Chapter 4

Summary and Future Work for Part I

The experimental results shown in the previous chapters of Part I will be summarized in this chapter. Lastly, several suggestions about future research directions to deepening the understanding of MTO reaction are made on the basis of my experimental results.

4.1. Overall Summary and Conclusion

Ethylene and propylene are the two most important hydrocarbon products which support the entire chemical industry and, by extension, the modern civilization. The MTO process using non-petroleum feeds is a promising technology that can cope with high oil prices and expected gaps between olefin demand and capacity. The commercialized catalyst SAPO-34 can produce ethylene and propylene with high selectivity over 80% in continuous fluidized-bed reactors equipped with co-operating catalyst regeneration units. The MTO process is completely commercialized nowadays, and many plants are under construction or on stream including the Shenhua Baotou coal-to-olefin process which started operation in 2010, located in Inner Mongolia of China.

Tremendous efforts have been made to elucidate the fundamental mechanism of MTO reaction. The hydrocarbon pool mechanism suggested by Dahl and Kolboe in the early 1990s is the most widely accepted by the scientific community. The hydrocarbon pool mechanism consists of a wide array of polymethyl aromatic intermediates. The sizes and numbers of methyl groups of aromatic carbenium intermediates which governs the final
product distribution are restricted by cage geometries. Many previous works tried to deduce the shape selectivity in the MTO reaction. However, the global structure-property relation between the topology and olefin product distribution on the basis of reliable metrics has yet to be reported.

To establish the general rule about the shape selectivity in MTO reaction, among 245 molecular sieve topologies which have been ever reported, 14 topologies having cage structures limited by pore windows consisting of 8 tetrahedral atoms were selected. 30 molecular sieves (17 zeolites and 13 AlPO₄-based) having those topologies were prepared. The crystal structures, morphologies, and elemental compositions were characterized on the basis of PXRD, SEM, and EDS, respectively. The MTO behaviors of all of these catalysts were investigated. All MTO reactions were conducted at the same reaction condition (T = 400 °C, WHSV(MeOH) = 1.3 h⁻¹) to make a valid comparison.

First, it was experimentally confirmed that the topology primarily determines the olefin selectivity distribution. Two topologies—CHA and AEI—were prepared as zeolites, SAPOs, CoAPOs, and MgAPOs. Impressive similarities in olefin selectivity distributions were observed among isostructural groups of catalysts. Several other topologies (AFX, SFW, LEV, LTA, RHO, and KFI) were prepared as both zeolites and SAPOs. Zeolite-based catalysts showed MTO behaviors similar to those of their SAPO-based counterparts. Regardless of elemental compositions, AFX and SFW showed transient ethylene-to-propylene ratios close to unity at all stages of reaction. SAPO-35 and Nu-3 sharing the same LEV topology showed sharply increasing transient ethylene-to-propylene ratios over time on stream. All LTA-, RHO-, and KFI-type molecular sieves showed very high butylene contribution ratios similar to or higher than 0.5.

Second, given that it is not the elemental composition, but the topology that dictates the final olefin selectivity distributions, the studied topologies were classified into 4 groups, and named as Category I, II, III, and IV. Category I consists of CHA, AFX, SFW, and other
GME-related topologies. These topologies gave ethylene-to-propylene ratios which are approximately one. The Category II topologies are ERI, LEV, and intergrowth of these two frameworks. These types of catalysts showed sharply increasing transient ethylene-to-propylene ratios and/or completely ethylene-dominating product distributions. The members of Category III are DDR, AEI, ITE, RTH, and SAV. Category III-type molecular sieves showed propylene selectivities which are almost twice higher than ethylene selectivities without exception. Topologies having LTA-type cages (LTA, RHO, KFI, and UFI) were grouped into Category IV which is characterized by their high butylenes selectivities.

Third, a geometric indicator that can correlate the cage structures to the four categories of catalytic results was suggested. On the basis of a thought experiment on a hypothetical cage having an ideally ellipsoidal shape, the most important metric that actually limits the size of hydrocarbon pool intermediates was extracted. Among three principal axes of an ellipsoidal cage, the ellipse defined by the shortest and second shortest principal axes was named the cage-defining ring, and the length of the second shortest axis was defined as the cage-defining ring size. Analogous procedures were applied to real cages based on the crystallographic data disclosed on the IZA database. The cage-defining rings and their sizes were determined for 14 topologies studied in this work. A strong correlation found between the cage-defining ring sizes and the categories of olefin product distributions.

This work may be the most extensive experimental study regarding the shape selectivity in the MTO reaction up to date. I believe that the concept of cage-defining ring will provide researchers a reliable way to estimate the product distributions from the crystal structures.
4.2. Proposed Future Work

As mentioned in Chapter I, recent trends of mechanistic studies about the MTO reaction are toward the dual-cycle concept, and the identification of carbenium intermediates formed within various types of cage topologies. According to the dual-cycle concept, the alkene cycle generates propylene with high selectivity from the cracking of higher olefins, and the aromatic cycle produces both ethylene and propylene. In Part I, it was experimentally demonstrated that ethylene-to-propylene ratios are
primarily dictated by the cage topology. Considering the result that ethylene is almost exclusively formed from the aromatic cycle, the shape selectivity of cages can be eventually accomplished by the confinement effect on this dual-cycle mechanism. For example, it was shown that SSZ-98 zeolite having an ERI topology gave a very high ethylene selectivity. Combined with the recent mechanistic studies, a hypothesis such as “the ERI topology may prefer the aromatic cycle and/or suppress the alkene cycle” can be established. Analogous hypotheses can be considered for all other topologies and/or categories of topologies.

![Figure 4.2](image_url)

Figure 4.2. Cage structures, maximum sizes of sphere that can fit within cages, and cage-defining ring sizes of topologies SAT, SWY, and AVL.

There are several remaining topologies which should be tested in respect of the cage-defining ring concept. I suggest three topologies (SAT, SWY and AVL shown in Figure 4.2) for future work. The framework SAT is a very interesting topology since it is expected to show a high ethylene-to-propylene selectivity because it belongs to Category II. Its cage-
defining ring size (6.60 Å) is smaller than that of ERI (6.76 Å). This framework was first reported as a MgAPO-based molecular sieve STA-2,107 and later, a pure SAT-type AlPO₄-based molecular sieve was reported.108 But this framework has not yet been synthesized as a pure SAPO form, and SAPO-56 (AFX) was always observed as an impurity phase in the SAPO system. I successfully synthesized pure CoAPO-based SAT phases, but no complete conversion of methanol was observed in the MTO reaction. It is also possible that this SAT cage is too narrow to possess the aromatic intermediates of MTO reaction.

The framework SWY is another cage-based topology which is expected to belong to Category II. Its cage-defining ring size (6.77 Å) is almost the same to that of ERI (6.76 Å). The only SWY-type molecular sieve which has ever been reported is a SAPO-based molecular sieve STA-20.109 I synthesized several STA-20 samples, but they showed very high selectivities of heavy hydrocarbons (C₅, C₆, etc.) presumably due to the presence of impurity phases. Optimization of synthesis recipes is required.

The framework AVL is a 2-dimensional framework whose cage structure is essentially a hybrid of CHA and LEV.56 The MTO behaviors of SAPO-59 were already reported in the literature,40 but the data were collected at a different reaction temperature (350 °C). The cage-defining ring size of AVL (7.53 Å) is very close to those of Category I (7.45 Å). But at the same time, the diameter of maximum sphere that can be included in the cage is 7.14 Å which is smaller than that of CHA (7.37 Å). I expect that SAPO-59 having an AVL topology will show product distributions similar to that of SAPO-34 at 400 °C. But due to its low channel dimensionality, I also expect that it will show a much shorter lifetime than SAPO-34, just like SAPO-35.
Steaming of zeolites is another interesting topic from the point of view of the MTO product distributions. There is a scientific agreement that the steaming process dealuminates zeolites, particularly from paired aluminum sites.\textsuperscript{110} The Davis lab has made many efforts to investigate the effects of zeolite steaming having different topology types on the resultant MTO behaviors.\textsuperscript{48, 69, 106, 111} Low-silica CHA,\textsuperscript{111} RHO, and KFI zeolites\textsuperscript{106} synthesized without use of OSDAs and an AEI-type zeolite SSZ-39\textsuperscript{69} were steam-treated at high temperatures (> 600 °C) and their MTO behaviors were investigated. For most of these zeolites, there was no significant change in olefin product distributions, but their lifetimes were significantly improved due to the suppression of coke formation from paired aluminum sites.\textsuperscript{64}

I investigated the MTO behaviors of steamed SSZ-13 (CHA), SSZ-16 (AFX), SSZ-52 (SFW) and SSZ-98 (ERI) at the same reaction condition (steaming condition: 750 °C for 8 hours with a bubbler temperature of 80 °C; MTO reaction: 400 °C). The changes of MTO behaviors of steamed AFX-, SFW-, and ERI-type zeolites have not been reported in the
literature. The frameworks were preserved after steaming without degradation (Figure A10). The \(^{29}\)Si NMR spectra of these zeolites before and after steaming shown in Figure A11 support that the framework Si/Al\(_T\) ratios were significantly increased due to dealumination. After steaming, the amounts of penta-coordinated and octahedral extra-framework aluminum species were substantially increased. (Figure A12) The formation of extra-framework aluminum is commonly observed in other steamed zeolites.\(^{106, 111}\)

Finally, the MTO time-on-stream charts of these selected zeolites (before and after steaming) were demonstrated in Figure A13. After steaming, SSZ-13 retained its even-balanced ethylene-to-propylene ratio (~ 1). But interestingly, SSZ-98 of Category II and SSZ-16/SSZ-52 of Category I showed propylene-dominant product distributions which are corresponding to Category III-type topologies. These inter-categorical transitions were graphically summarized in Figure 4.3. I believe that this inter-categorical transition induced by steaming has something to do with the presence of secondary minor cages of ERI, AFX, and SFW frameworks; AFX and SFW have GME cages as minor cages, and ERI has smaller CAN cages. My hypothesis is that the steaming process of zeolites having minor cages results in an effective increase in cage-defining ring size. Extra-framework aluminum species can retreat into such small cages that are not MTO-active. The frameworks show no inter-categorical transitions such as CHA and AEI have no secondary cage-like units. I believe that further investigation of this inter-categorical transitions induced by steaming will deepen the understanding of the nature of the steaming process regarding the shape selectivity of the MTO reactions.