



CHAPTER IV

RESULTS AND DISCUSSION

4.1 Catalyst Characterizations

4.1.1 Catalyst Acidity and Acidic Strength

Table 4.1 summarizes the characterization of catalysts investigated, including the density of acid sites, which was determined from the integration of the TPD of absorbed ammonia. A clear trend was observed for the acidity of different proton form zeolites, which results from a different Si/Al ratio as follows: BEA > FAU > MFI, as well as WZ. As previously observed (Kubička *et al.*, 2004), the impregnation with Pt results in a loss of acid sites resulting from the interactions between platinum crystallites and acid sites.

Table 4.1 Acidity of catalysts

Sample	Total acidity ^a ($\mu\text{mol/g-cat}$)
Bare catalysts	
MFI	680
BEA	1617
FAU	1109
WZ	158
CBV400	2224
CBV720	1317
Pt supported catalysts	
Pt/MFI	630
Pt/BEA	1021
Pt/FAU	795
Pt/WZ	48
Pt/CBV400	1594
Pt/CBV720	944

^a Total acidity measured by TPD of NH_3

The profiles of temperature-programmed desorption of adsorbed ammonia over various fresh catalysts are shown in Figure 4.1. Different desorption peaks were observed on the TPD profiles at different temperature ranges. Peaks shown at low and high temperatures can be attributed to ammonia desorbed from weak and strong acid sites, respectively (Lónyi and Valyon, 2001). The desorption peak at 470 K represents the very weak acid sites, which are due to an octahedral Al ion formed by dealumination (Nakao, *et al.*, 2004). The desorption peak at about 650 K represents the acid site formed by Al in the zeolite lattice structure.

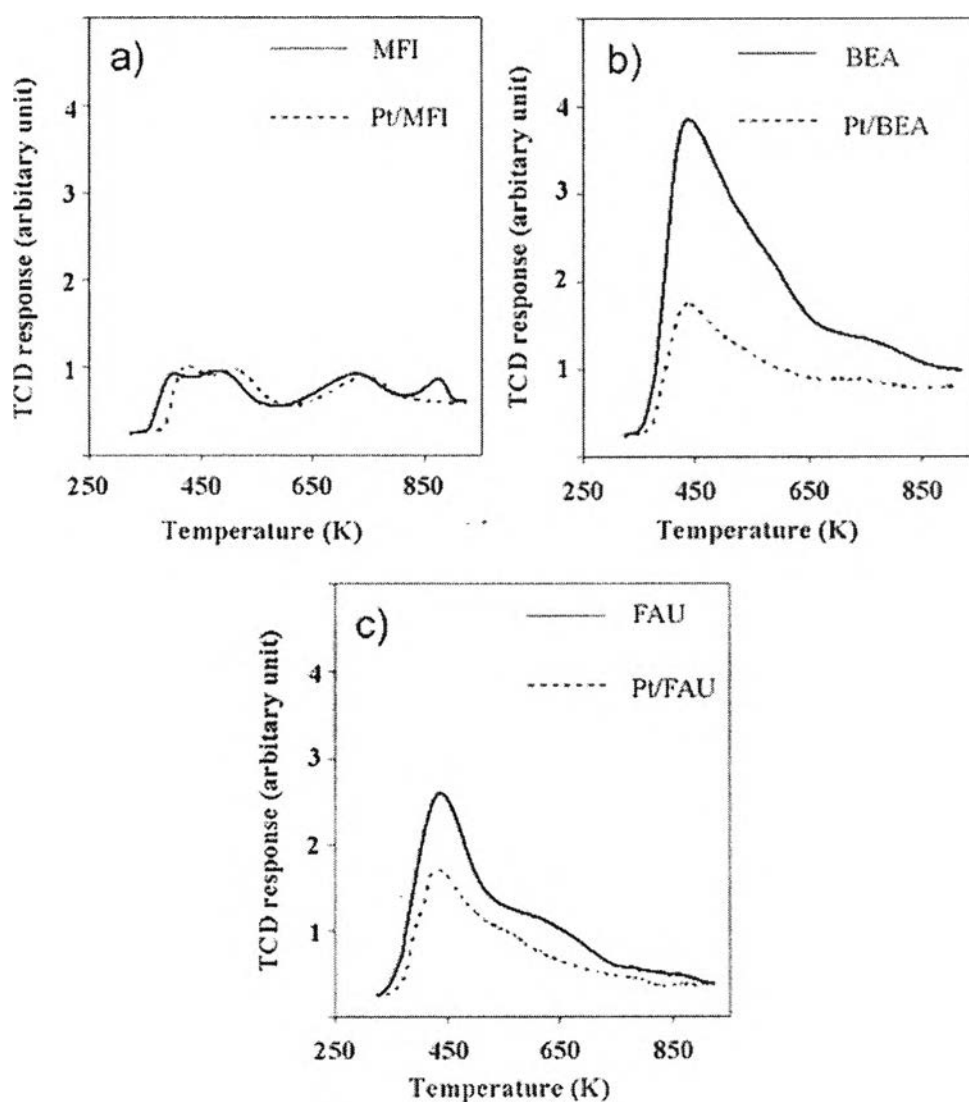


Figure 4.1 TPD profile of ammonia on (a) MFI (b) BEA, and (c) FAU zeolites.

In addition, the peak found at a higher temperature of about 800 K is assigned to strong acid sites, which result from the interaction between Al ions in framework and octahedral Al ions (Miyamoto *et al.*, 2000). Each temperature at the peak maximum corresponds to zeolite types, which depend on structure, and the peak area corresponds to the Si/Al molar ratio.

Tungsten oxide-based materials comprise another interesting class of solid acids (Barton *et al.*, 1999). The small and highly charged W^{+6} cations are found in several solid acids: heteropolyoxoanion compounds, such as 12-tungstophosphoric acid, oxygen-modified tungsten carbides, and WO_x dispersed on γ - Al_2O_3 and ZrO . Interestingly, WO_x dispersed on ZrO_2 (WO_x - ZrO_2), first reported to be superacids (Arata and Hino, 1990). These authors suggested, based on color changes by Hammett indicators, that acid sites stronger than 100% sulfuric acid may exist ($H_0 \leq 14.52$).

Among these catalysts, the acid strengths are in the order of WZ, MFI, BEA and FAU zeolites, while the number of acid sites is in the order of BEA, FAU and MFI zeolites corresponding with the Si/Al molar ratios of each zeolite and it is lowest in WZ. In addition, the TPD profiles of ammonia for Pt-containing catalysts gave the same order as proton form zeolites, which mean the impregnation of metal does not change the properties of the parent zeolites.

4.1.2 Structure of Surface W Species Determined by Raman Spectroscopy

Raman spectroscopy, in this work, was used to characterize the types of bonds formed on the zirconia surface. The Raman spectra taken under ambient condition for bare and Pt supported WZ are shown in Figure 4.2. The spectra of catalysts were observed in the 100-1200 cm^{-1} region. A band at 647 cm^{-1} is characteristic of tetragonal zirconia can be observed in both samples. We did not observe a band at ca. 600 cm^{-1} assigned to monoclinic zirconia. Bands ranged in between 170-180 cm^{-1} associated to crystalline WO_3 species on the surface. A band at about 810 cm^{-1} attributed to W-O-W stretching modes and the higher frequency bands at ca. 1000 cm^{-1} assigned to W=O stretching modes that unequivocally indicated the presence of hydrated interconnecting polyoxotungstate (Scheithauer *et al.*, 1998). These polyoxotungstate clusters spread on the surface of tetragonal

zirconia have been generally associated with the formation of acid sites displaying high catalytic activity for acid-catalyzed reactions. Pt supported WZ revealed a little shift of a band at ca. 1000 cm^{-1} and its higher intensity.

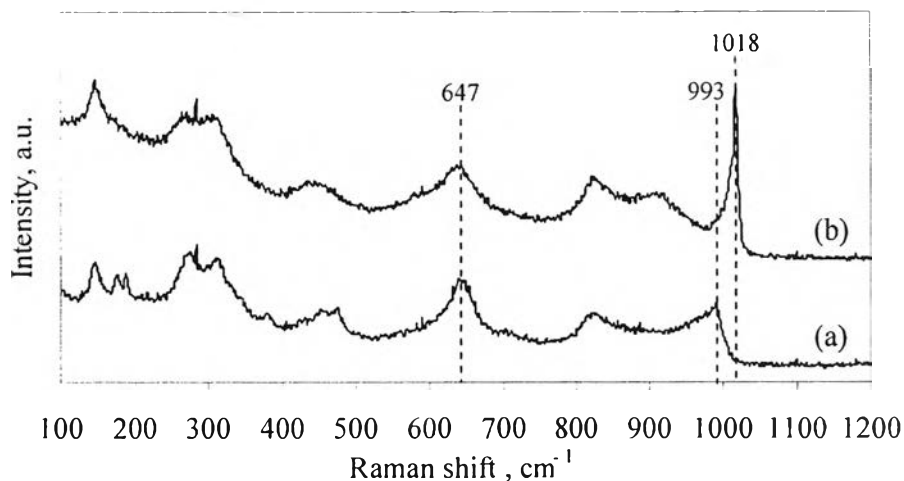


Figure 4.2 Raman spectra of bare (a) and Pt supported (b) WZ.

4.2 Catalytic Activity Measurements

The products derived from isomerization and ring opening reactions with a trace dehydrogenation reaction of MCH were classified into 4 families. The first is monobranched (ethylcyclopentane; ECP) and dibranched (dimethylcyclopentanes; DMCPs) cycloalkanes, denoted as ring-contraction products (RC). The second is monobranched (e.g. 3-methylhexane) and multibranched (e.g. 2,4-dimethylpentane) alkanes with 7 carbon atoms, noted as ring opening products (RO). The third is aliphatic and alicyclic compounds with less than 7 carbon atoms, known as cracking products (CR). The last is dehydrogenation products, which are called heavy products (HP) (Appendix A). However, under the mild reaction conditions (i.e. high pressure and low temperature) and the high molar ratio of H_2/feed , in addition to RC, the remains (CR, RO, and HP) were found in insignificant amount.

Over bare and Pt-supported zeolites, cracks were observed in a traced amount. Hence, the small deactivation has been seen. Unlike zeolites, 5 to 10% of

cracks, and also deactivation were found over bare WZ (Appendix B). Besides, the presence of Pt revealed the enhancement of MCH conversion over all kinds of catalysts (Appendix C).

4.3 Selectivity of MCH Ring-Contraction Isomers over Bare Acidic Catalysts

The difference in selectivity to the individual RC isomers on acidic catalysts can be assigned to the difference in the acidic strength and pore geometry (sizes and structures) of catalysts, as well as the residence time of the intermediates. It is interesting to investigate the effects of these parameters on the RC isomers, which are the primary and major products at these reaction conditions. The equilibrium mixture of RC isomers is shown in Figure 4.3.

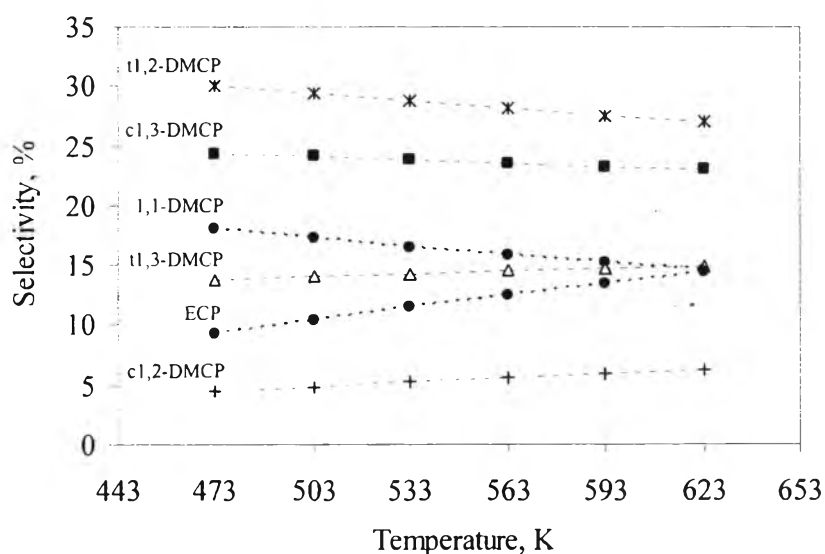


Figure 4.3 RC products selectivity as a function of temperature. The composition at thermodynamic equilibrium was simulated by using SimSci PRO/II PROVISION. Reaction conditions: Total pressure = 2 MPa; H_2 /feed molar ratio = 40.

Obviously, the selectivity to *cis*-1,2-dimethylcyclopentane was the lowest due to the most steric hindrance, the two methyl groups at the same side. The RC isomers found in this study consist of ethylcyclopentane, 1,1-dimethylcyclopentane,

cis-1,3-dimethylcyclopentane, *trans*-1,3-dimethylcyclopentanes, and *trans*-1,2-dimethylcyclopentane, but *cis*-1,2-dimethylcyclopentane.

The acid-catalyzed branching isomerization of alicyclic hydrocarbon compounds on solid acids is generally rationalized by the formation of protonated cyclopropane intermediates after the formation of a carbenium ion (Martens *et al.*, 1997) and each branching isomer (RC) requires the formation of carbocation at different positions as shown in Figure 2.4. The monobranched ECP is formed via the rearrangement of a tertiary transition state (intermediate A), which is the most stable transition state, involving the internal alkyl shifts, in which the three C-atoms of the cycloproponium intermediates are involved (Martens *et al.*, 2001). High yield of ECP (high selectivity) is due to the easiest formation of this type of an intermediate on the weak acid sites. In addition, the shortening of the residence time will even increase the formation of ECP, resulting in high selectivity to ECP at low conversions (small reactor sizes). Unlike ECP, the dibranched DMCPs are preceded via corner-protonated cyclopropane (CPCP) intermediates (B, C, and D) (Martens *et al.*, 2001), which have a less stable transition state and require a strong Brønsted acid site (McVicker *et al.*, 2005). These types of intermediates are least favored. Therefore, the formation of ECP is faster than the formation of DMCPs, and ECP can be produced on the weaker acid sites.

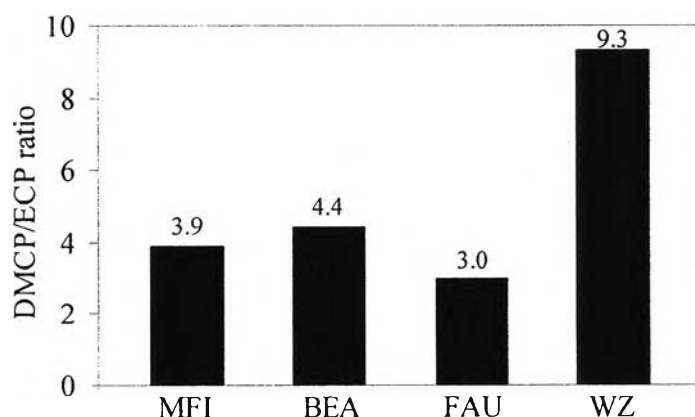


Figure 4.4 The DMCPs/ECP ratio over MFI, BEA, FAU zeolites and WZ at the same conversion (~3%).

In other words, the formation of DMCPs needs stronger acid sites or a longer surface residence time than an ECP, especially 1,3-DMCP isomers (Belatal *et al.*, 2004). Consequently, the acid strength can be relatively compared by the DMCPs/ECP ratio.

As shown in Figure 4.4, the ratio on FAU zeolite (3.0) is less than that of the BEA (4.4) and MFI (3.9) zeolites resulting from the relatively weak acid sites of the FAU zeolite. The strongest acid sites, obviously, goes to WZ (9.3).

The selectivity to individual RC isomers as a function of the MCH conversion were plotted in Figures 4.5 (for MFI), 4.6 (for BEA), 4.7 (for FAU), and 4.8 (for WZ). Also, the selectivity to individual RC isomers as a function of W/F for all kinds of catalysts was shown in Appendix C.

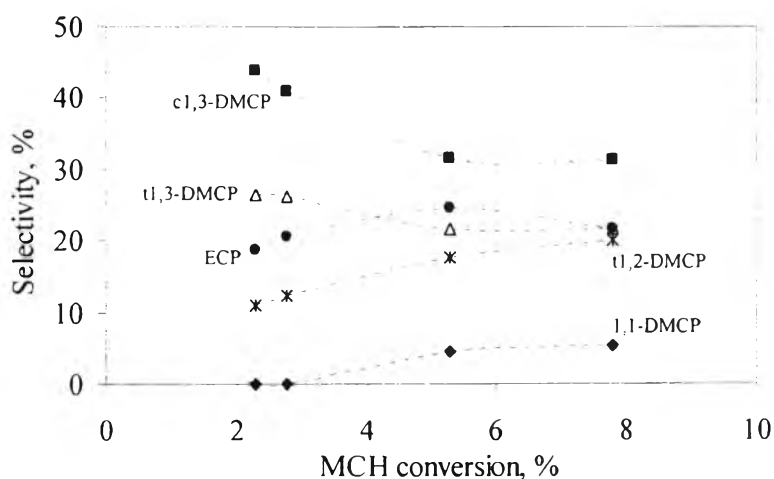


Figure 4.5 Selectivity to RC products vs. MCH conversion over MFI zeolite at different space velocities. Reaction conditions: Total pressure = 2 MPa; Temperature = 533 K; H_2 /feed molar ratio = 40.

For strong acid strength zeolites (MFI and BEA), the selectivity to 1,3-dimethylcyclopentane isomers (*cis*-1,3-DMCP and *trans*-1,3-DMCP) are higher than that to *trans*-1,2-dimethylcyclopentane (*trans*-1,2-DMCP) at all conversion ranges. But for WZ, the strongest acid catalyst, the selectivity to 1,3-DMCPs is high at low conversion, and at higher conversion (>30%), the selectivity is dominated by *trans*-1,2-DMCP which is more thermodynamically preferential (Figure 4.3). Unlike these

strong acidic catalysts, the selectivity to ECP on FAU zeolite (~25%, Figure 4.7) is very high at low conversions and this value is higher than that on MFI and BEA (~19%, Figures 4.5 and 4.6), as well as WZ (~10%, Figure 4.8).

From Appendix C, considering at the same W/F (0.5h), MCH conversion over MFI was the lowest (~5%), whereas theirs of others are higher (~23% for BEA, ~22% for FAU, ~23% for WZ). It can be ascribed that the reaction might take place only the outside surface not inside the pores of MFI due to its pore restriction (see Appendix D)

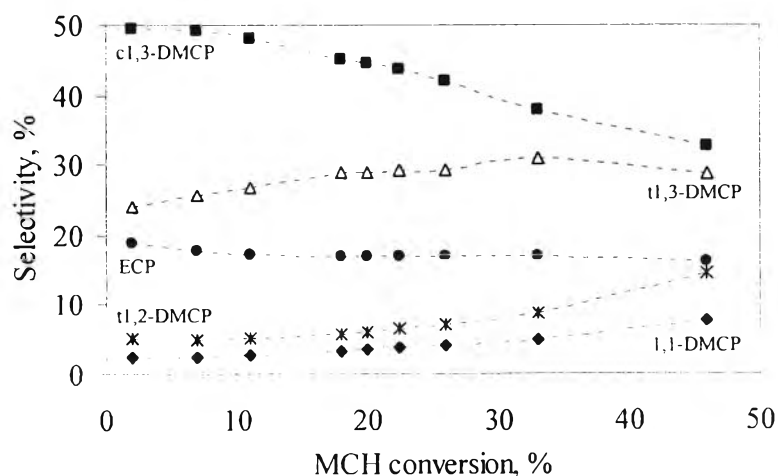


Figure 4.6 Selectivity to RC products vs. MCH conversion over BEA zeolite at different space velocities. Reaction conditions: Total pressure = 2 MPa; Temperature = 533 K; H_2 /feed molar ratio = 40.

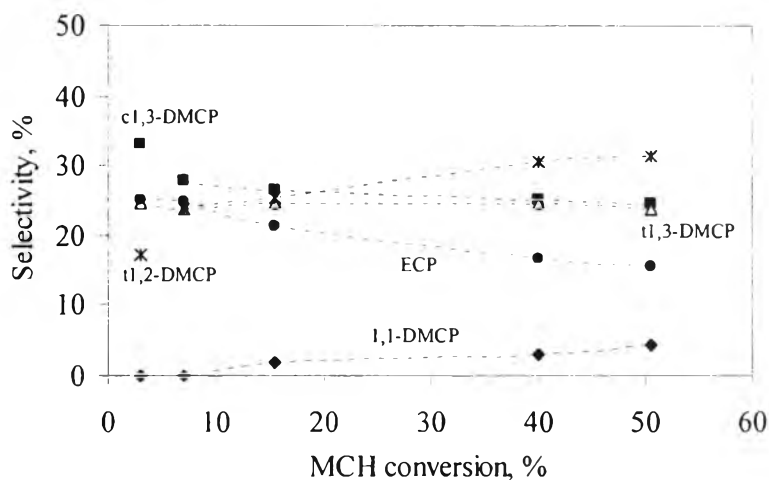


Figure 4.7 Selectivity to RC products vs. MCH conversion over FAU zeolite at different space velocities. Reaction conditions: Total pressure = 2 MPa; Temperature = 533 K; H_2 /feed molar ratio = 40.

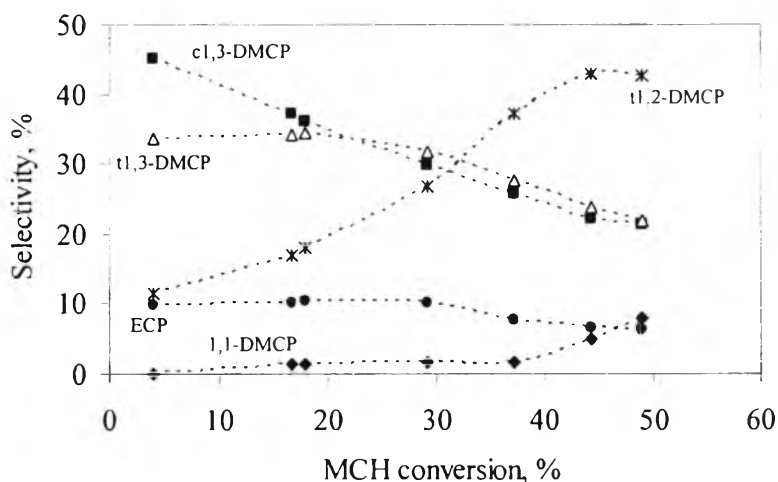


Figure 4.8 Selectivity to RC products vs. MCH conversion over WZ zeolite at different space velocities. Reaction conditions: Total pressure = 2 MPa; Temperature = 533 K; H_2 /feed molar ratio = 40.

Shape selectivity speaking, the bulkiest *trans*-1,2-DMCP exhibits the most difficulty for transport in the channels or pore mouth with a high constraint. When considering the selectivity of 1,2-DMCP over large pore size (BEA and FAU

zeolites), the selectivity to *trans*-1,2-DMCP on the FAU zeolite is higher than that on the BEA zeolite. The smaller in the selectivity to *trans*-1,2-DMCP on the BEA zeolite was ascribed to the pore size restriction. Even though both FAU and BEA are 12-ring zeolites, the FAU zeolite contains the supercages. In addition, the selectivity to *trans*-1,2-DMCP on amorphous WZ which has a plenty of space for reactions can reach up to ~40%. Interestingly, The formation of both *trans*-1,2-DMCP and 1,1-DMCP requires the same intermediate (B in Figure 2.4), but all of these acidic catalysts give the lowest selectivity toward 1,1-DMCP over all conversion ranges. This infers that there should be another effect that plays an important role for this intermediate. A similar situation was found on the isomerization of *n*-hexane over highly acidic WO_x/ZrO_2 -based catalysts by Santiesteban *et al.* (2001). They found that the 2,2-dimethylbutane isomer was not formed on this acidic catalyst due to the high kinetic barrier associated with the intermolecular hydride transfer to the sterically-hindered intermediate (i.e., 2,2-dimethyl-3-butyl cation). Therefore, if the same situation occurs on the isomerization of MCH, it would be due to the suppression of the intermolecular hydride transfer of 2,2-dimethylcyclopent-1-yl cation with an electroneutral molecule (Santiesteban *et al.* 2001). This effect will be discussed later. In the case of *cis*- and *trans*-1,3-DMCPs, the selectivity to *cis*-1,3-DMCP is clearly higher than that to *trans*-1,3-DMCP over MFI and BEA zeolites, while they are close together over FAU zeolites and WZ. This can be explained by the means of transformation from cycloproponium intermediates to *cis*- and *trans*-1,3-DMCPs. To achieve *cis*-1,3-DMCP, flat surfaces (i.e., restricted areas) are required in order to allow both methyl groups faced away from the surface and shown up at the same side. Unlike *cis*-1,3-DMCP, *trans*-1,3-DMCP was hard to sit on the surface due to the 2 branches with the opposite sides. They might be a barrier for intermolecular hydride transfer step. The selectivity to *trans*-1,3-DMCP is, therefore, less favorable. In contrast, the possibilities to obtain *cis*- and *trans*-1,3-DMCPs are relatively equal to each other for the catalysts with huge reaction spaces (i.e., supercages and amorphous structures).

4.4 Effect of Metal (Pt) on the Selectivity to RC Isomers over Acidic Catalysts

As discussed above, the low amount of 1,1-DMCP found on bare acidic catalysts may be due to the limitation of the hydride/hydrogen transfer. Thus, to elucidate the effect of metal (Pt) on a hydride transfer step, the MCH reaction was performed over the Pt supported on the acidic catalysts (MFI, BEA, FAU zeolites, and WZ) under the same reaction conditions. The Pt loading on supports was constant at 1 wt% in this study. This value was found to be good enough for the isomerization activity for n-heptane (Pope *et al.*, 2002). On these Pt catalysts, RC products are the dominant products with a selectivity > 95% at a reaction temperature of 533 K. The results obviously showed that the selectivity to the RC isomers over the Pt catalysts (Figures 4.9, 4.10, 4.11, and 4.12) differs from the selectivity to the RC isomers over the bare zeolites (Figures 4.5, 4.6, 4.7, and 4.8). These results suggest that Pt metals have an influence on the product distribution of RC isomers.

A significant difference was the selectivity to ECP. For all kinds of the Pt supported zeolites, higher selectivity to ECP was found at low conversion. It then decreased as the conversion increased, while that to the dibranched isomers (DMCPs) increased. This trend may be explained considering that, at low conversion, ECP is easily formed via the internal alkyl shifts (Martens *et al.*, 2001) and desorbs right away from the surface. Unlike zeolites, the selectivity to ECP is low on Pt/WZ. In addition, for all acidic catalysts, the increase in the selectivity to the thermodynamically favored DMCP isomers observed at higher space times may be due to a stepwise isomerization (Mignard *et al.*, 1994).

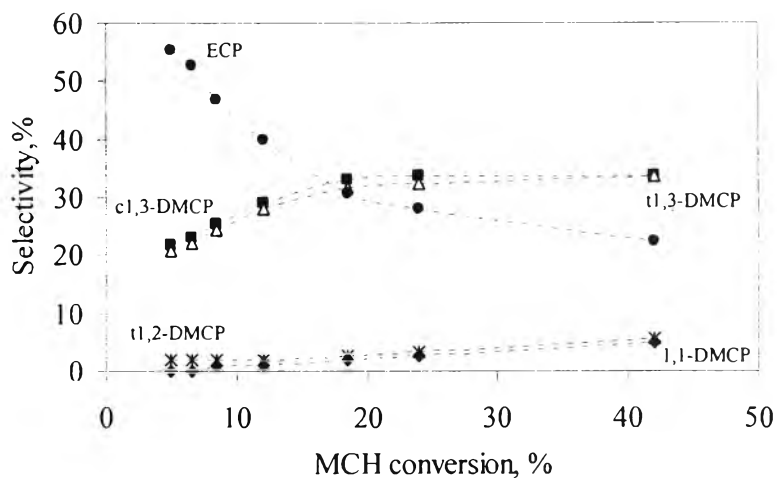


Figure 4.9 Selectivity to RC products vs. MCH conversion over Pt/MFI catalyst at different space velocities. Reaction conditions: Total pressure = 2 MPa; Temperature = 533 K; H_2 /feed molar ratio = 40.

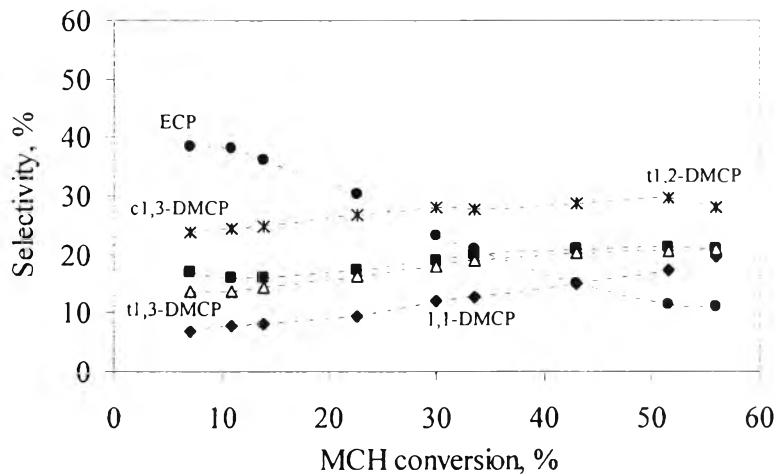


Figure 4.10 Selectivity to RC products vs. MCH conversion over Pt/BEA catalyst at different space velocities. Reaction conditions: Total pressure = 2 MPa; Temperature = 533 K; H_2 /feed molar ratio = 40.

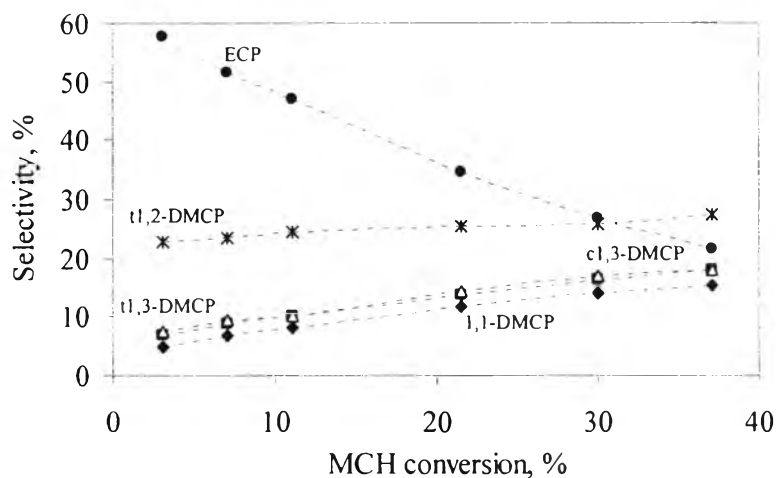


Figure 4.11 Selectivity to RC products vs. MCH conversion over Pt/FAU catalyst at different space velocities. Reaction conditions: Total pressure = 2 MPa; Temperature = 533 K; H_2 /feed molar ratio = 40.

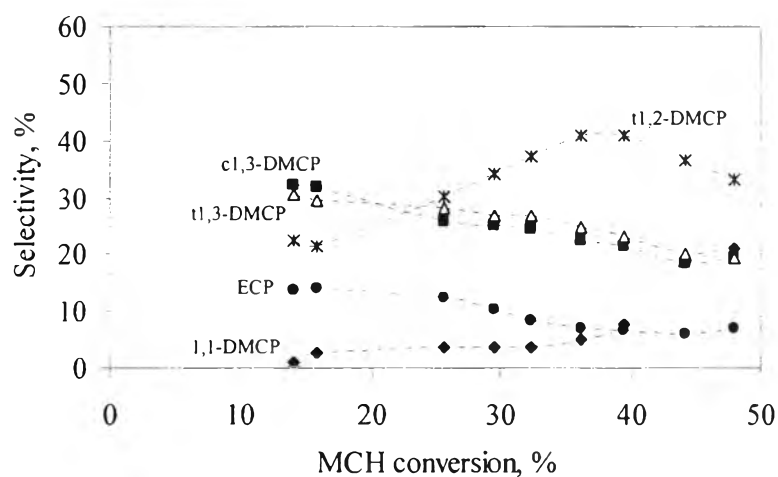


Figure 4.12 Selectivity to RC products vs. MCH conversion over Pt/WZ catalyst at different space velocities. Reaction conditions: Total pressure = 2 MPa; Temperature = 533 K; H_2 /feed molar ratio = 40.

In the case of 1,1-DMCP resulting from a bulky 2,2-dimethylcyclopent-1-yl cation intermediate, its selectivity was found in larger amounts over Pt/BEA, Pt/FAU, and Pt/WZ but not over Pt supported on medium pore (Pt/MFI) when compared to the corresponding bare zeolites. The hydride transfer from an

electroneutral RH molecule is sterically unfavorable and one can expect this step to be slow, which result in the very low production of 1,1-DMCP. However, the absolute amount of 1,1-DMCP over Pt/MFI was higher than that over MFI. A similar situation was reported by Santiesteban *et al.* (2001) investigated that the isomerization of n-hexane on highly acidic WO_x/ZrO_2 -based catalysts and found that the 2,2-dimethylbutane isomer was not formed in the absence of Pt, but it was produced in significant amounts when Pt was added to the catalyst. They suggested that the presence of Pt gives rise to a high concentration of atomic hydrogen on the surface, enough to overcome the high kinetic barrier associated with the intermolecular hydride transfer to the sterically-hindered intermediate (i.e., 2,2-dimethyl-3-butyl cation).

When comparing the selectivity to *trans*-1,2-DMCP (the bulkiest RC isomer) over MFI (Figure 4.5) and Pt/MFI (Figure 4.9), the selectivities to these compounds over both catalysts are about the same. The presence of Pt does not enhance the formation of the *trans*-1,2-DMCP isomer due to a shape selectivity effect of this support (a 10 member-ring medium-pore structure; MFI). Unlike MFI zeolite, the selectivity to the *trans*-1,2-DMCP isomer are different over the large pore zeolites with Pt (Pt/BEA; Figure 4.10 and Pt/FAU; Figure 4.11) and without Pt (BEA; Figure 4.6 and FAU; Figure 4.7). On the Pt/BEA and Pt/FAU catalysts, the selectivity to *trans*-1,2-DMCP was the highest, but this value was very low on the MFI zeolite and WZ. This confirms that the presence of Pt plays an important role in the hydrogen transfer step on the zeolites, but WZ. However, on Pt/MFI, the hydrogen transfer rate is higher than bare MFI since MCH conversion and the selectivity to ECP is still high, but this effect may be suppressed on the selectivity to *trans*-1,2-DMCP due to the shape restriction.

As mentioned above, the enhancement of the formation of ECP, *trans*-1,2-DMCP, and 1,1-DMCP over the Pt supported catalysts should be derived from the enhancement of the hydrogen transfer step, which results in decreasing surface residence time of the intermediates (Iglesia *et al.*, 1993). On an acidic catalysts, the desorption of an intermediate (alkylcarbenium ions) on the surface to form RC isomers occurs by a bimolecular hydride transfer with the electroneutral molecules, mostly reactant. In this case, the hydride transfer step is slow, and it results in the

slow desorption of intermediate transition states. On Pt catalysts, Pt metals are very active for the hydrogenation/dehydrogenation reaction that would accelerate the desorption rate, which decreases the lifetime for the intermediate. These lead to the difference in the distribution of RC isomers. In addition, Santiesteban *et al.* (2001) suggested the new pathways in the hydride transfer reaction step for the isomerization reaction for *n*-hexane over the Pt supported catalysts. Pt metals activate hydrogen (H₂) to form a large amount of hydrogen atoms on the surface, and these hydrogen atoms accelerate the hydride transfer rate resulting in decreasing surface residence time. Thus, 1,1-DMCP is merely found because of a high kinetic barrier of 2,2-dimethylcyclopent-1-yl cation in the bimolecular hydride transfer step with an electroneutral molecule. However, unlike zeolites, the selectivity patterns of MCH isomers over bare and Pt promoted WZ are similar. Therefore, it can be suggested that the hydride transfer step does not play an important role over WZ based catalysts.

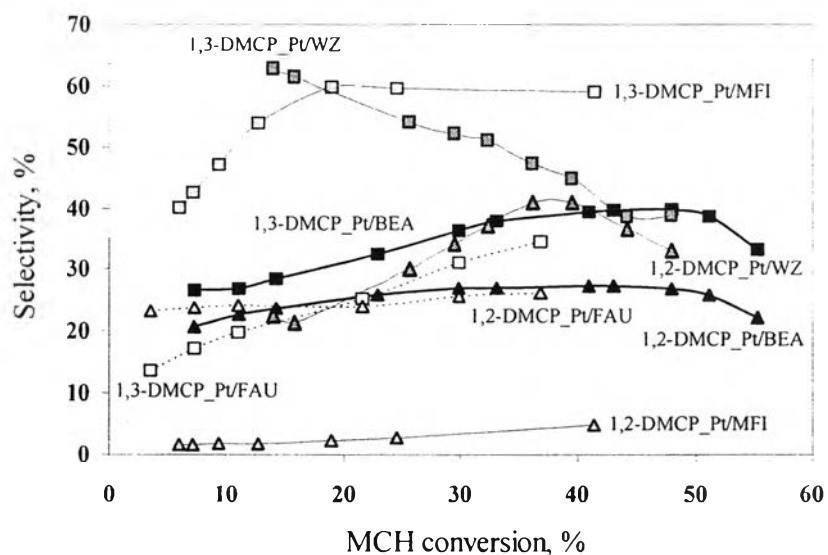


Figure 4.13 Selectivity to 1,2- and 1,3-DMCP (%) plotted vs. MCH conversion (%) over Pt supported catalysts at 2 MPa and 533 K.

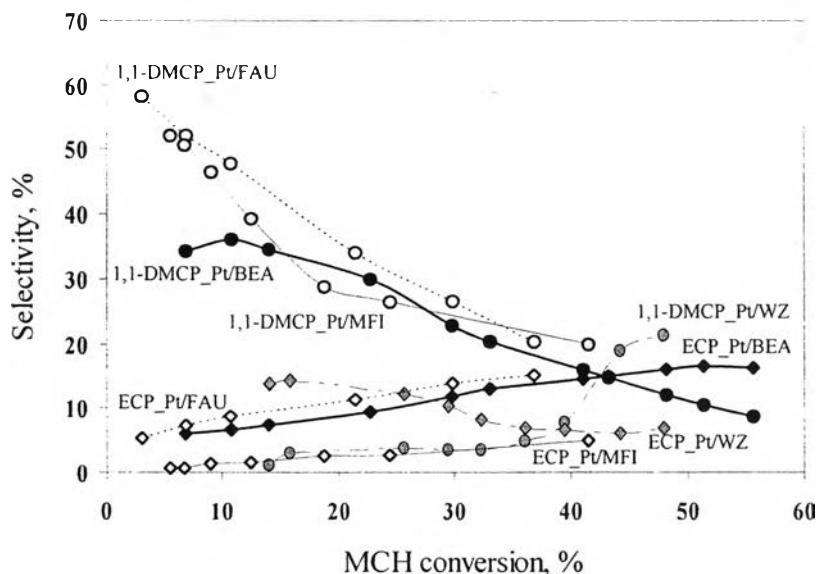


Figure 4.14 Selectivity to ECP and 1,1-DMCP (%) plotted vs. MCH conversion (%) over Pt supported catalysts at 2 MPa and 533 K.

To clearly understand the influences on the formation of RC isomers, the selectivities of RC isomers over Pt-supported catalysts were plotted together in Figures 4.13 and 4.14. Among the Pt supported catalysts, at low conversion, the selectivity to 1,3-DMCP decreases in the order of Pt/WZ > Pt/MFI > Pt/BEA > Pt/FAU as following the acidic strength. As explained, the formation of 1,3-DMCP requires a stronger acidic strength than that of ECP. However, the selectivity to ECP is slightly different due to the ease of its formation and the fast desorption rate of the intermediate. The presence of Pt significantly enhances the formation of 1,1-DMCP, the most sterically hindered carbenium ion intermediate, except on Pt/MFI (due to the shape selectivity effect) and Pt/WZ (due to less effective hydrogen transfer step). As stated above, Pt metal provides a large amount of surface hydrogen atoms, which readily undergo the hydride transfer with the carbenium ions. In the case of the formation of 1,2-DMCP, Pt metal increases the desorption rate of the carbenium ion intermediate and the isomerization reaction. However, the formation of *trans*-1,2-DMCP does not increase on Pt/MFI or MFI alone due to shape selectivity. A *trans*-1,2-DMCP shows the highest difficulty for the diffusion in channels or on pore mouths of the most restricted structure, due to its bulkiest structure.

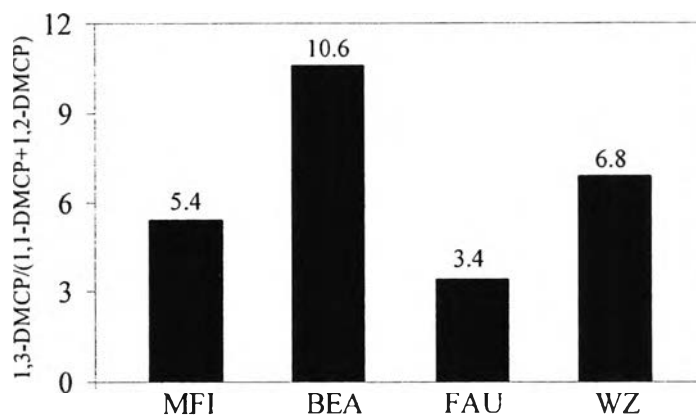


Figure 4.15 The 1,3-DMCP/(1,2-DMCP+1,1-DMCP) ratio over MFI, BEA, FAU zeolites and WZ at the same conversion (~3%).

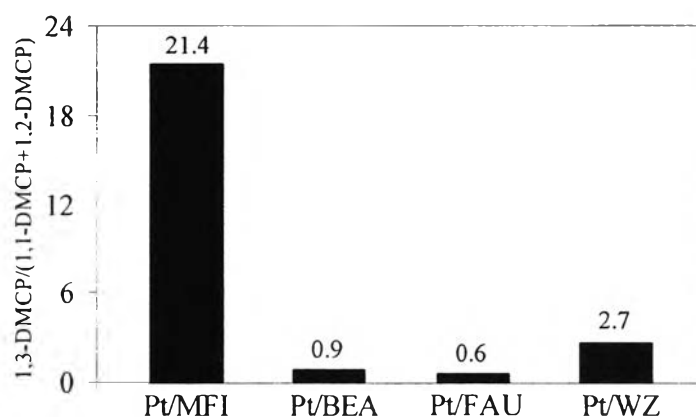


Figure 4.16 The 1,3-DMCP/(1,1-DMCP+1,2-DMCP) ratio over Pt supported catalysts at the same conversion (~13%).

Figures 4.15 and 4.16 show the huge difference on the ratio of 1,3-DMCP and the sum of 1,1-DMCP and 1,2-DMCP over bare and Pt supported acidic catalysts. For large pore zeolites (BEA, FAU, Pt/BEA and Pt/FAU) and amorphous WZ with a minor or no shape selectivity effect, the 1,3-DMCP/(1,1-DMCP+1,2-DMCP) ratios on Pt catalysts are lower than that on zeolites alone due to the increase in bulky (1,2-DMCP) and less kinetically favored (1,1-DMCP) molecules. This result confirms that Pt metal enhances the ability of hydrogen transfer. In contrast, for

Pt/MFI, this ratio is dramatically high due to the difficulty of the transportation inside the small pores or shape selectivity effect.

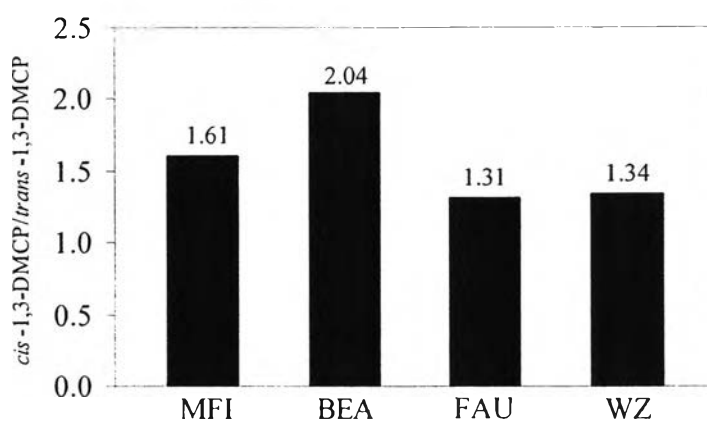


Figure 4.17 The *cis*-1,3-DMCP/*trans*-1,3-DMCP ratio over MFI, BEA, FAU zeolites and WZ at the same conversion (~3%).

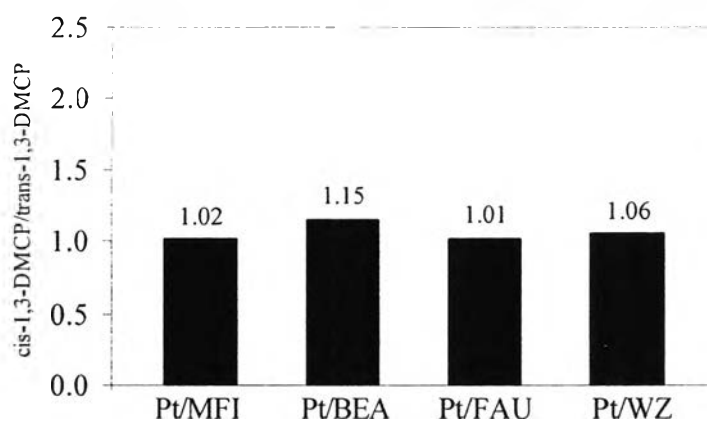


Figure 4.18 The *cis*-1,3-DMCP/*trans*-1,3-DMCP ratio over Pt supported catalysts at the same conversion (~13%).

An interesting change in the *cis*/*trans*-1,3-DMCP ratio was observed in the product between bare (Figure 4.17) and Pt supported (Figure 4.18) acidic catalysts. This ratio was significantly decreased on Pt supported catalysts. This result may be due to both *cis*-to-*trans* isomerization and the enhancement of hydrogen transfer. The

formation of *cis*-1,3-DMCP is easier than that of *trans*-1,3-DMCP due to its conformation. The methyl groups are both in the equatorial type positions.

4.5 Effect of Acid Density on the Selectivity to RC Isomers over CBV400 and CBV720 Zeolites with and without Pt Metal

Both CBV400 (Si/Al = 2.5) and CBV720 (Si/Al = 30) zeolites were used to study the effect of acid density on the MCH isomerization. The conversion of MCH and product distribution was shown in Appendix A. The conversion showed the order CBV400 > CBV720 and Pt/CBV400 > Pt/CBV720, which is the same order of the acid density. The main products are RC isomers. The selectivity to RC isomers for the MCH reaction over Pt free catalysts is shown in Figures 4.19 and 4.20. Both catalysts show a slightly different selectivity to RC isomers. This implies that the acid density has a little effect on isomerization if there are no other effects involved (i.e., shape selectivity). In addition, the selectivity to RC isomers for the MCH reaction on the Pt supported catalysts is presented in Figures 4.21 and 4.22. There is no change in the selectivity to RC isomers, which suggests the enhancement of isomerization.

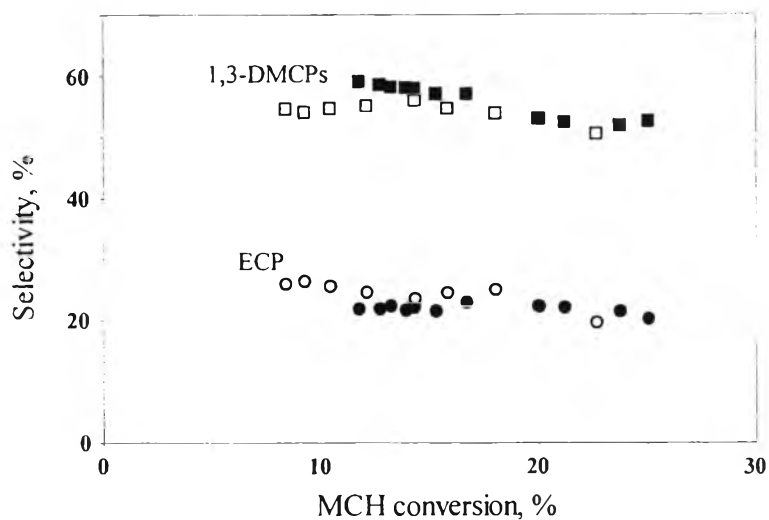


Figure 4.19 Selectivity to RC products (%) plotted vs. MCH conversion (%) over CBV400 (■ 1,3-DMCPs, ● ECP) and CBV720 (□ 1,3-DMCPs, ○ ECP) at 2 MPa and 533 K.

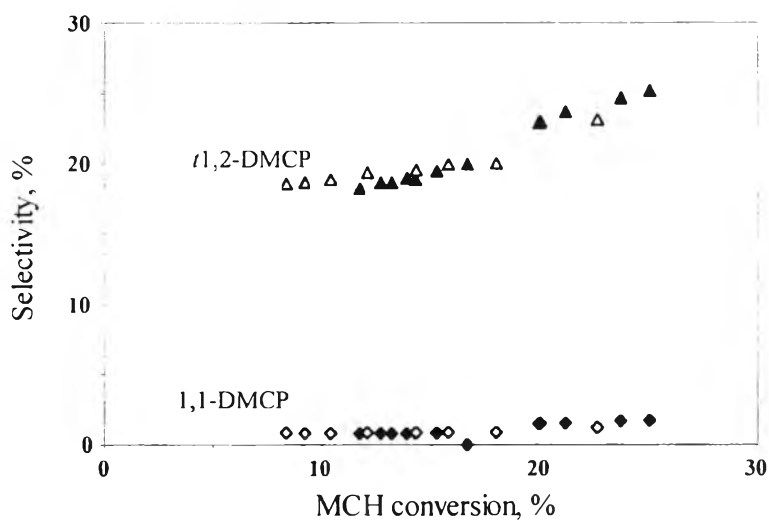


Figure 4.20 Selectivity to RC products (%) plotted vs. MCH conversion (%) over CBV400 (▲ *trans*-1,2-DMCP, ◆ 1,1-DMCP) and CBV720 (△ *trans*-1,2-DMCP, ◇ 1,1-DMCP) at 2 MPa and 533 K.

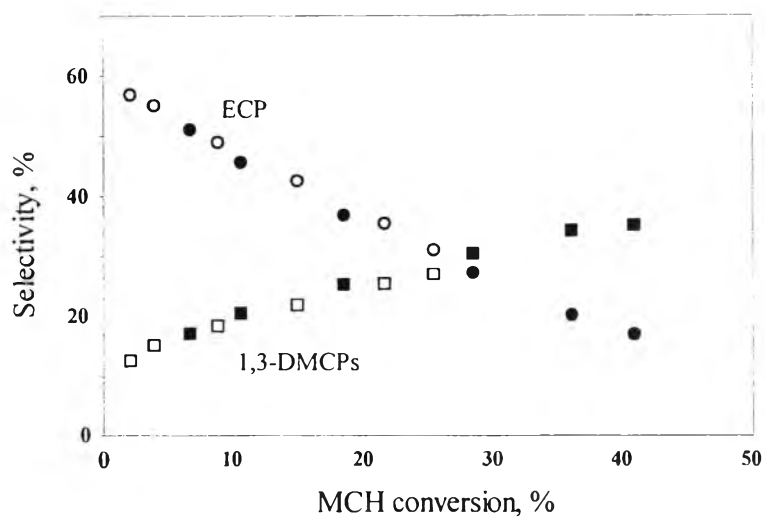


Figure 4.21 Selectivity to RC products (%) plotted vs. MCH conversion (%) over Pt/CBV400 (■ 1,3-DMCPs, ● ECP) and Pt/CBV720 (□ 1,3-DMCPs, ○ ECP) at 2 MPa and 533 K.

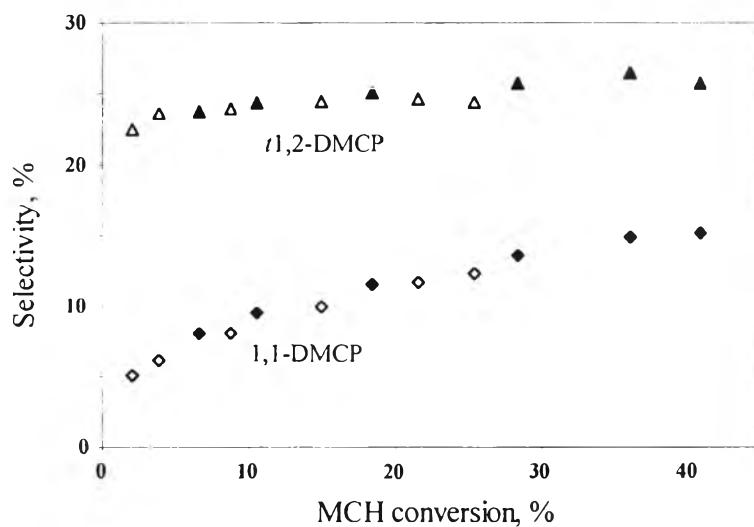


Figure 4.22 Selectivity to RC products (%) plotted vs. MCH conversion (%) over Pt/CBV400 (▲ *trans*-1,2-DMCP, ◆ 1,1-DMCP) and Pt/CBV720 (△ *trans*-1,2-DMCP, ◇ 1,1-DMCP) at 2 MPa and 533 K.