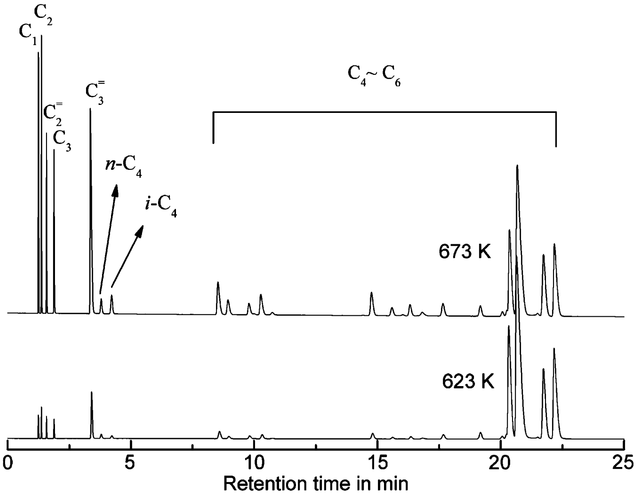


Fig. 10 GC results of tail gas out of adsorber at adsorption temperature of 623 K and 673 K, 1-hexene partial pressure of 30 kPa and adsorption time of 1 h

the pores with smaller diameters are more easily blocked. The pore diameter distributions (Fig. 9) indicate clearly that small pores disappeared in the deactivated sample. In consideration of the larger measured pore sizes compared to that of the eight-member-ring, the differences in S_{BET}, V_p and d_p suggest that coke also deposits outside of the α-cages. The changes in pore diameter distributions can be attributed to the blockage of some small pores as well as the contribution of the pores existing in coke.

S_{BET}, V_p, and d_p of regenerated zeolite treated under 883 K are also given in Table 2. Although the crystal structure is not destroyed under the regeneration conditions, S_{BET} and V_p of the zeolite increase while d_p decreases after regeneration. This trend is mainly due to pore shrinkage and deformation.

As far as 5A zeolite is concerned, coke can be formed from 1-hexene molecules under two kinds of acid sites: the Lewis acid sites formed by Ca^{2+} and the Brønsted acid sites resulting from the dissociation of H_2O molecules (Thomazeau et al. 1996).

The compositions of tail gases from the adsorber were analyzed using gas chromatography. At 673 K, GC results given in Fig. 10 display the large contents of hydrocarbons with carbon number less than three or more than five, suggesting that the cracking reaction will also take place as coke is being formed during 1-hexene adsorption on 5A zeolite. The same adsorption experiment was also performed at 623 K and the GC results are presented in Fig. 10. A comparison of GC results between 623 K and 673 K indicates that the contents of C_1–C_3 rise while the contents of C_5^+ decline with increasing temperature. Meanwhile, hydrogen was also detected in the tail gases. This means that further cracking reactions take place among the cracked products or oligomerization products, and the cracking reactions can be intensified by raising temperature. Small hydrocarbon molecules escape from the oligomers by strand breakage, hence decreasing the saturation degrees of the oligomers. Then, coke is formed through hydrogen transfer, cyclization and further polymerization of the unsaturated oligomers.

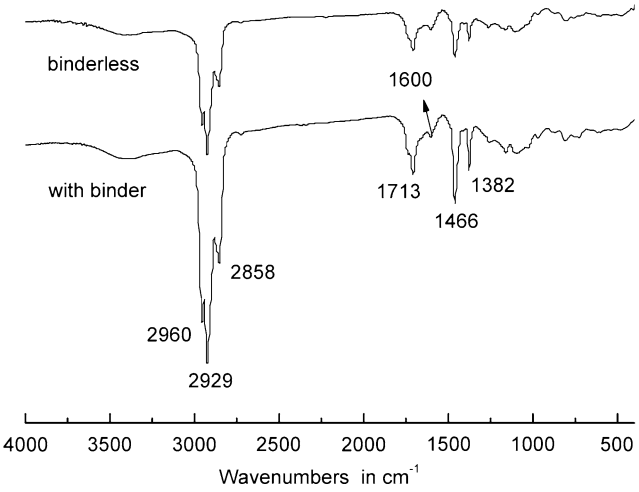


Fig. 11 FT-IR spectrum of exaction with dichloromethane from deactivated binderless 5A zeolite

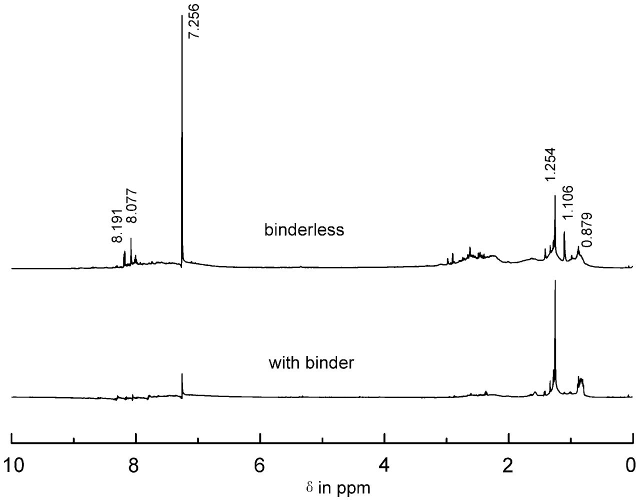


Fig. 12 ^{1}H NMR spectra of exaction with dichloromethane from the two deactivated 5A zeolites

Meanwhile, the coke was isolated from the two coked zeolite samples by treating them with a hydrofluoric acid solution and extracting the solution with dichloromethane. Hereafter, the isolated coke was analyzed using FT-IR; the I FT-IR spectra of the coke dissolved in dichloromethane are shown in Fig. 11. The peaks at 2960 cm^{-1} and 1382 cm^{-1} assign to the methyl group, the peaks at 2929 cm^{-1}, 2858 cm^{-1} and 1466 cm^{-1} assign to the methylene group, the peak at 1600 cm^{-1} assign to the skeletal vibration of aromatic ring. The FT-IR results suggest that the two samples of coke from the two zeolites are composed of the similar compounds. Meanwhile, the coke was analyzed using ^{1}H NMR method. The ^{1}H NMR results of the two samples are shown in Fig. 12. There two types of ^{1}H assigning to the saturated structure ($\delta = 0$–2 ppm) and the aromatic structure ($\delta = 6$–8 ppm) appear in both of the spectra; this is in agreement with the FT-IR results. For the coke derived from the binderless 5A zeolite, the ratio of the peak area of saturated ^{1}H to that of aromatic ^{1}H is 1.57. As for the coke sample from 5A zeolite with binder, the ratio is 2.17. The coke from binderless zeolite has a higher content of aromatic hydrogen than that from zeolite with binder because the two zeolite samples have undergone different time of coking. In order to obtain the coked binderless sample with the same coke content as the sample with binder, the time of coking was kept for more long. Hence, the coke from binderless zeolite is more aromatic than that from zeolite with binder.

As a result, the formation of coke during 1-hexene adsorption on zeolite can be explained using the carbonization-cyclization mechanism (Масагутов et al. 1992). Under the acid sites of adsorbents, 1-hexene molecules polymerize based on the carbeniumions mechanism then transform into unsaturated oligomers. The unsaturated oligomers then crack into small olefin molecules. In addition, olefin carbeniumions can be formed by hydrogen transfer reactions taking place between oligomer carbeniumions and olefin molecules. Finally, polyaromatic coke molecules can be formed by polymerization, cyclization, and hydrogen transfer reaction.

3.6 Kinetics of deposit and oxidative removal of coke on binderless 5A zeolite

The formation of coke on 5A zeolite during 1-hexene adsorption can be considered as Eq. (3). The reactant 1-hexene, the lumping of coke product and the lumping of cracked low molecule hydrocarbons are denoted with *hex*, *cok* and *cra* respectively.

$$hex \rightarrow cok + cra \tag{3}$$

Furthermore, coke deposit kinetics could be expressed using Eq. (4), considering coking as n-order reaction for 1-hexene and introducing the residual adsorption activity.

$$\mathrm{d}C/\mathrm{d}t_\mathrm{C} = k_\mathrm{C} p_\mathrm{H}^n (1 - D/100) \tag{4}$$

where k_C is the kinetic constant, g/(g Pa^n h), p_H is the partial pressure of 1-hexene, Pa, and the item of $(1 - D/100)$ denotes the residual adsorption activity with a coke content of C. For a high enough p_H, the item of p_H^n can be regarded as constant during the formation of coke. Then the integral expression of Eq. (4) can be written as Eq. (5) with the initial conditions of $t_\mathrm{C} = 0$, $C = 0$, and $D = 0$.

$$C/(1 - D/100) = k_\mathrm{C} p_\mathrm{H}^n t_\mathrm{C} \tag{5}$$

The kinetic curve of coke deposit on binderless 5A zeolite is depicted in Fig. 13 and the value of $k_\mathrm{C} p_\mathrm{H}^n$ was extracted from the slope as 1-hexene pressure equals to 30 kPa. In the conditions of adsorption temperature at 623 K and adsorption time of 30 min, another experiment was executed by performing the adsorption at 1-hexene partial pressures

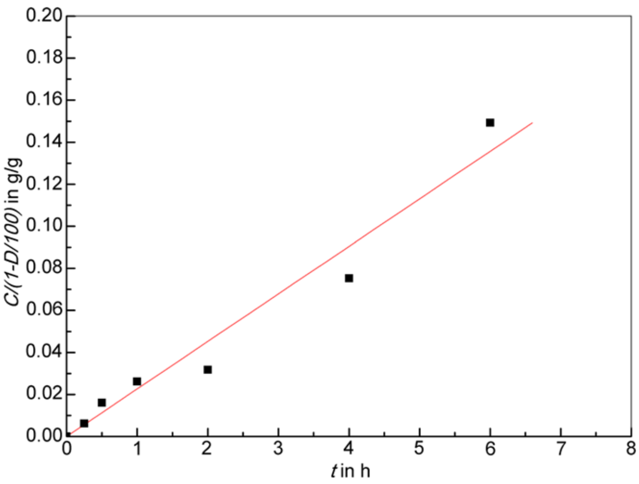


Fig. 13 Kinetic curve of coking from 1-hexene adsorption on binderless 5A zeolite at 623 K and 1-hexene partial pressure of 30 kPa

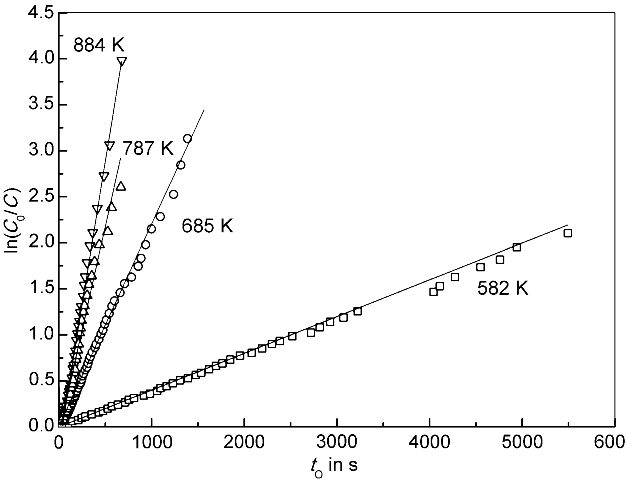


Fig. 14 Kinetic curves of oxidation removal of coke in deactivated binderless 5A zeolite

of 40 kPa. For 30 kPa and 40 kPa, corresponding coke contents on binderless 5A zeolite are observed to be 0.014 g/g and 0.019 g/g, while deactivation degrees are 12.7 % and 16.4 %, respectively. Furthermore, n and k_C could be observed from the coke content with p_H of 40 kPa and t_C of 0.5 h in Eq. (5). At a temperature of 623 K, the coke contents on binderless 5A zeolite during 1-hexene adsorption can be expressed as Eq. (6):

$$C = 1.37 \times 10^{-3}(1 - D/100)\, p_H t_C \tag{6}$$

Oxidative removal of coke molecules on deactivated zeolite can be expressed as Eq. (7). Assuming that oxidation reaction is irreversible, the rate equation of oxidation reaction can be written as Eq. (8). Kinetic curves of oxidation removal of coke in deactivated samples are shown in Fig. 14 and kinetic results obtained are listed in Table 3.

Table 3 Macrokinetic results for oxidative removal of coke on deactivated zeolite

T (K)	$k_{\mathrm{oxi}} p_{\mathrm{O_2}}^{n1}$ (1/s)[a]	k_{oxi} (1/(Pa$^{0.32}$ s))	$k_{\mathrm{oxi},0}$ (1/(Pa$^{0.32}$ s))	E (J/mol)
685	0.0021 (0.994)[b]	8.83×10^{-5}	0.013	28122.1
787	0.0045 (0.976)	1.89×10^{-4}		
884	0.0063 (0.995)	2.65×10^{-4}		

[a] Condition: $p(O_2) = 20$ KPa

[b] The values in bracket relate to the correlation coefficients

$$C_\alpha H_\beta + \left(\alpha + \frac{\beta}{4} - \frac{\gamma}{2}\right) O_2 \rightarrow \gamma CO + (\alpha - \gamma) CO_2 + \frac{\beta}{2} H_2O \tag{7}$$

$$-\mathrm{d}C/\mathrm{d}t_O = k_{\mathrm{oxi}} p_{\mathrm{O_2}}^{n1} C^{n2} \tag{8}$$

where k_{oxi} is the apparent reaction rate constant, $C = C_0$ while $t_O = 0$.

Only rate constants at temperature above 685 K were used to calculate activation energy for the oxidation reaction. As a result, the macrokinetic equation for oxidative removal of coke from binderless 5A zeolite is obtained as follows:

$$\ln(C_0/C) = 0.013 \exp(-28122.1/T)\, p_{\mathrm{O_2}}^{0.32} t_O \tag{9}$$

4 Conclusions

The present study indicates that the temperature as well as the binder existing in adsorbents significantly affects coke deposits and deactivation of 5A zeolite. Coke contents and deactivation degrees illustrate the distinct increases with rising the temperature. Zeolite samples with binder display higher coke contents and deactivation degrees than binderless samples because of the influence of the amorphous compounds contained in the binder. The fact is that the activity sites offered by the amorphous compounds catalyze the formation of coke precursors, hence exaggerate the rate of coking. As compared to the coke formed in zeolite with binder, the coke in binderless zeolite is more aromatic. Coke is formed during 1-hexene adsorption on binderless 5A zeolite along with series of reactions including polymerization, cracking, cyclization, and hydrogen transfer. Deactivation degrees of zeolite samples display a damped increase with increasing coke contents. The coke consists of inflammable and nonflammable parts, and can be removed completely by oxidative treatment under the temperature of 787 K. No destruction in zeolite crystal structure was observed in the regenerated binderless sample. At 623 K, the rate equation of coke formation on binderless 5A zeolite during 1-hexene adsorption can be expressed as $C = 1.37 \times 10^{-3}(1 - D/100) p_{\mathrm{H}} t$. In the temperatures range of 582 to 787 K, the macrokinetic of oxidative removal of coke from binderless 5A zeolite can be expressed as $\ln(C_0/C) = 0.013 \exp(-28122.1/T)\ (P_{\mathrm{O}_2})^{0.32} t$.

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