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Mechanism of methanol-to-olefin (MTO) reaction

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Abstract. The full name of MTO is methanol to olefin, which is a new chemical reaction process to gain an important chemistry industry raw material. In this paper, we mainly talk about several general reaction process as well as the mechanism of the reaction. The use of molecular sieve catalytic process is a key point where the new MTO process different form the original simple petroleum cracking in order to again olefin. In this work we mainly discuss how the MTO process could happen with the assist of the molecular sieve catalyst. There are direct mechanism Carbene mechanism and Methane-formaldehyde mechanism. The effect of the direct mechanism is to gain some simple and short Carbon-Carbon product. And then the indirect mechanism will take on to control the rate of the reacting process and the ration of different products. By studying on the mechanism of the MTO reaction, we can figure out how a powerful catalyst, molecular sieve catalyst, works in the reaction. Also, the MTO process is a meaningful way to take place of the origin cracking process to gain olefin, as the storage of petroleum is decreasing fast recently.

Keywords: Olefins, MTO, molecular sieve catalytic process.

1. Introduction

Olefins are a very important raw material in organic synthesis, and have a very important position in the raw materials of China's chemical industry, polyolefins and synthetic rubber are inseparable from basic low-carbon olefins. With the development of the speed of light in China's chemical industry, the demand for olefins is also increasing. In the traditional chemical industry, the main source of olefins is high-temperature thermal cracking of petroleum; However, at a time when demand is extremely high, the efficiency of this production method cannot meet the requirements, and the increasingly scarce oil in the world has led to a sharp decline in the supply of oil. In this context, the MTO process came into being. The use of natural resources such as coal and natural gas available in China through MTO process, while ensuring energy supply, while providing necessary raw materials for the chemical industry, is the future development direction of the olefin chemical industry. From the discovery of MTG Industries by American companies in 1975: the catalysis of methanol into gasoline by molecular sieves, followed by the discovery and improvement of this innovative method in countries around the world, gradually improving the new industrial chain of olefins. So far, the relatively complete industrial chain can be summarized to more than 85% of ethylene propylene types. The new type of molecular sieve catalysis has changed the status quo of China's chemical industry and is an innovative change. In this work, the direct mechanism and indirect mechanism of the molecular sieve catalytic process of MTO are mainly studied, and the principle of reaction is studied at different mechanism levels.

2. Reaction mechanism

The whole picture of the reaction mechanism of MTO still needs more in-depth study, so far there have been many discoveries in the process of converting alcohols into C-C short chains, but the reaction mechanism corresponding to the general reaction process can be divided into two parts: direct mechanism and indirect mechanism.

2.1. Direct mechanism

The direct mechanism is mainly about how the C atoms in alcohols recombine and form a chain structure of the C-C structure. After decades of research, scientists have proposed more than twenty different reaction mechanisms, including but not limited to carbene mechanism, methane-formaldehyde mechanism and methylene oxy mechanism. Of all the direct mechanisms, the surface methoxy group (SMS) formed by methanol adsorption at the B acid site is the intermediate that appears most frequently in mechanistic experiments [1,2]. This review mainly analyzes the reaction mechanism of two key points, carbene mechanism and methane-formaldehyde mechanism. Figure 1 shows several different direct mechanism reaction flow diagrams.

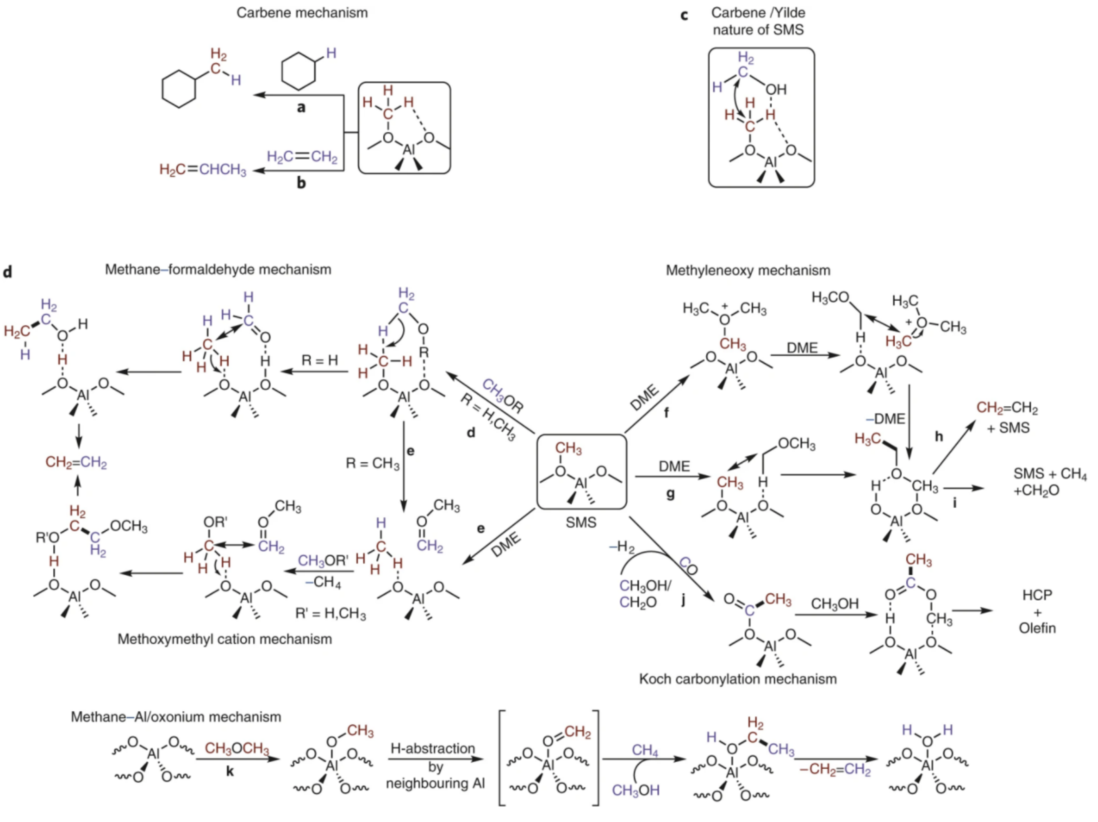

Figure 1. Several direct mechanisms of MTO reaction to form C-C bonds catalyzed by molecular sieve reaction [3]

2.1.1. Carbene mechanism. The basis of the carbene mechanism is the change of methoxy groups: the surface-stable carbene species formed by the deprotonation of methoxy groups on acidic zeolite are the key to the formation of corresponding olefins. This theory was first discovered by Hunger and his colleagues [2,4] through experiments in nuclear magnetic spectroscopy and carbide collection. As shown in Figure 1.1a-c, the carbene properties of the methoxy group are due to the polarization of the C-H bond corresponding to the upper methoxy group by O molecules in the zeolite lattice [5,6]; In this process, both the alcohol group and the intermediate C are attracted by the polarized H and combined into olefins in the form of SP3 before subsequent reactions. Using the isotopic distribution of C,H and the corresponding infrared spectroscopic analysis in the H-ZSM-5 catalyzed ethylene methylation experiment, Kondo's team proposed this carbene mechanism reaction [7] as the reaction mode in Figure 1.1b. However, due to the lack of necessary intermediate components, the presence of carbene is still not recognized. However, the presence of surface methoxy groups is key to the formation of the initial dimethyl ether and the subsequent formation of the C-C chain structure: carbene species are inserted into adjacent methoxy groups and bound as shown in Figure 2 [8]. The formed olefins then react with further methoxy groups by rapid diffusion to form a chain bond structure of C-C under SAPO-34. At higher temperatures, CO can be inserted into acetyl groups and bound to methoxy groups, but these substances do not directly form intact olefins and further reactions are required.

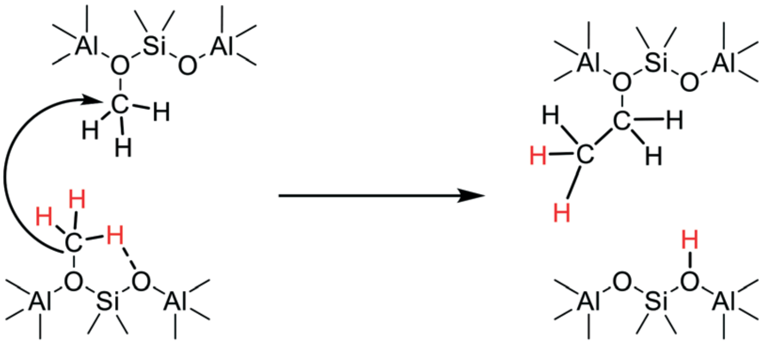

Figure 2. Reaction of carbene species to adjacent methoxy groups[8]

2.1.2. Methane-formaldehyde mechanism. The underlying methane-formaldehyde mechanism comes from the hypothesis of Hunter's team in 1987 [6]. In 1998, Hirao et al. proposed a relatively complete methane-formaldehyde mechanism [9]. In it, he simulated the formation of methane formaldehyde as a process from a methyl C atom of a surface methoxy group in ethanol through three T-skeleton atoms. The mechanism of methane formaldehyde is mainly divided into two parts, as shown in the two large branches of Figure 1.1d: one is the formation of methane formaldehyde, and the other is the formation of ethylene. The first is that the methyl hydrogen atoms in methanol are attracted to methoxy groups and thus transfer, which is necessary to form the corresponding methane and formaldehyde. The second is that the first step is for the production of methane to decompose into hydrogen and methyl groups, and combine with the oxygen atoms on the molecular sieve skeleton and the carbon atoms on the formaldehyde in the first step, and finally obtain ethanol, which is dehydrated to form ethylene. Due to the relatively complex and lengthy process of this reaction mechanism, the high demand for reaction activation energy and a large number of intermediate products, the reaction process is relatively unstable, and this direct mechanism of reaction is not recognized. Therefore, the formation of the first C-C chain bond is still unknown, but experiments have proved that the direct mechanism does exist in the early process of reaction with MTO, so it is still of research significance.

3. Indirect mechanism

While studying the principle of C-C bonds and carbon chain formation, new discoveries have also been made about how methanol is converted into other substances and the reaction mechanism of molecular sieve from catalysis. Among them, the two most important indirect mechanisms are the hydrocarbon pool mechanism and the dual cycle mechanism, which play a role in the process of cracking to form the corresponding olefins.

3.1. Hydrocarbon pool mechanism

The essence of the hydrocarbon pool mechanism is the mixing between methanol, dimethyl ether and alkenes and the tendency to autocatalyze, as shown in Figure 3, which contains many different hydrocarbon pool species and different olefin species formed after molecular sieve cleavage catalysis. In 1979, Reagan [10] found that these three substances can produce autocatalytic phenomena under the catalysis of ZSM-5, and the reaction rate of the formation of olefins is nearly 50 times faster than the process of obtaining ethylene from the first two substances alone. Subsequently, in 1982 and 1986, Dessau's [11,12] team studied H-ZSM-5 catalyzed methanol conversion reactions with 13C labeling, and found that the ethylene produced was not a simple C1 synthetic, but a product of more advanced olefin cracking. In 1983, Mole's [13] team found that if aromatic hydrocarbons were present in the reaction system, the conversion rate of methanol fixed on the dealuminized Y zeolite of H-ZSM-5 and zinc ion exchange would be greatly improved. Therefore, aromatic hydrocarbons have proved to be the catalyst for this reaction and can greatly accelerate the reaction rate. Then, between 1993 and 1996, Dahl and Kolboe [14-16] team, knowing that SAPO-34 can catalyze the methanol reaction and raise the type of ethylene propylene produced by 13C labeling, investigated the source of carbon from this reaction product. It was found that the C in most hydrocarbon products was derived from labeled methanol carbon, and the reactivity of olefins was relatively low. Thus, the hydrocarbon pool mechanism was discovered. However, the hydrocarbon pool mechanism is only a conclusive law at present, and there is no specific conclusion on the cause of the source of carbon chain molecules and the corresponding mechanism, and there is no very specific model of the reaction structure.

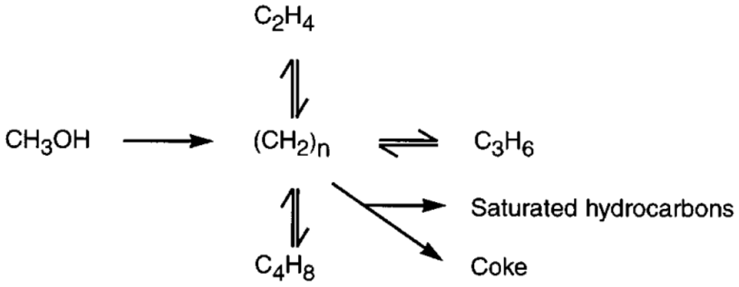

Figure 3. Specific flow of hydrocarbon pool mechanism[16]

3.2. Dual cycle mechanism

According to the reaction process of the hydrocarbon pool mechanism, the organic matter of the higher olefin or aromatic intermediate produced by the MTO reaction will be fixed in the molecular sieve pores and react with the inorganic skeleton of the molecular sieve as a catalyst. The final low-carbon olefin is a product of reaction between the substance immobilized on the molecular sieve and methanol in the autocatalytic stage, and the chain structure is continuously combined and grown, and cracking occurs. So far, Bjorgen have proposed that the dual cycle mechanism of [17,18], including aromatic hydrocarbon cycle and olefin cycle, is the most internationally recognized and reliable reaction mechanism, as shown in Figure 4. For the aromatics cycle, the two main mechanisms are the side chain cyclic hydrocarbon mechanism and the contraction and expansion cycle mechanism [19-21]. In the side chain alkylation mechanism, the initial hydrocarbon pool species will generate ethylene and propylene after undergoing the most important methylation in the differentiation stage, and subsequent reactions such as deprotonation, hydrogen transfer, and alkyl cracking. In the subsequent contraction-expansion cycle mechanism, the initial hydrocarbon pool species will shrink the ring to form the corresponding alkyl substituent after the first step of methylation reaction, and then react after the substituent is cracked to generate low-carbon olefins. Reduction back to the original hydrocarbon pool species. In this way, the aromatics cycle realizes the cyclic transformation of substances. While the mechanism of olefin cycle was first proposed by Dessau [22]. For the olefin cycle, its reaction mechanism is similar to that of the aromatic hydrocarbon cycle. After a certain stage of conversion, substituents that can be cracked will be generated, and the corresponding substituents can return to the stage after being cracked into high-carbon olefins. Transform the previous state and implement the loop.

However, although two cycles have a similar cycle mechanism, the products of two cycles are not the same. The main products of olefins and aromatics are not the same, and ethylene, the main product of the aromatic hydrocarbon cycle, is formed by the methylation reaction of the same low-carbon organic matter followed by a cracking reaction [23]. The main source of olefins with high carbon olefins such as C3+ is the olefin cycle. According to the C13 labeling study of Bjorgen. [24], the C13 isotope distribution of ethylene was found to be similar to that of xylene in the reaction of methanol propylene and xylene, while the reaction product of high olefins was different from ethylene. Thus, it can be obtained that the aromatic hydrocarbon cycle mainly corresponds to the product low carbon olefin, and the olefin cycle mainly corresponds to the product high carbon olefin. Because of this difference, the proportion of corresponding products can be controlled by adjusting the participation ratio of the aromatic cycle to the olefin cycle. In other words, the product of MTO reaction can control the selectivity of the product through the adjustment of the mechanism.

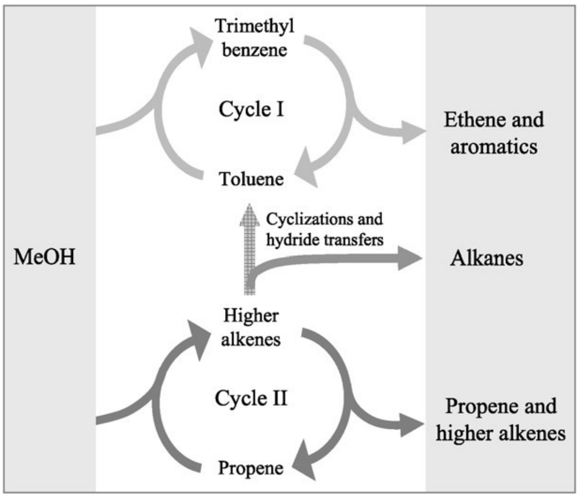

Figure 4. Dual cycle mechanism[22]

4. Conclusion

The main research in this paper is to summarize the reaction mechanism of MTO reaction, that is, methanol to olefin. The basic origin and reaction mechanism of C-C chain structure, carbene mechanism and methane-formaldehyde mechanism, as well as the reaction rate and origin of carbon atoms, hydrocarbon pool mechanism and double cycle mechanism in the catalytic process of zeolite are described. Although the formation of the first C-C bond and the specific reaction process of the hydrocarbon pool mechanism still need to be studied, the summary obtained still plays a very large role in the study of the reaction mechanism.

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