

Computational study on the product selectivity of FCC zeolitic catalyst

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Abstract

Reactive adsorption of olefins on the FCC zeolitic catalysts was studied computationally in an attempt to estimate the selectivity toward the olefins. The chemistry of the adsorption of butenes on the zeolite was studied by means of MO calculations. Ionic states were located as the local minima, rather than the transition states, with the stability of 10–20 kJ/mol lower than that of corresponding π -complexes. The simulation protocol based on the molecular mechanics with systematic sampling, proposed in our previous report, was applied to estimate the adsorption strength of all the carbenium ion isomers that can be derived from C_4 – C_6 olefins on Y, mordenite, ZSM-5 and β . A small pore of ZSM-5 was found to adsorb C_4 – C_5 olefins strongly, while a super cage of Y will allow $C_6 <$ to escape from the reaction. MOR and β were predicted to be suitable for high C_4 – C_5 olefin selective catalysts. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

As the blend stock for environment-friendly gasoline, the demands for ethers such as methyl tertiary butyl ether (MTBE) produced from the reaction of isobutene and methanol and tertiary amyl methyl ether (TAME) produced from isopentene and methanol and for alkylates produced from isobutane and butenes, are expected to be spurred in near future. C_4 – C_5 olefins, which are the elemental ingredients in these compounds, depend mostly on the by-product from the fluid catalytic cracking (FCC) process

at present. Commercial FCC catalysts today are mixtures of zeolite and amorphous silica–alumina matrix. Faujasite (Y) base zeolites, e.g. rare earth metal exchanged zeolite (REY) and ultrastable Y (USY), are commonly used for FCC catalysts. In addition, ZSM-5 is often added to the catalyst to boost the octane number of gasoline. However, to meet the anticipated expansion of the demand for C_4 – C_5 olefins, development of the zeolitic catalysts with higher selectivity toward these fractions is an urgent task. Zeolites are the microporous materials consisting of silica and alumina and a number of them possessing different pore structures are currently known. The pore structure of zeolite controls the diffusion of reactants and products and the stability of the transition states (TS), or

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in other words, the activation energy, thus influences the catalytic activity and particularly selectivity.

On the other hand, the latest progress of the computational chemistry techniques have enthusiastically promoted the theoretical studies on the zeolites [1,2]. Kazansky et al. [3] studied the cracking mechanism of paraffins using a simple cluster model $\text{H}_2\text{OAl}(\text{OH})\text{H}_2$ in combination with ab initio molecular orbital (MO) method, and determined the transition states and the activation energies. Martin et al. [4] studied the protonation of olefins by means of MO using a cluster model $\text{H}_3\text{SiOAlH}_2\text{OHSiH}_3$. They reported that the π -complex would be activated to the ionic transition state following the proton transfer, where the barrier height is about 30 kcal/mol, then would relax to more stable alkoxide-type structure. Santilli et al. [5] calculated the adsorption energy of straight and branched C_6 alkanes on several types of zeolites by means of Monte Carlo (MC) method using empirical force field and reproduced successfully the behavior of the adsorbed straight C_6 /branched C_6 ratio as a function of pore size. They also discovered the correlation between the ratio of the amounts of adsorption and the ratio of these compounds in the product of $n\text{-C}_{16}$ cracking. Although MC is a powerful technique to simulate the adsorption, as the molecular size of the adsorbate becomes larger, the acceptance ratio for the trial movement decreases and the computational inefficiency becomes problematic. In order to cope with this difficulty, configurational-bias MC (CBMC) was proposed [6,7], and was successfully applied to simulate the adsorption of long straight chains. This technique, however, cannot be applied to the ring compounds. In our previous work [8], in an attempt to elucidate the relationship between the heat of adsorption and the pore structure, we estimated the former by simulating the interaction energy between the zeolite framework and adsorbate. Computational protocol based on the molecular mechanics (MM) with systematic sampling was proposed there to ob-

tain the adsorption structure rapidly. In the present study, this computational procedure was applied to estimate the adsorption strength of olefins on zeolites so as to assist the selection of the zeolite which will improve $\text{C}_4\text{-C}_5$ olefins yield based on the following idea.

The reaction of olefins is 1 to 4 orders of magnitude faster than that of paraffins [9]. Therefore in order to achieve a high selectivity toward $\text{C}_4\text{-C}_5$ olefins, one must retard the side reactions such as decomposition or oligomerization from once produced $\text{C}_4\text{-C}_5$ olefins. These reactions are believed to proceed via carbenium ions formed by the protonation of olefins, thus the pore structure which destabilizes these carbenium ions, i.e. which adsorbs these cations weakly, would increase $\text{C}_4\text{-C}_5$ olefin output because the formation of these undesired intermediates would be suppressed. On the other hand, if it also adsorbs $\text{C}_6 <$ olefins weakly, these larger molecules will not be decomposed and will remain in the product, which will lead to a poor selectivity toward $\text{C}_4\text{-C}_5$ fractions. Our strategy is therefore to search for the zeolite type which adsorbs the carbenium ions derived from $\text{C}_4\text{-C}_5$ olefins weakly, but those from C_6 olefins strongly.

At first, the chemistry of the adsorption of butene isomers on the zeolite was studied in detail by means of ab initio MO calculations, adopting a large cluster model (vide infra) so as to take into account the stabilization effect on the carbenium ions by the zeolite framework. Ionic states were located as the local minima, rather than the transition states, with the stability of 10–20 kJ/mol lower than that of corresponding π -complexes. In addition, all the carbenium ion isomers that can be derived from the protonation of butenes, pentenes and hexenes were calculated in the gas phase by MO to determine their stability. Primary cations were, as known well, found prohibitively unstable and were omitted from the following simulations. The adsorption of aforementioned carbenium ions on four types of zeolites, namely, Y, mordenite (MOR), ZSM-5 and β , were then simu-

lated according to our MM protocol and the adsorption strength were calculated. The small pore of ZSM-5 was found to adsorb C_4 – C_5 olefin strongly, while super cage of Y will allow C_6 to escape from the reaction. MOR and β were predicted to be superior in the C_4 – C_5 olefin selectivity.

2. Computational details

2.1. Characterization of carbenium ions (MO)

All the carbenium ion isomers that can be derived from the protonation of butenes, pentenes and hexenes are sketched in Figs. 1–3. In order to examine their stability, the structures were optimized and the energies were determined in vacuo by ab initio MO calculations at RHF/6-31G* level. Furthermore, to characterize the olefinic species adsorbed on the zeolite, adsorption of butenes on the cluster model extracted from Y zeolite (Fig. 4) was studied in detail by means of MO as well. This cluster was constructed, based on the crystal data of Y, as follows. One T site was taken as the center (note that all the T sites are equivalent in case of Y) and replaced by Al, then the atoms up to the fourth from the center were extracted and of outermost atoms (9 Si's), those connected to only one oxygen (6 Si's) were replaced by H and two H's were attached to the rest (3 Si's) toward the direction where the oxygens originally were. Then O–H and Si–H bond lengths

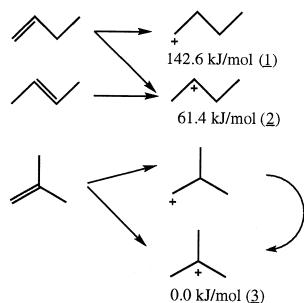


Fig. 1. Carbenium ions derived from butenes.

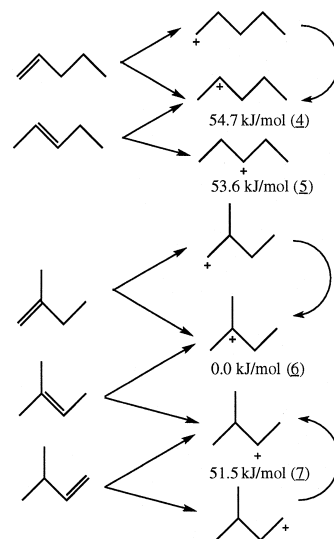


Fig. 2. Carbenium ions derived from pentenes.

were modified to be 0.946 and 1.474 Å, respectively. Hydroxyl (acidic) proton was placed on one of four oxygens connected to Al that gave the lowest energy (Fig. 4). The initial structures of butene–zeolite π -complexes were then built by placing butenes on this cluster so that the distance between the acidic H and one of two π -bonded carbons becomes 1.7 Å. The initial structures of ionic states (protonated butene or carbenium ion–deprotonated zeolite) were constructed by stretching the acidic OH up to 2 Å and placing butenes so that the distance between this hydrogen and the carbon to be protonated becomes 1.1 Å. Only the geometry of butenes and the hydroxyl proton were optimized keeping zeolite part (including terminal H's) frozen at RHF/6-31G*. All the ab initio calculations were carried out by Gaussian94 [10].

2.2. Adsorption structure and strength of carbenium ions (MM)

In order to elucidate the relationship between the selectivity toward C_4 – C_5 olefins and the pore structure of zeolites, according to the idea described in Section 1, the computational protocol based on the molecular mechanics with

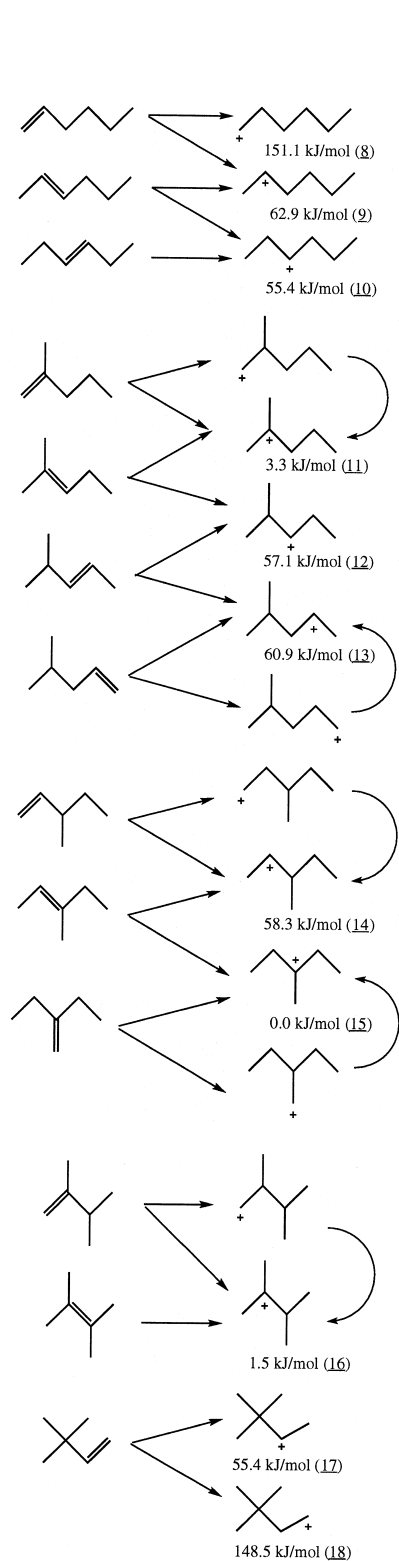


Fig. 3. Carbenium ions derived from hexenes.

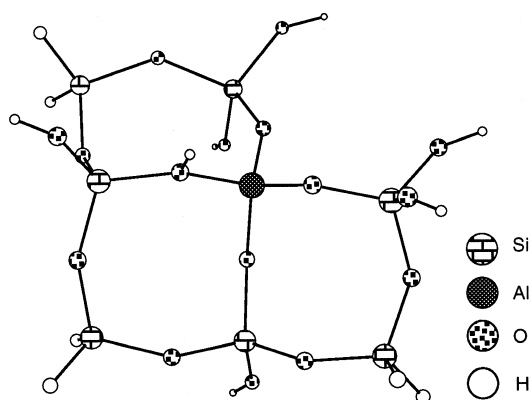


Fig. 4. Zeolite cluster model extracted from Y to be used for ab initio MO calculations.

systematic sampling established in our previous work [8] was applied to investigate the adsorption profile of carbenium ions derived from the protonation of C_4 – C_6 olefins on four types of zeolite: Y, MOR, ZSM-5 and β . The same force field parameters as the previous report [8] were employed, i.e. burchart [11] for the zeolite part and DREIDING [12] for the adsorbate (burchart-DREIDING). Atomic charges were also determined in the same manner as the previous report [8], i.e. $0.3 \times$ formal charges were assigned to the atoms belonging to zeolite ($Si = 1.2$, $Al = 0.9$, $O = -0.6$ a.u.) and the atomic charges of the adsorbate were calculated by charge equilibration (QEq) method [13] inside the zeolite field. Note that the total charge of adsorbate is 0.3 a.u., while zeolite bears a net charge of -0.3 a.u. because there is only one Al site in our zeolite models, as described below.

MO results revealed that primary cations are prohibitively unstable and in most cases hydrogen was transferred spontaneously during the optimization to yield secondary or tertiary cation, thus they were excluded from the consideration. One unit cell was taken as a simulation cell for Y, two unit cells stacked along the c axis were used for MOR and ZSM-5, and four unit cells stacked along the a and b axes were employed for β . For every possible H type model, where only one T site was replaced by

Al while all others were kept as Si and one charge compensating proton was placed on one of four oxygens connected to Al, the initial structure was set up by placing the olefin molecule in the vicinity of hydroxyl proton and transferring the proton from zeolite to olefin. From each initial structure, the adsorption structure was obtained by the energy minimization of carbenium ion while the zeolite was held rigid. Finally, assuming Boltzmann distribution, the adsorption strength at working condition was estimated by averaging the energies of all the adsorption structures derived from each initial structure with the appropriate weight, namely $C \times \exp(-E/RT)$ ($T = 600$ K), where C is the normalization factor. Although the statistical significance should be calculated, strictly speaking, according to the free energy rather than the enthalpy, the entropic effect was neglected in this simulation. Detail procedure to calculate the adsorption structure is explained below taking mordenite as an example.

In case of mordenite, there are four unequivalent T sites, each of which is connected to four oxygen atoms. Therefore, there are 16 (4×4) possible configurations of Al and proton, which are obtained by replacing one T site by Al and placing one proton on one of the oxygens bonded to Al (Note that Y, ZSM-5, and β consist of 1, 12 and 9 unequivalent T sites, respectively, and the numbers of possible Al and proton configurations are 4 (1×4), 48 (12×4) and 36 (9×4), respectively). 16 H-MOR's were then obtained by optimizing only the coordinate of proton. For each of 16 H-MOR's, the initial structure of adsorption was built by placing the olefin above the hydroxyl proton and transferring this proton from the zeolite oxygen to the carbon. For instance, in case of the adsorption of carbenium ion derived from the protonation of 1-butene at C^1 (**2**), a bond was created between the hydroxyl proton and C^1 with the length of 1.1 Å. Then 1-butene was rotated so that the plane defined by three atoms bonded to C^1 (two H's and one C) becomes perpendicular to OH and the plane defined by Si–O–Al also becomes

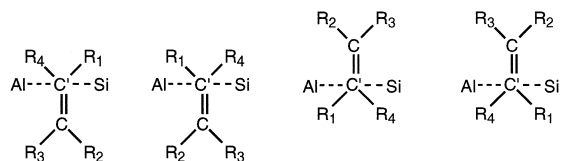


Fig. 5. Four initial conformations of olefins over the acid site (top view). Al–O–Si are beneath the olefins. C' is the carbon to be protonated and right under C' are the hydroxyl proton and oxygen.

perpendicular to the C=C double bond. There are four possible conformations as shown in Fig. 5 and all the structures corresponding to each case were constructed (64 (16×4) structures). Finally a bond between the zeolite oxygen and the proton was stretched up to 2 Å and cleaved. Starting from each initial structure, only carbenium ion was optimized until RMS force becomes less than 0.01 and the final adsorption structure was obtained. Here SP3 hybrid parameter was assigned to one of π -bonded carbons which was protonated, while SP2 hybrid was assigned to the other. In the course of optimization, atomic charges of the carbenium ion were recalculated every 30 steps by QEq while charges on the zeolite were fixed. Cerius2 was used for all the MM calculations.

3. Results and discussion

3.1. Characterization of carbenium ions

The calculated gas phase energies of carbenium ion isomers derived from C_4 – C_6 olefins are given under each structure in Figs. 1–3. The values are the differences from the most stable isomer. Those transformed spontaneously during the geometry optimization are indicated by curly arrows. In all but three primary cations, **1**, **8** and **18**, hydrogen was transferred spontaneously to yield secondary or tertiary cation. Secondary cations were found about 50–60 kJ/mol less stable than tertiary cations. These results are consistent with the experimental findings [9] that the reactions involving tertiary cations are the fastest, followed by those involv-

ing secondary cations while reactions involving primary cations are very slow.

In order to characterize the carbenium ions adsorbed on the zeolite, adsorption structures and energies of protonated butenes (carbenium ions) on the cluster model extracted from Y zeolite were calculated by ab initio MO (Fig. 6). Although C² protonated 1-butene (**1**) was located in the gas phase, this cation was converted to C¹ protonated isomer (**2**) following the spontaneous hydrogen transfer over the zeolite. This indicates that, because the zeolite catalyzes the hydrogen transfer, unstable isomers will be transformed to the stable ones more easily over zeolite than in vacuo. Conclusively, primary cations hardly exist even over the zeolite. The isomer **2** was 61.4 kJ/mol less stable than **3** in vacuo, but this relative stability was reversed upon the adsorption on the zeolite, probably due to the large stabilization effect on **2**. The difference of the stabilization effects on **2** and on **3** by the zeolite can be interpreted as follows. The cation center C² of the straight chain **2** is allowed to approach the zeolite oxygen (C–O = 1.65 Å), which results in a great stabilization, but in case of branched chain **3**, three methyl groups are surrounding C² and are hindering it to approach the zeolite oxygen (3.18 Å), thus only a small stabilization is gained. This result indicates that the relative stability of carbenium ions may change upon the adsorption on zeolites.

Also π -complexes were calculated using the same cluster model and were compared with the ionic states (Fig. 6). Optimization from the initial structures where 1-butene or isobutene approaches the hydroxyl proton through C² lead to the structures with butenes approaching the proton through C¹. This also implies that C¹ is preferably attacked by proton, thus the primary cations are scarcely formed. The π -complex of 1-butene was found less stable than the corresponding ionic state, which may be due to the low stability of 1-butene itself. In fact, the energy of 1-butene calculated at the same level in vacuo was 11.4 kJ/mol higher than that of

2-butene and this energy difference was almost unchanged even after the adsorption on the zeolite (12.1 kJ/mol). One may thus infer that over the zeolite, 1-butene will be protonated easily, and will be isomerized to more stable 2-butene. The π -complexes were found more stable than the ionic states in case of 2-butene and isobutene. However, ionic states were located as the local minima, contradicting Martin's report [4] that these states correspond to the transition states. Furthermore, they reported the barrier height of about 130 kJ/mol from the π -complexes to the ionic states, while the energy gaps found here were merely 10–20 kJ/mol. Low energy of our protonated 2-butene may be attributed to its adsorption structure, where the distance between C² and the zeolite oxygen is particularly short, and falls between the corresponding atomic distances in the TS (2.15 Å) and the stable alkoxide (1.50 Å) of propene adsorption reported by them. In case of protonated isobutene, however, C²–zeolite O interatomic distance is much longer than the corresponding distance in the TS (2.44 Å) of isobutene adsorption in their report. There are three notable differences between Martin's calculations and ours which are possibly responsible for the inconsistent results. First of all, we employed a large cluster model to take into account the stabilization effect on the carbenium ions by the zeolite framework, while their model consists of only two oxygens that may stabilize the cation. Another difference is the basis set: we adopted 6-31G*, which is the minimal requirement to get a reasonable picture of the anionic state (additional diffuse functions is even recommended), while they used small 3-21G, which may have contributed to the underestimation of the stability of ionic states. Finally, although they partially optimized the zeolite cluster imposing some symmetric constraints, the geometry of zeolite part was completely frozen in our calculations. In H- and alkoxide-types, H or C are covalently bonded to one of four oxygens connected to Al. This would induce more distorted structure with one long

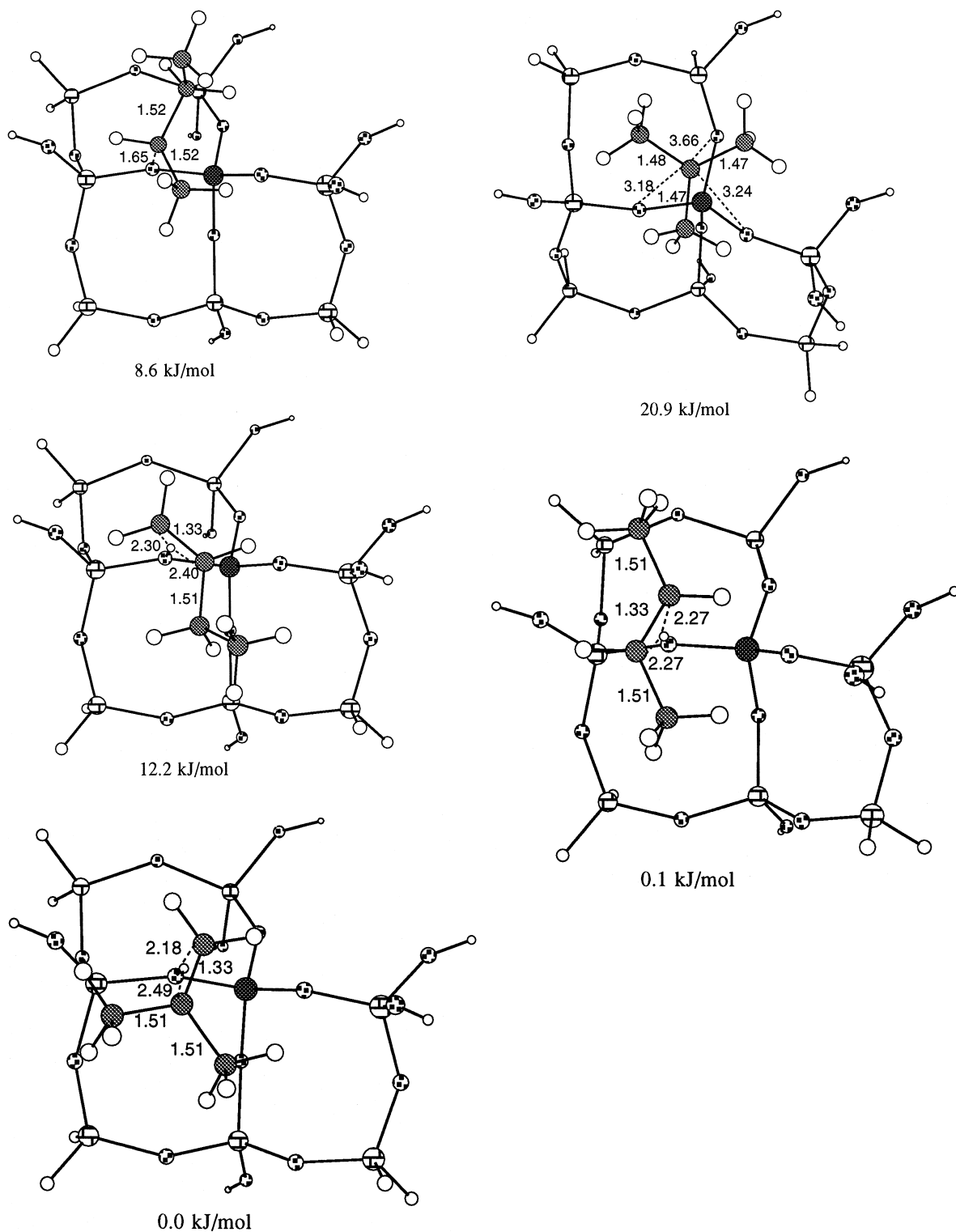


Fig. 6. Adsorption structure of 2, 3, 1-butene, 2-butene and isobutene on the cluster model extracted from Y.

Al–O bond than that of ionic states. Therefore, the influence of fixing the geometry will be more harmful to H- and alkoxide-types than to ionic states, and the stability of the former will thus be underestimated, which may have led to appreciate the stability of ionic state comparatively higher.

According to our results, transition states lie in the course of proton transfer from zeolite to olefin, and if the activation barrier of this reaction is high, carbenium ion would never be formed. Whatever, carbenium ions are indeed unstable compared to π -complexes, hence are still considered to be reactive. Zeolites possessing a pore structure that stabilizes these carbenium ions would thus promote the side reactions from the once produced olefins and to prohibit the formation of them would be a key to improving the selectivity. Our idea described in the introduction should therefore be reasonable.

3.2. Adsorption structure and strength of carbenium ions

Most stable adsorption structures of both carbenium ion isomers derived from butenes, **2** and **3**, (hereafter simply called butenes) on Y were found when they are confined in the sodalite cage (Fig. 7). Carbenium ion isomers derived from pentenes and hexenes (later also simply called pentenes and hexenes, respectively) were, on the other hand, too large to enter the sodalite cage and were bound to the super cage in the most stable structures (Fig. 7). The super cage of Y is so widely open that still a lot of space is left between the framework and the adsorbate when C₅ or C₆ are adsorbed, thus only weak interaction can be expected. In the usual case, as the size of adsorbate molecule becomes larger, unless it is too large to fit inside the pore, the framework–adsorbate interaction becomes stronger due to the increase of interacting points. In the case of Y, however, butenes perfectly fit inside the sodalite cage, thus are expected to be adsorbed more strongly than pentenes or hexenes. The smaller difference between the ad-

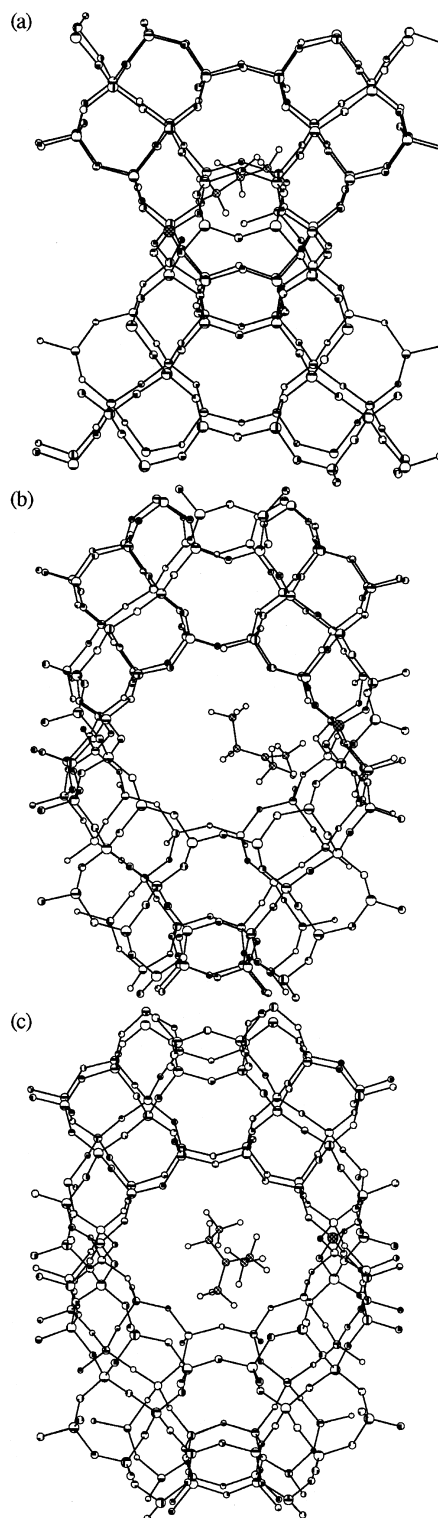


Fig. 7. Adsorption structures of the most stable isomers of C₄–C₆ olefins on Y. (a) **3**, (b) **6** and (c) **15**.

sorption energy of butenes on Y and that on MOR or on β as compared to the adsorption of longer chains may be attributed to this effect (Table 1). The question arises, however, if butenes can really enter the sodalite cage, since it consists of only 6- and 4-membered-ring. To examine this point, a molecular dynamics simulation was performed on the models where butenes are adsorbed in the sodalite cage of Y. The force field parameters used here were the same as those used for the molecular mechanics calculations, but to take into account the flexibility of zeolite all atoms were allowed to move. The simulation was performed at high temperature (1000 K) to save the computational time because it is believed that it takes a long time (order of ns) for the transition between the stable adsorption states [14]. During 100 ps of simulations, both **2** and **3** changed their conformation and orientation but could not escape from the sodalite cage, which means that butenes cannot enter the sodalite cage by diffusion either. The averages of the adsorption energies were, therefore, also calculated excluding the

Table 1
Adsorption energies of carbenium ions derived from C₄–C₆ olefins on zeolites (kJ/mol)

	MOR	ZSM-5	β
2	11.7	25.5	7.5
3	14.9	18.3	8.3
2^a	19.5	33.3	15.3
3^a	16.7	20.0	10.0
4	23.7	38.4	18.8
5	25.8	41.8	20.7
6	20.7	26.8	15.3
7	26.2	32.9	21.7
9	24.7	41.3	19.0
10	28.2	46.1	25.2
11	24.6	36.1	19.1
12	33.4	43.9	27.4
13	30.7	40.9	26.6
14	29.1	37.5	24.6
15	33.6	42.3	27.9
16	30.7	38.5	24.2
17	28.4	35.5	22.3

Values are differences from y.

^aWhen butenes adsorbed in the sodalite cage of Y were excluded from the calculation.

Table 2
Adsorption energies per carbon atom of carbenium ions derived from C₄–C₆ olefins on zeolites (kJ/mol)

	MOR	ZSM-5	β
2	2.92	6.37	1.88
3	3.74	4.57	2.07
2^a	4.87	8.31	3.83
3^a	4.17	5.01	2.51
4	4.74	7.67	3.75
5	5.17	8.35	4.14
6	4.14	5.35	3.05
7	5.23	6.58	4.34
9	4.12	6.89	3.17
10	4.69	7.69	4.21
11	4.10	6.01	3.18
12	5.56	7.31	4.57
13	5.12	6.82	4.43
14	4.85	6.25	4.11
15	5.59	7.06	4.65
16	5.12	6.42	4.04
17	4.73	5.92	3.71

Values are differences from y.

^aWhen butenes adsorbed in the sodalite cage of Y were excluded from the calculation.

structures where adsorbates reside in the sodalite cage (Tables 1 and 2).

Examination of the most stable adsorption structures of C₄–C₆ on ZSM-5 interestingly revealed that the straight chains prefer the zigzag channel while the branched chains are fond of the straight channel without exceptions (Fig. 8). Because passing a zigzag channel is expectedly more difficult than passing a straight channel, straight chains would be trapped and react while branched chains would go through. Meanwhile, as the blend stock of gasoline, the octane number of the branched chains is higher than that of the straight ones. Our results indicate that ZSM-5 would crack the straight chains selectively and leave the branched ones unreacted, resulting in a high concentration of the branched chains in the product, and ZSM-5 is, in fact, used commercially as the octane booster today. Besides the difference in the adsorption structures of straight and branched chains, no other significant differences were observed when the adsorption structures of different-sized molecules are compared.

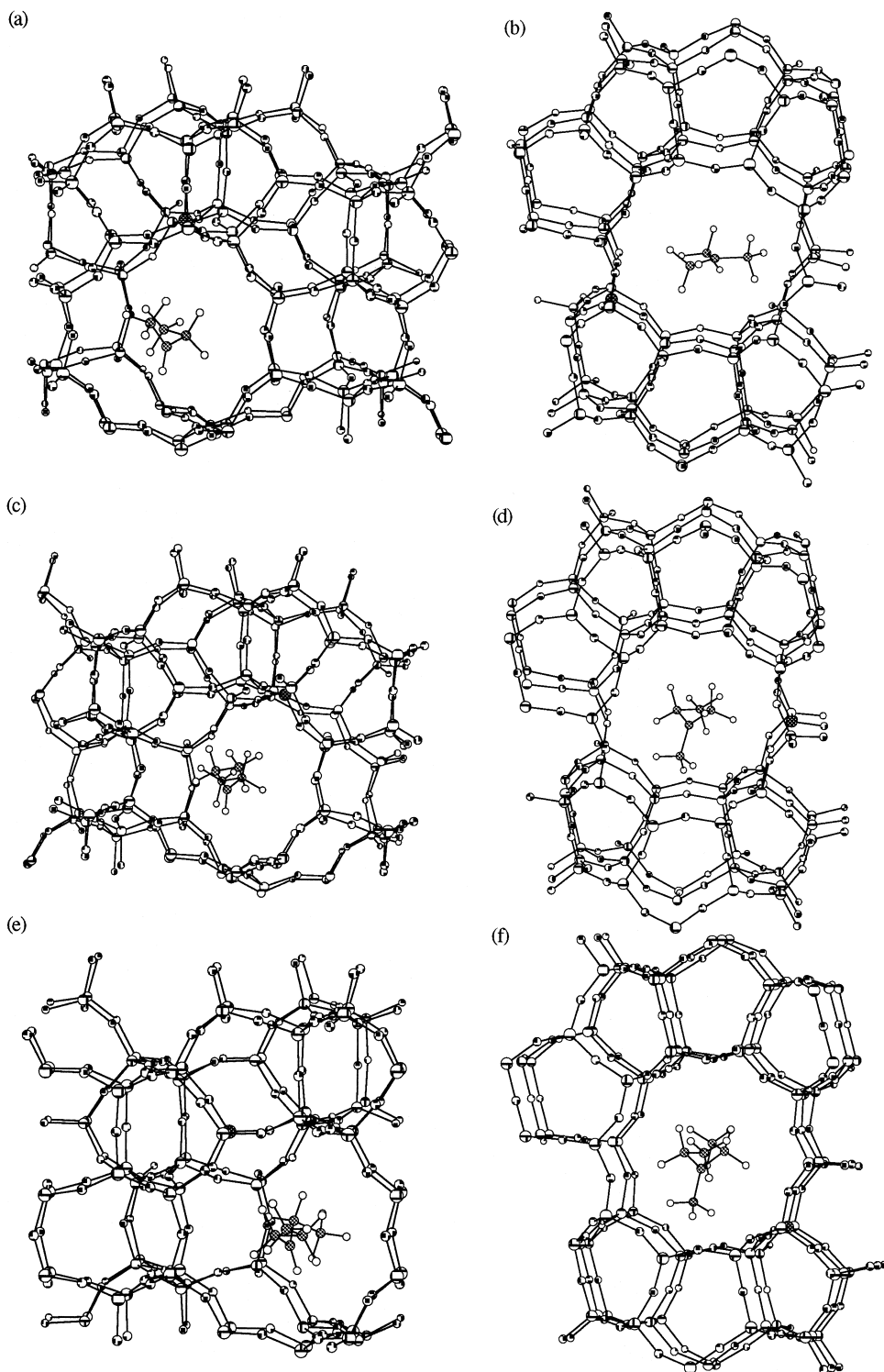


Fig. 8. Adsorption structures of the most stable isomers of straight and branched C_4 – C_6 olefins on ZSM-5. (a) 2, (b) 3, (c) 5, (d) 6, (e) 10 and (f) 15.

In the most stable adsorption structures of the carbenium ion isomers derived from C_4 – C_6 olefins on MOR, the adsorbates were all located in the 12-membered-ring main channel (Fig. 9). In our previous work [8], the most stable adsorption structure of ammonia on MOR was found when the adsorbate is captured in the 8-membered-ring side pocket. In the present simulations, some structures where a part of the chain is inside the side pocket were obtained, but none of them corresponded to the lowest energy. Therefore the adsorption profile of ammonia and that of olefins are different (particularly ammonia is thought to be special because of its small size and the ability to form the hydrogen bonds). Furthermore, the calculated adsorption strength of ammonia on MOR was higher than that on ZSM-5, while it is opposite in case of olefin adsorption. This result gives a warning that the acid properties evaluated by the heat of ammonia adsorption do not always correlate with the catalytic activity in the target reaction.

No significant differences were observed when the most stable adsorption structures of C_4 – C_6 on MOR (Fig. 9) or on β (Fig. 10) were compared and the adsorbates are always located at the similar site of the pore. Both types possess the 12-membered-ring pores, but do not have a roomy cage like the super cage of Y. Therefore, as the size of molecule adsorbed on MOR or β becomes larger, the interaction between the framework and adsorbate would increase more significantly than in case of Y. The tendency of the calculated adsorption strength (Table 1), that larger deviations from Y are found as the molecular size increases, agrees with this expectation.

Adsorption strength of carbenium ion isomers derived from C_4 – C_6 olefins on Y, MOR, ZSM-5 and β are summarized in Table 1, where the values are the differences from Y. Also, the data are given when butenes adsorbed in the sodalite cage of Y, which hardly seem to occur (*vide supra*), were excluded. The relative adsorption strength are, in all cases, $Y < \beta <$

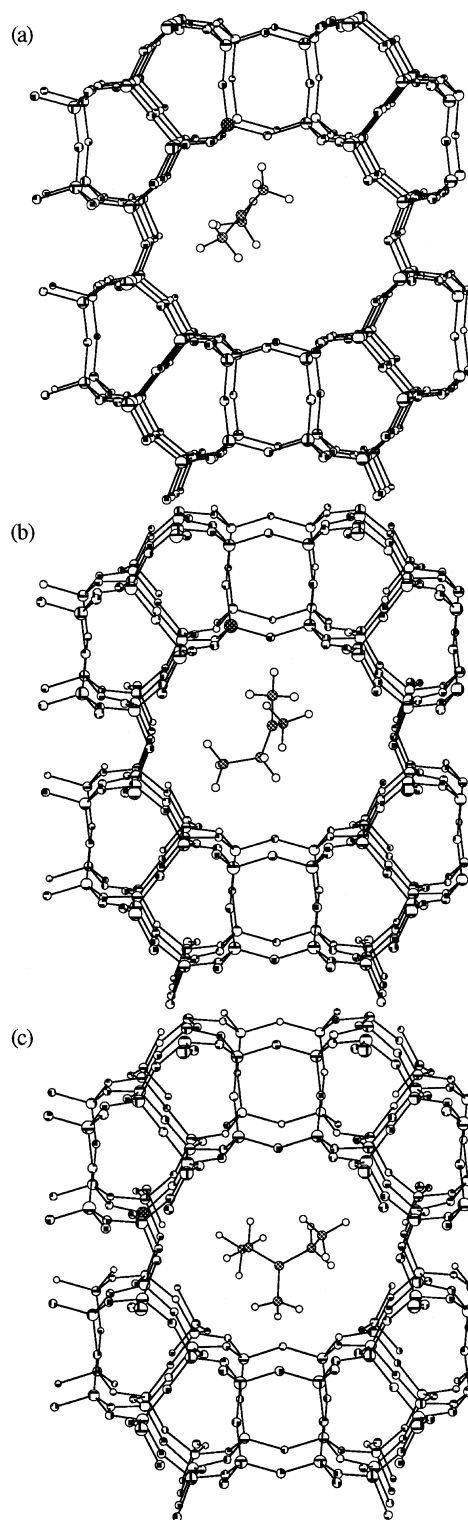


Fig. 9. Adsorption structures of the most stable isomers of C_4 – C_6 olefins on MOR. (a) 3, (b) 6 and (c) 15.

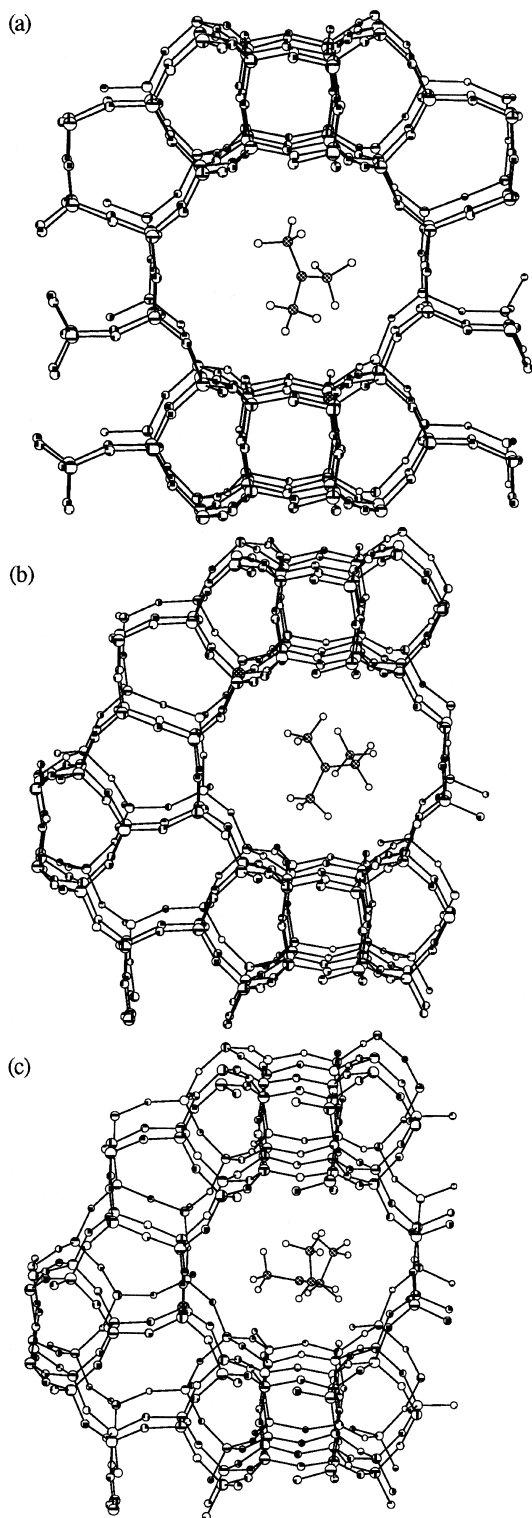


Fig. 10. Adsorption structures of the most stable isomers of C_4 – C_6 olefins on β . (a) 3, (b) 6 and (c) 15.

ZSM-5. The larger the molecule, the more the interacting points. Therefore, for the fair comparison of the different-sized molecules, the interaction energies per carbon atom were calculated by dividing the adsorption energies by the number of carbon atoms (Table 2, where values are the differences from Y). Higher interaction energies per carbon atom are obtained as the molecular size becomes larger in case of MOR and β , as compared to Y. In case of ZSM-5, on the other hand, the highest interaction energies per carbon atom were found with the adsorption of C_4 and C_5 . From this result, ZSM-5 adsorbs C_4 – C_5 more strongly than Y does, thus would promote the side reactions from once produced C_4 – C_5 olefins, resulting in a low selectivity toward the target fraction. MOR and β , on the other hand, adsorb C_6 more strongly than C_4 and C_5 , as compared to Y does, thus would trap and crack the former species while allowing the latter to pass through and give a higher concentration of the desired fraction in the product. Reciprocally, Y would not suffer from the side reactions from C_4 – C_5 olefins, but let $C_6 <$ also be unreacted and remain in the product, due to the weak adsorption strength of C_6 on Y as compared to that on MOR or on β . Furthermore, although the adsorption profile of MOR and β are similar, MOR consists of unidimensional 12-membered-ring main channel (with 8-membered-ring side pocket) and is expected to degrade instantly once used as the FCC catalyst, because if one point of the pore is blocked by coke, gas have no alternative way and it would be completely choked up. β possesses the same 12-membered-ring but two dimensional channel, thus gas can escape even if one point is blocked and the durability against coking is expected to be higher than that of MOR. Therefore, if degradation by coke formation is taken into account, which is an important factor in FCC catalyst, β is expected to be superior to MOR. Our preliminary experiment using micro activity test (MAT) revealed that the performance of MOR as FCC catalyst is not satisfactory due to the poor conversion. Among Y,

ZSM-5 and β , C₄–C₅ olefin selectivity was the highest when β was used as the catalyst, which is consistent with our prediction from the simulation.

4. Conclusion

The selectivity of FCC zeolitic catalysts toward the C₄–C₅ olefins was estimated by the simulation of the adsorption strength. All the carbenium ion isomers that can be derived from the protonation of butenes, pentenes and hexenes were calculated in gas phase by ab initio MO and primary cations were found prohibitively unstable. The adsorbed species were studied in detail also by MO calculations, adopting butenes adsorbed on the cluster model extracted from Y. The relative stability of carbenium ions were found to change upon the adsorption on zeolites, due to the different stabilization effect. Ionic states were located as the local minima, rather than the transition states, but their stability was 10–20 kJ/mol lower than that of corresponding π -complexes, and they were expected to be reactive. The adsorption structures and energies of C₄–C₆ carbenium ions on Y, MOR, ZSM-5 and β , were calculated according to the simulation protocol based on the molecular mechanics with systematic sampling. The small pore of ZSM-5 was found to adsorb C₄–C₅ olefins strongly, while the super cage of Y will allow C₆ to escape from the reaction. MOR and β were predicted to be superior in the C₄–C₅ olefin selectivity.

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