ADSORPTION OF OXYGENATE OF NAPHTHA BY ZEOLITE: AN EXPERIMENTAL AND THEORETICAL STUDY

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Abstract:

Adsorption of oxygenate, including MTBE and methanol, to silica gel, activated alumina, zeolite 4A and 13X were investigated and found that the availability of active sites and shape selectivity were two important factors influencing adsorption behaviors. Among all studied adsorbents, zeolite 4A possessed the highest amount of active site while exhibited the lowest adsorption capacity to MTBE, which can be attributed to the relatively smaller channel diameter (4.1×4.1 Å) compared to the dimension of MTBE (6.0×4.8 Å). Considering that this phenomenon was insignificant in methanol adsorption (3.6×3.5 Å), it was likely that the confinement of adsorption site is important in controlling the adsorption of aprotic adsorbate.

Keyword: adsorption, oxygenate, naphtha, active sites, shape selectivity

1. Introduction

Ethylene is an important raw material in the synthesis of synthetic fiber, synthetic rubber and other synthetic plastics. This means the high quality of naphtha, which is the raw material for ethylene production, is highly desired[1, 2]. The oxygenates contaminant in naphtha is an issue of concern, which is known to result in increasing carbon dioxide and carbon monoxide and consequently compromises the operation of caustic washing system, hydrogenator and methanator. The associated worst scenario would be the concentrated superscale of acetylene and thereby emergency shutdown[3, 4]. As a result, the remove of trace oxygenates from naphtha is the crucial step in efficient utilization of naphtha for ethylene production. In the traditional process, rectification or extractive distillation is widely applied to separate and purify naphtha. Given both rectification and extractive distillation are more effective in removing high content of oxygenates in naphtha, they are difficult to deal with trace amount of oxygenates (< 10 mg·L^{-1}) contaminant[5]. In this case, adsorption would be an effective alternative to solve this demand[6, 7].

Due to the large surface area, regular pore structure and framework composition, zeolites are receiving great attention for the removal of organic compounds and other hazardous ions[8]. Generally, the capacity of oxygenates adsorption is expected proportionally to the number of active sites of an adsorbent. In the case of zeolites, the active sites are distributed inside the three dimensional (3D) structure of zeolites, meaning the fate of oxygenate molecules should be regulated by their molecular dimensions and adsorbent channel structure too. This speculation was examined in this work. The concentration of active sites of four adsorbents

(silica gel, activated alumina, zeolite 4A and 13X) were first determined. Then the molecular dimensions for complex molecules (methyl tert-butyl ether (MTBE) and methanol) have been calculated with the aid of ACD/ChemSketch 12.01 (freeware version offered by Advanced Chemistry Development. Inc.). Combined with experiments, the aim of this paper is to compare the sizes of molecules and pore channels to find how the shape selectivity influence the adsorption.

2. Experimental

2.1 Materials

Naphtha was produced by Maoming Petrochemical Company (MPCC). All adsorbents were provided by Green Source Company. MTBE and methanol were purchased from Sinopharm Chemical Reagent Co., Ltd., China.

2.2 Adsorption experiments

100 mL naphtha was placed in 250 ml erlenmeyer flask and once the adsorbent was included in this system the naphtha mixture was sealed and continuously vibrated for three days. The naphtha samples were taken and filtered and analyzed to determine oxygenates concentration using gas ../../../../Program Files (x86)/Youdao/Dict/7.1.0.0421/resultui/dict/?keyword=chromatography-mass ../../../../Program Files (x86)/Youdao/Dict/7.1.0.0421/resultui/dict/?keyword=spectrography (Agilent 7890A-5975C, America).

3. Results and discussion

The surface active sites is expected responsible for the adsorption. In the case of removing oxygenates, polar adsorption site on the surface of adsorbent plays a key role in adsorption. The functional groups at zeolite surface include -O-Al-O- and -O-Si-O-. Thereby, the protonation and deprotonation of surface group would decide the maximum adsorption capacity. To determine the concentration of active sites, acid-base titration was conducted. The concentration of active sites was estimated by considering the following equation[9]:

$$SOH = \frac{moles\ of\ H\ added\ (solid + system) - moles\ of\ H\ added\ (system)}{2} \quad (1)$$

It is important to note that Eq. (1) works only when the titration starts with fully protonated surface and ends with fully deprotonated SOH sites.

As shown in Table 1, zeolite has the highest active site concentration over others, while the active site concentration of silica gel with sole -O-Si-O- and activated alumina with sole -O-Al-O- are respectively 0.0010 and 0.0016 mol·g^{-1}, which is one magnitude lower than that of zeolites. It is thus expected that zeolite would likely have the highest adsorption. While for zeolites, the narrow channel structure is the critical factor leading to whether oxygenates can be transported to the corresponding active sites. The pore diameter of zeolite channel can be found in the literature, while no relevant data for oxygenates is available. The descriptions of the critical dimensions involve the diameter of the circumscribed circle of the cross-section of minimum area of a molecule. The evaluation of these values was calculated from the available bond lengths, bond angels and Van der Waals radius[10].

First, the molecular model was structured through ACD/ChemSketch as shown in Fig. 1.

During adsorption, molecule with polar functional group would be preferentially assimilated at the surface of adsorbent, resulting in the separation of oxygen from naphtha. Particularly, oxygen is more possibly to serve ../../../../Program Files (x86)/Youdao/Dict/7.1.0.0421/resultui/dict/?keyword=as adsorbing key atom compared with other atoms[11, 12]. Thereby, the oxygen is preferentially adsorbed at active sites. Based on the optimized 3D geometry, the flat determined by hydrogen 1, 2 and 10 is closest to oxygen, which is more likely to firstly gravitate with the surface of adsorbent. Obviously, the spatial position of hydrogen 1, 2, 4, 7, 5 (or 6) and 8 (or 9) determined the minimum area of cross-section of MTBE, in which the choice of hydrogen atom between 5 and 6 (or 8 and 9) could be related ../../../../Program Files (x86)/Youdao/Dict/7.1.0.0421/resultui/dict/?keyword=to the distance from this hydrogen to the $plane_{1,2,10}$.

As shown in Table 2, the distance from hydrogen 5 and 8 to $plane_{1,2,10}$ were far than that of hydrogen 6 and 9. Obviously, the molecular dimension can be defined by projections of hydrogen 1, 2, 4, 7, 5 and 8 at the plane, which plane is almost vertical to $plane_{1,2,10}$ and $plane_{13,16,18}$. The coordinate of hydrogen projection could be confirmed by the distance from the corresponding hydrogen to $plane_{1,2,10}$ and $plane_{13,16,18}$ as shown in table 2. Obviously, the length of D1 and D2 determined minimum area of cross-section of a molecule, in which D1 = max(D1-13,16,18, D4-13,16,18,D5-13,16,18)+max(D2-13,16,18, D7-13,16,18,D8-13,16,18) and D2 = max(D5-1,2,10,D8-1,2,10).

Based on these data, the minimum diameter of MTBE structure can be estimated to 4.323×2.972 Å. Because D is the distance between centres of hydrogen atoms, the radius of molecules should be confirmed through what is D plus twice Van Der Waals radius of

hydrogen atom (r_H = 1.2 Å). As a result, the minimum diameter of MTBE can be calculated to 6.723×5.372 Å. According to the Lennard-Jones potential, the critical dimensions are given by $r_{min} = 2^{1/6}r$ (r is defined as kinetic diameters or Lennard-Jones potential constants)[13]. The kinetic diameter of MTBE during adsorption is 5.989 ×4.788 Å.

From three different directions, the optimized molecular model of methanol was shown in Fig. 2, and the distances from hydrogen to the specific plane were listed in Table 3.As described above, the minimum diameter of methanol structure can be estimated through D1 = max (D1-3,5,6, D4-3,5,6) + D2-3,5,6 and D2= max (D3-1,2,6, D4-1,2,6) to 1.814×1.058 Å. Similarly, the critical dimensions and kinetic diameter of methanol during adsorption were respectively determined with 4.214×3.908 and 3.754×3.475 Å.

Fig. 3 shows adsorption of adsorbents from 100 mg·L^{-1} MTBE naphtha with different adsorbent loading. Adsorption of zeolite is much less than that of the maximal adsorption capacity (~880 mg·g^{-1}), which can be concluded from the adsorbent active site. With adsorbent/naphtha ratio of 1:200, zeolite 4A exhibited lower adsorption caption (1.98 mg·g^{-1}) than zeolite 13X (14.68 mg·g^{-1}) despite of similar active site. This can be attributed to the limitation of pore structure 4.1×4.1 Å, which is not favor for transportation of MTBE born with 5.989 × 4.788 Å as shown in previous calculation. The poor adsorption may be derived from the active site of the particle surface rather than that in channels of zeolite 4A. Meanwhile, this adsorption is far below that of silica gel and activated alumina. The increasing adsorbent/naphtha ratio would decrease adsorption of all adsorbent. Particularly, the decreasing trend of zeolite 4A is the lowest. When the adsorbent/naphtha ratio increase to 1:100, the adsorption caption of zeolite 4A maintains about 2 mg·g^{-1} of maximal adsorption capacity,

which can be attributed to fewer active sites available compared with excess MTBE. With further increase the ratio to 1:20, the adsorption caption of zeolite 4A decrease to 1.28 mg/g. This great distinction between zeolite 4A and others derives from dimensional limitation between molecular dimension of 5.989 ×4.788 Å and its channel structure of 4.1 × 4.1 Å.

Fig. 4 shows adsorption of adsorbents from 100 mg·L^{-1} methanol naphtha with different adsorbent loading. This ../../../../Program Files (x86)/Youdao/Dict/7.2.0.0511/resultui/dict/?keyword=tendency of adsorption caption of zeolite 4A is different from that of MTBE adsorption. This huge discrepancy can be attributed to the distinction of two kinds of molecular diameter. Kinetic diameter of methanol in sorption were 3.754 × 3.475 Å, which can freely transmit in the channel of zeolite 4A. As a result, adsorption performance trend of zeolite 4A is similar with others. As the adsorbent/naphtha ratio increase from 1:200 to 1:20, the adsorption of all adsorbents decrease to ~2 mg·g^{-1} from ~12 mg·g^{-1}. A higher concentration of naphtha with 500 mg·L^{-1} methanol is designed to measure the adsorption capacity of adsorbents as shown in Fig.5. With an increase in methanol concentration, the adsorption capacity of zeolite 4A and 13X rapidly increase to ~52 mg·g^{-1} from ~12 mg·g^{-1} at adsorbent/naphtha ratio of 1:200. While the adsorption capacity of silica gel and activated alumina remained a low level of 28 and 38 mg·g^{-1}, which can be attributed to the limitation of relatively lower active sites (0.0010 and 0.0016 mol·g^{-1}, the corresponding maximum adsorption capacity of 32 and 51 mg·g^{-1} respectively). With the increasing adsorbent/naphtha ratio, the gap of adsorption capacity between two groups would decrease, implying the limitation of active sites for silica gel and active alumina gradually insignificant.

Fig.6 shows the adsorption of adsorbents for naphtha. Due to the large size of MTBE

compared with the restrained channel of zeolite 4A, MTBE concentration after adsorption is still 13.1 mg·g^{-1}. As for methanol adsorption, a higher removal rate of ~95 % is observed in all adsorbents, and the methanol concentration after adsorption decrease to ~ 2 mg·L^{-1}. As a result, the total concentration of oxygenates, including MTBE and methanol, reduce to ~ 2 mg·L^{-1}, which can be satisfied with the demands of production.

4 Conclusion

During adsorption of oxygenates, channel structure and active sites are two important factors: pore diameter of adsorbent and molecular ../../../../Program Files (x86)/Youdao/Dict/7.2.0.0511/resultui/dict/?keyword=dimension is the critical factor to decide whether the molecular could be transported through channel of adsorbent and then be removed to meet manufacture requirement; the maximum adsorption capacity of adsorbents is proportional to the number of active sites. Particularly, the kinetic diameter of MTBE and methanol during adsorption were respectively calculated as 5.989 ×4.788 and 3.754×3.475 Å via the aid of ACD/ChemSketch. During adsorption, zeolite 4A with pore structure of 4.1×4.1 Å would allow the transportation of methanol but forbid that of MTBE, thus leading to the huge difference of adsorption../../../../Program Files (x86)/Youdao/Dict/7.2.0.0511/resultui/dict/?keyword= between adsorption of two oxygenates. Meanwhile, despite of high active sites, the rejection of MTBE for zeolite 4A is inferior ../../../../Program Files (x86)/Youdao/Dict/7.2.0.0511/resultui/dict/?keyword=to that of silica gel and activated alumina. However, the rejection of methanol for zeolite 4A would keep similar level of others. With the increasing methanol concentration, due to the limitation of active sites,

the adsorption capacity of silica gel and activated alumina perform the poorer effect than that of zeolite adsorbent during methanol adsorption. At last, the adsorption capacity of adsorbents for naphtha is measured, and the results point out that the total concentration of oxygenates reduce to ~ 2 mg·L^{-1}, which can be satisfied with the demands of production.

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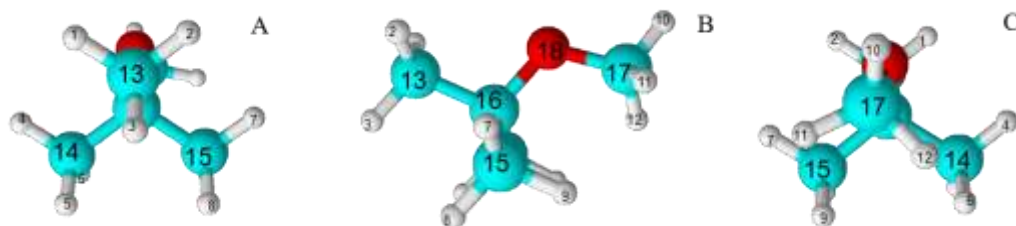
Figure 1 optimized molecular model of MTBE (white: hydrogen; blue: carbon; red: oxygen)
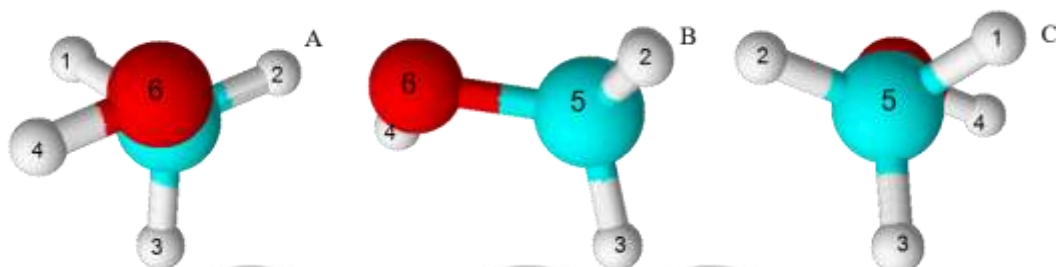

Figure 2 optimized molecular model of methanol (white: hydrogen; blue: carbon; red: oxygen)
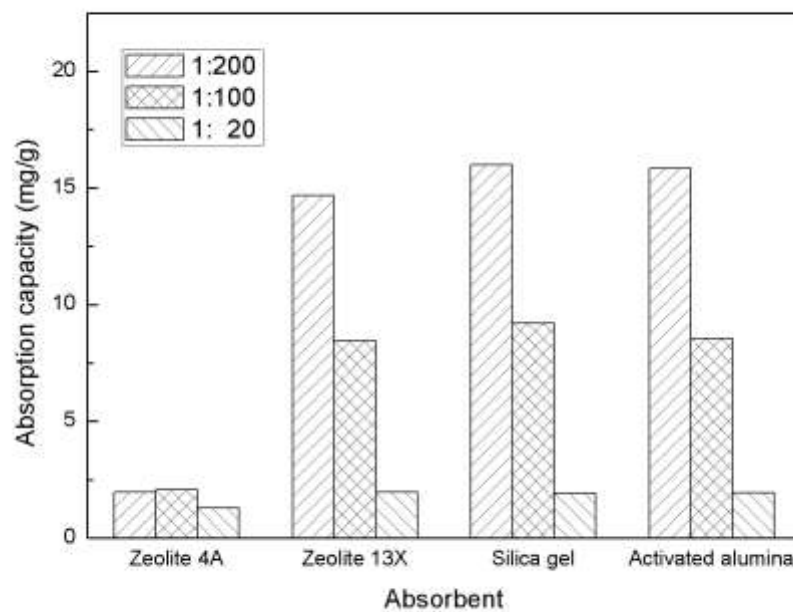
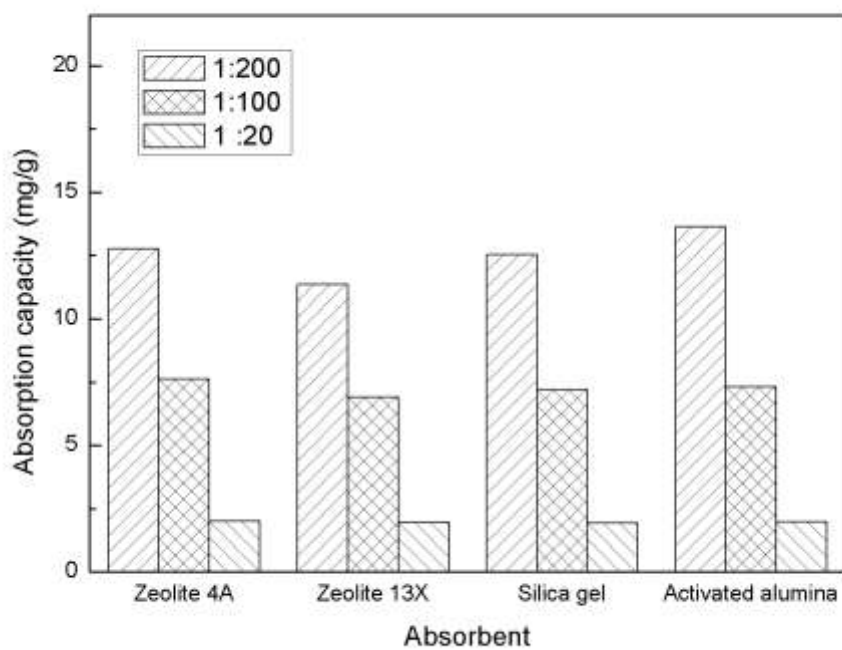**Figure 3 adsorption of adsorbents from 100 mg·L^{-1} MTBE naphtha with different adsorbent loading**

Figure 4 adsorption of adsorbents from 100 mg·L^{-1} methanol naphtha with different adsorbent loading
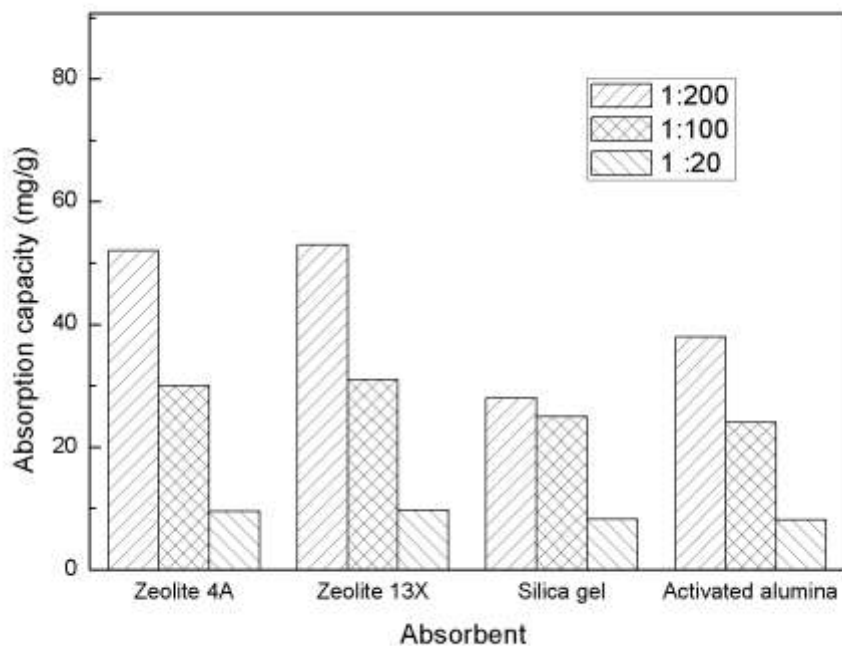
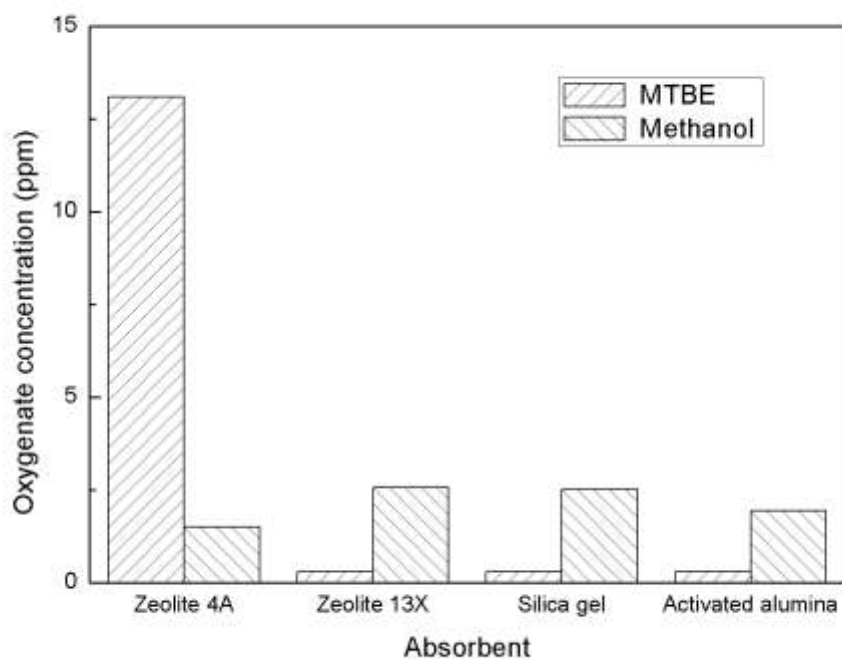**Figure 5 adsorption of adsorbents from 500 mg·L⁻¹ methanol naphtha with different adsorbent loading**

Figure 6 adsorption of adsorbents with adsorbent/naphtha ratio of 1:20 (component concentration: MTBE 16 mg·L⁻¹; Methanol 43 mg·L⁻¹)

Table 1 the concentration of active sites of four adsorbents

adsorbent	4A	13X	Silica gel	activated alumina
Active sites (mmol·g^{-1})	9.7	10.3	1.0	1.6

Table 2 distances (Å) from hydrogen atom to plane

	Distance (Å)
D4-1,2,10	1.569
D7-1,2,10	1.628
D5-1,2,10	2.952
D8-1,2,10	2.972
D6-1,2,10	2.785
D9-1,2,10	2.758
D1-13,16,18	0.908
D2-13,16,18	0.895
D4-13,16,18	2.170
D7-13,16,18	2.153
D5-13,16,18	1.300
D8-13,16,18	1.219

Table 3 distances (Å) from hydrogen atom to plane

	Distance (Å)
D3-1,2,6	1.508
D4-1,2,6	0.373
D1-3,5,6	0.902
D2-3,5,6	0.912
D4-3,5,6	0.806