

Ab initio MO studies on protonation mechanism of ethylene over catalyst HZSM-5

Zhang Guiling, Li Gang, Dai Baiqing *

Department of Chemistry, Harbin Normal University, Harbin 150080, China

Abstract

Four calculation models (I–IV) were proposed for studying the protonation mechanism of ethylene over catalyst HZSM-5. Ab initio SCF-MO calculations were carried out at the STO-3G basis set level. From the calculation results of geometry optimization and Mulliken population of these models, it has been shown that the *cis*-four-centered reaction mechanism (model I) is the most reasonable one, while the vertical complex reaction mechanism (model II) is of no effect, and models III and IV are possible for the terminal radical absorption. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The zeolite catalyst HZSM-5, as a molecular sieve, is able to effect a number of industrially significant conversions. Its catalytic activity depends mainly on Brønsted –OH groups. One of the most important conversions is the protonation of olefins. This molecular sieve is characterized by a system of straight channels paralleling crystal face [010] and sine channels paralleling [100] (as shown in Fig. 1) [1], and straight channels are the main ones. This special framework structure also provides a good space environment for its catalytic activity. Some experiments have shown that these protonation reactions are carried out in a carbonium ion mechanism [2,3]. Therefore, to study protonation

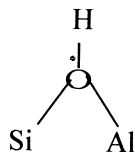
mechanism and the absorbed state of ethylene over HZSM-5 zeolite plays an important role in understanding the mechanism of a series of organic catalytic reactions. Here, we report an ab initio MO study on this mechanism. Such kind of work has not been reported.

2. Calculation details

According to the HZSM-5 zeolite cluster structure and the experimental models of olefin addition reactions, we suggest four models for the calculation (Fig. 2). H atoms are verified by experimental results to be connected with bridged oxygen atom of the Si–O–Al units to form bridged –OH groups, and these –OH groups are in the same environment. Considering certain –OH, for example, –O₁H₂, except for the Si₃ and Al₄ atoms which are connected directly to it (Fig. 1), the other Si or Al atoms

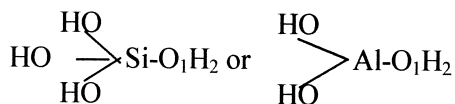
* Corresponding author. Tel.: +86-451-6329924; Fax: +86-451-6329591; E-mail: bqdai@postoffice.hrbnu.edu.cn

take weak long-range effect on it, so taking the dimer of



for calculations is reasonable.

In order to simplify the calculations and not to influence the zeolite activity, we took H as the terminal atom to close the end cluster unit because it has little effect on Brönsted $-O_1H_2$ activity. In the case of models I and II, we chose $-OH$ to close Si and Al, but for models III and IV (designed to examine the possibility of terminal absorption if we also chose $-OH$ to close Si or Al), the formed



will be unstable and will destroy the activity of the terminal $-O_1H_2$, so for closing Si or Al, using H is suitable.

Calculations of full geometry optimization were carried out at STO-3G basis set level by using Gaussian-94 program on Pentium-II computer. Although STO-3G is the minimum basis set, it is acceptable and good enough here. Because for comparing models I–IV the most important value is the qualitatively relative en-

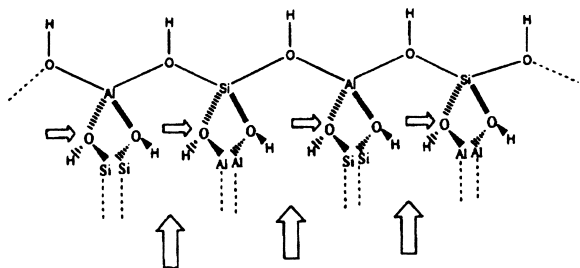


Fig. 1. Framework of HZSM-5 (\uparrow) straight channel, (\Rightarrow) sine channel.

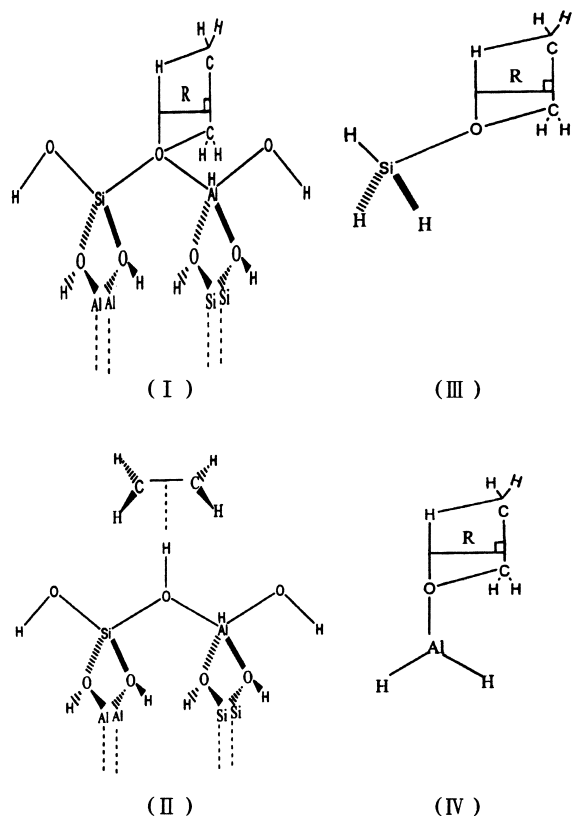


Fig. 2. Four absorption models I–IV.

ergies rather than the quantitatively accurate absolute energies, and the order of stabilities will keep no change with basis set levels.

3. Results and discussions

The optimized results are listed in Table 1.

Model I is set for *cis*-four-centered reaction mechanism, whose SiO_1H_2Al plane and $O_1H_2C_3C_4$ plane are perpendicular to each other, and the ethylene plane is parallel to straight channels and perpendicular to sine channels. In the course of calculation, we took the perpendicular distance R (from the center of O_1-H_2 to C_3-C_4) as the parameter to describe the absorption process. While R changed, the angle $\angle H_2O_1C_4$ is always kept at 53.16° which is the ultimate optimized result.

Table 1
The optimized geometries and Mulliken populations of various models

Models	Bond length (Å)				Mulliken population			
	O ₁ -H ₂	H ₂ -C ₃	C ₃ -C ₄	O ₁ -C ₄	O ₁ -H ₂	H ₂ -C ₃	C ₃ -C ₄	O ₁ -C ₄
I	2.696	1.087	1.544	1.443	-0.001	0.383	0.355	0.264
II	0.972	2.320	1.310		0.275	0.004	0.605	
III	0.729	1.086	1.551	1.425	-0.001	0.384	0.352	0.271
IV	2.422	1.086	1.559	1.417	-0.002	0.382	0.351	0.274

The results of optimizations showed that the zeolite and ethylene begin to interact when R reached about 1.5 Å from farther distance, at first C₃=C₄ bond is weakened at $R = 1.52$ Å

then O₁-H₂ starts to loose at $R = 1.44$ Å. These two bond lengths have approximately linear relationship with R : as R became shorter, they get longer, and the O₁-H₂ bond does

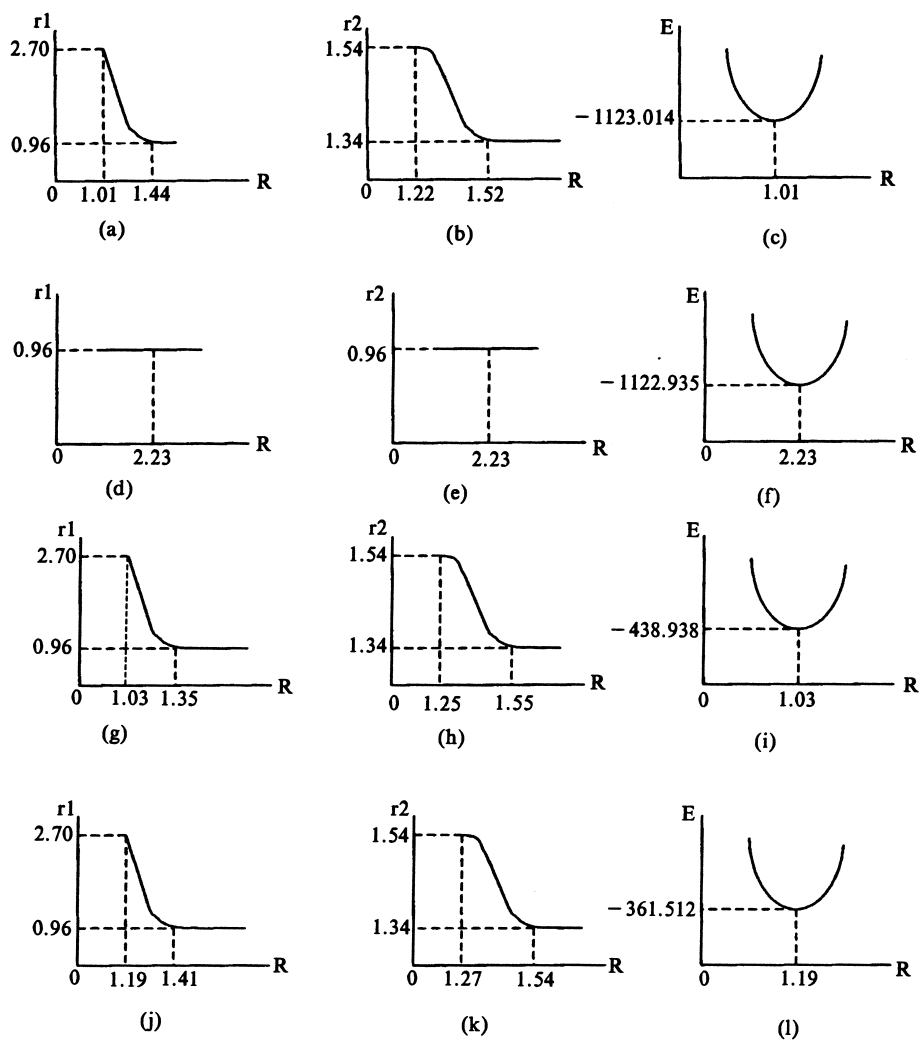
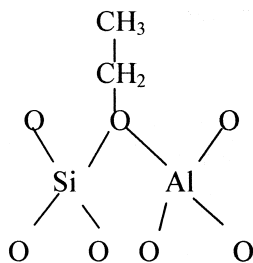


Fig. 3. Changes of bond lengths and absorption energy with distance R for various models.

rapidly. At $R = 1.2 \text{ \AA}$, the $C_3=C_4$ double bond changes to single, and the O_1-H_2 bond gets longer continuously. The stationary configuration is obtained at $R = 1.01$. (Fig. 3a,b). At this distance, the absorption configuration (Fig. 3c) gets the lowest energy (-1123.014 Hartree). Data in Table 1 also show that the O_1-H_2 bond broke and the $C_3=C_4$ bond turned into single C_3-C_4 . In the meantime, O_1-C_4 and H_2-C_3 bonds are formed. These mean that the H_2 atom transferred to ethylene in which carbon atoms converted from sp^2 into sp^3 hybrid leading to the protonation of ethylene. The stable absorption configuration is in accordance with the



experimental result. Propylene absorption mechanism over DZSM-5 zeolite had been studied by using IR, D-exchange tracer and impulse methods and it has been shown that the $-OD$ 2665 cm^{-1} peak disappears immediately and the $-CH_2D$ 2165 cm^{-1} peak appears simultaneously [4].

Model II is set for the vertical complex reaction mechanism, i.e., $-O_1H_2$ is perpendicular to the ethylene plane, which is parallel to sine channels and perpendicular to straight channels. Here we use the distance R (from the center of $C=C$ to H_2 atom) to describe the absorption process. According to Fig. 3d and e, it can be seen that when R changes the O_1-H_2 and $C_3=C_4$ bond lengths are always kept at 0.96 and 1.32 \AA , respectively. At $R = 2.23 \text{ \AA}$, the stable absorption configuration is obtained. The

lowest energy of model II is 0.079 Hartree higher than that of model I. Compared with the data of model I (Table 1), it is apparent that the O_1-H_2 bond does not break, $C_3=C_4$ is still double, the ethylene and zeolite cannot combine with each other, so this absorption model is of no effect.

Models III and IV are designed on the basis of model I to describe the terminal radical absorption. Because the 2750 cm^{-1} peak in IR of $\equiv SiOD$ experimentally disappears, this absorption can occur over terminal $-O_1H_2$. The calculated results of models III and IV indicate that terminal radical absorption is possible. Parameter R is also chosen to deal with the absorption process, which is right similar to model I. The $C=C$ bond loses first, then O_1-H_2 begins to break (see Fig. 3g–m) just like model I. At $R = 1.03 \text{ \AA}$ and $R = 1.19 \text{ \AA}$, the stable absorption states are obtained for model III ($\angle H_2O_1C_4 = 54.06^\circ$) and IV ($\angle H_2O_1C_4 = 62.92^\circ$), respectively. The data in Table 1 of these two models are also in accordance with model I.

From the above discussion, it can be concluded that the *cis*-four-centered absorption is helpful to the bond formation not only of C_3-H_2 but also of C_4-O_1 . This concerted action leads to the weakened of $C=C$ double bond and the protonation of ethylene.

Acknowledgements

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