CHAPTER VII
OXIDATIVE DEHYDROGENATION OF PROPANE OVER VS-1 ZEOLITE SYNTHESIZED FROM SILATRANE

7.1 Abstract

The catalytic properties of VS-1 zeolite, synthesized from silatrane precursor, for oxidative dehydrogenation of propane have been studied. Propane conversion increases with an increase in vanadium content, while selectivity slightly decreases. Temperature strongly affects both conversion and selectivity. Selectivity decreases with increasing temperature due to free radical formation at high temperature. Interestingly, use of a high concentration of sodium in the VS-1 synthesis, which results in lower structural incorporation of vanadium, produces higher conversion and higher selectivity. Tetrahedral vanadium within the zeolite crystal structure is believed to be responsible for selective oxidative dehydrogenation, whereas extrinsic vanadium or polymeric species are responsible for over oxidation, selectively giving high carbon monoxide and carbon dioxide. Balancing the space velocity versus the propane/oxygen ratio provides a compromise of good selectivity with adequate conversion. Shorter contact time gives higher product yield and conversion though lower in selectivity.

7.2 Introduction

The high demand for olefins and the low olefin content of natural gas have stimulated much research aimed at enhancing the dehydrogenation reaction of paraffin. However, this reaction is highly endothermic. Thus, it is usually performed at temperatures exceeding 600°C, causing many unfavorable side-reactions, such as, a high yield of coke and smaller hydrocarbon molecules. Oxidative dehydrogenation (ODH) is a thermodynamically favorable alternative method to avoid high temperature reaction. While ODH seems to be a promising route, it is difficult to prevent total oxidation to carbon monoxide and carbon dioxide. A variety of different catalysts, such as, metal oxide on various oxide supports, have been tested over the past two decades. Among the catalyst systems studied, vanadium has great versatility in oxidative reactions of organic compounds, as reviewed by Swierkosz [1]. It is well known that the catalyst support strongly affects the catalytic behavior of the vanadium site [2]. In addition, a number of other factors influence the catalytic behavior, such as, the structure and dispersion of metal oxide on the support. It has been proposed that the distance between vanadium sites influences the selectivity of ODH [3] by increasing the possibility of over oxidation by near-neighbor active sites.

Microporous and mesoporous materials with reactive centers of redox metal catalyst are a potential candidate for converting propane to propene via selective oxidation. Vanadium on various types of porous zeolites, including MCM41 [4], FAU [5], MFI [6-7] have been studied. Different methods have been used for incorporating vanadium into the zeolite structure. These can be divided into two main approaches, viz. post-synthesis modification, e.g. via solid state reaction [8-9], chemical vapor deposition [10] or wet-impregnation methods [11], and hydrothermal synthesis [12-14], which gives a higher probability to obtain isolated V species in the framework [15], and involves fewer synthesis steps.

Using the novel precursor silatrane, VS-1 zeolite was successfully synthesized and investigated to find optimal formulation conditions in our previous work [16]. In this paper, the catalytic activity and selectivity of VS-1 zeolite in the oxidative dehyrogenation of propane, is studied, in terms of the effect of synthetic formulation, namely, vanadium concentration, sodium hydroxide concentration and effect of intrinsic and extrinsic vanadium. The operating conditions, such as space velocity and temperature, have also been taken into account.

7.3 Experimental

Materials

Fumed silica (SiO_2) with 99.8% silica content was supplied from Sigma Chemical. Triethanolamine (TEA, $N[CH_2CH_2OH]_3$) was supplied by Carlo Erba reagenti. Ethylene glycol (EG), as reaction solvent, was obtained from J.T. Baker. Vanadium (III) chloride, 99%, was supplied by ACROS Organics. Sodium hydroxide (NaOH) was purchased from EKA Chemicals. Tetra-propyl ammonium bromide (TPA) was obtained from Fluka Chemical AG. All chemicals were used as received. Acetonitrile (CH_3CN) was obtained from Lab-Scan Co., Ltd. and distilled using standard purification methods prior to use.

Instrumentation

FTIR spectroscopic analysis was conducted on a Bruker Instrument spectrometer (EQUINOX55) with a resolution of 2 cm^{-1} to measure the functional groups of materials. The solid samples were mixed and pelletized with dried KBr. Thermal properties and stability were analyzed on a Perkin Elmer TGA7 analyzer at a scanning rate of 10 K/min under nitrogen atmosphere from 303 to 1023 K and hold at 1023 K for 10 min under oxygen atmosphere. Thermogravimetric/ differential thermal analyzer was conducted on Perkin Elmer Pyris Diamond TG/DTA. The crystal morphology was studied using a JEOL 5200-2AE scanning electron microscope. UV-visible measurements were performed on Shimadzu UV-2550 with the ISR-2200 Integrating sphere attachment, and $BaSO_4$ was used as reference sample. Crystal structure was characterized using a Rigaku X-Ray Diffractometer at a scanning speed of 5 degree/sec, with CuKα line as incident radiation and a filter. The working range was 3-50 theta/2theta, with 1 degree and 0.3 mm setting of divergence for the scattering and receiving slits, respectively. Reduction of VS-1 was performed on Thermo Finnigan TPDRO 1100 with 20 ml/min of 5.32% hydrogen in nitrogen at 10 K/min. Hydrothermal treatment by microwave heating technique was conducted using MSP1000, CME cooperation (Spec 1,000 W and 2450 MHz). Samples were heated in a Teflon tube, using the inorganic digestion mode, with time-to-temperature programming.

Methodology

Preparation of vanadium containing silicalite-1 (VS-1)

Four samples with different ratios of Si/V, viz. 122, 281, 384 and 1024, were synthesized according to reference 16. Variation of initial vanadium and sodium hydroxide concentration in the synthesis mixture gives different levels of vanadium incorporation in the MFI structure, as shown in the previous work. After treating samples with 1 N ammonium acetate, the mole ratio of silica/vanadium increases to 284, 477, 880 and 1268, respectively. Ammonium acetate treated and un-treated samples were used in the catalytic testing.

Catalyst Testing

Oxidative dehydrogenation reaction using the synthesized VS-1 catalyst was performed via a pack bed reactor equipped with online gas chromatography under atmospheric pressure and isothermal conditions. GS-Alumina column was used to separate the obtained hydrocarbon products using an FID detector. Other gas products were separated using Plot-Q and Molsieve connected in series through a by-pass switching valve and equipped with a TCD detector. The reaction achieved steady state 30 min after initiation. The reactivity remained constant even when the reaction was continuously run for 20 h. Errors in carbon balance were less than 10%. The catalyst tests were conducted using 0.1 g of VS-1 zeolite in 8mm inner-diameter quartz tube reactor with low dead volume. The catalyst was pretreated in the reactor prior to the reaction with a mixed gas of nitrogen and oxygen at 550°C for 2 h before cooling down to the reaction temperature of 450°C. The reaction mixture contained 10 vol.% propane and 5 vol.% oxygen diluted in nitrogen gas (total flow rate = 200 cm^3/min). Catalytic behavior was then determined as a function of temperature. The catalyst study herein is reported, based on the VS-1 zeolite synthesis parameters and space velocity.

7.4 Results and Discussion

Synthesis of VS-1 zeolite using silatrane as the precursor and and the microwave heating technique was reported in ref 16. Many factors, including both reaction conditions and chemical formulation, were found to influence the amount of vanadium incorporated into the structure of zeolite. Contrasting silicalite versus VS-1 zeolite syntheses, there are some different types of crystal morphology produced when varying formula and reaction conditions. Decrease of water produces smaller zeolite crystals in the silicalite synthesis, due to an enhancement of nucleation rate. However, larger crystal sizes are obtained forVS-1 zeolite under the same conditions, because zeolite nucleation is obstructed by the presence of vanadium ion in solution. This has the effect of promoting more vanadium incorporation into VS-1 zeolite. Synthesis temperature is another factor, which affects the vanadium content in VS-1 zeolite. A higher synthesis temperature promotes higher condensation of vanadium into the structure of VS-1 zeolite. A third important factor that influences the thermal stability of VS-1 zeolite and the location of vanadium in the zeolite structure is the sodium hydroxide concentration in the synthesis formulation. It was found that at an appropriate concentration of sodium hydroxide, viz. NaOH/Si =0.3, good results were obtained for both vanadium content in the structure and the thermal stability of VS-1 zeolite. A lower sodium hydroxide concentration results in incomplete formation of zeolite due to the presence of amorphous silica in the product. On the other hand, too high sodium hydroxide concentration causes lower thermal stability of VS-1 zeolite and enhances the formation of extrinsic vanadium, which is extractable with ammonium acetate treatment, as described in reference 16. The amount of vanadium present in the VS-1 zeolite structure is correlated to the concentration of vanadium loading, as shown in figure 7.1. The relationship is almost linear in the samples treated with 1 N ammonium acetate (figure 7.1b). Figure 7.1 indicates that the higher the vanadium loading, the higher the vanadium deposition in zeolite; however, it seems that the higher level of deposition also creates a higher level of extrinsic vanadium species, which are removed after treatment. These samples were used to study the activity in oxidative dehydrogenation of propane. Several parameters associated with VS-1 synthesis can have a potential influence on the activity of catalysis, as described below.

Effect of synthesis formula to the activity of catalyst

Effect of vanadium loading concentration

Vanadium loading is proportional to the amount of vanadium catalyst, as shown in figure 7.1, and has an influence on the catalytic behavior, as illustrated in figure 7.2. After treating the as-synthesized VS-1 zeolite, the Si/V ratio became 1268, 477 and 284, according to figure 7.1b, thus only intrinsic vanadium specie responsible for this study. Propane conversion moderately increases, while the selectivity slightly decreases with increase of vanadium in the zeolite. However, a dramatic increase in conversion, and a dramatic decrease in selectivity, were observed with increase of temperature.

It is well known that the production of free radicals at higher reaction temperature causes unfavorable reactions, such as cracking of paraffin, exothermic oxidation and combustion, that are possible causes of the dramatic decrease in selectivity with increasing temperature, generating increasing amounts of carbon monoxide and carbon dioxide. Surprisingly, we are unable to detect any species of aromatics, as reported by Centi et al [7]. It is also well known that aromatization from polypropylene proceeds by cyclization via bifunctional reaction [17]. In the case of VS-1 catalyst, vanadium species are responsible for dehydrogenation, and certain available acid sites of zeolite are responsible for oligomerization, cyclization and cracking. However, we observe only cracking of propane in our experiment yielding ethylene and methane products with selectivities at around 30 and 25%, respectively (see Fig. 7.3). A difference in experimental methodology may be responsible for the different behavior of the catalyst and product selectivity, since our experiment was performed at a higher space velocity than the work in reference [7]. The cracking of propane in our experiment might come not from the catalyst itself. The selectivity of the cracking species is possibly due to an auto-thermal reaction since the selectivity increases only slightly (<3%) although the reaction temperature is increased from 450° to 550°C. More evidence to support this conclusion is that the reaction carried out without catalyst gives a similar value of the cracking selectivity.

The reactive sites in ammonium acetate treated VS-1 zeolites are known to concist of both octahedrally and tetrahedrally-coordinated vanadium, as described in ref 16. It was claimed that tetrahedral vanadium is responsible for more selectivity in dehydrogenation than the octahedral species, which is able to transform olefinic intermediate into selective and nonselective oxidation products [2, 3]. The slight decrease in C_3H_6 selectivity at higher temperature, evident in Figure 7.2, may reflect an increase of vanadium tetrahedral species, as described in ref 16. This correlates to the observation that the highest Si/V ratio gives the highest selectivity due to the absence of polynuclear vanadium, which acts as a strong oxidizing agent, giving oxygenated products. Thus, only well-dispersed vanadium is responsible for the oxidative dehydrogenation.

Effect of sodium hydroxide concentration

The role of sodium hydroxide in the synthesis of silicalite, ZSM-5 and VS-1 using the silatrane precursor, as explained in a series of articles [16, 18-19], strongly influences the quantity of vanadium deposited in the MFI topology. Specifically, vanadium incorporation into the structure is lowered with increasing sodium hydroxide concentration. Figure 7.3 illustrates the catalytic behavior of two VS-1 catalysts synthesized using the same synthetic formulation, but with different sodium hydroxide concentrations. The Si/V ratios in VS-1 after treatment with ammonium acetate are 477 and 880 for low (NaOH/Si=0.3) and high (NaOH/Si=0.5) sodium hydroxide concentration, respectively. Increase of sodium hydroxide in the synthesis mixture increases the conversion of both propane and oxygen, though the amount of vanadium in the VS-1 zeolite is lower than the other by half. VS-1 zeolite obtained using a high sodium hydroxide concentration gives not only conversion of oxygen higher than that of propane, but also a higher yield of carbon oxide species. Noting that the dehydrogenation reaction is a stoichiometric reaction of one oxygen molecule with two molecules of propane and produces two molecules of water, we deduce that the percent conversion of propane and oxygen should be almost equivalent in our experiment, since the theoretical propane to oxygen ratio is equal to 2. This is in good agreement with our results.

The higher percentage of the conversion obtained using VS-1 zeolite synthesized with high sodium hydroxide, may arise from reaction of propane with defect sites in the form of hydroxyl nests in the zeolite structure. This is not surprising since high concentrations of sodium hydroxide are able to dissolve zeolite crystal back into supersaturation under high temperature, consequently generating hydroxyl nest defects in the crystal. This effect also weakens the zeolite structure, making it less sustainable under high temperature during calcination, as reported in previous work [16]. These hydroxyl nests might control the reaction, causing over-oxidation to give carbon oxide species, which dominate even at low reaction temperatures.

Effect of intrinsic and extrinsic vanadium species

Hydrothermal synthesis of zeolite, such as VS-1 in previous work, is an easy and flexible preparation method. Loading vanadium into the zeolite structure has limitations, particularly that over-loading is possible, generating extrinsic vanadium, which may be present either as monomeric dispersion or polymeric species; however, as mentioned previously, the extrinsic species can be removed by chemical treatment with 1 N ammonium acetate. The catalytic behavior of the as-synthesized zeolite (Si/V= 281) and ammonium acetate treated VS-1 (Si/V=477) was studied and is compared in figure 7.4. A slight decrease in propane conversion, and a larger decrease in oxygen conversion, was observed for the ammonium acetate treated VS-1, as compared to the as-synthesized one. This is in agreement with observation of increasing carbon monoxide and carbon dioxide selectivity in the as-synthesized VS-1 (figure 7.4).

Many studies have elucidated the effect of vanadium loading on the selectivity of the oxidative dehydrogenation, and demonstrate that higher vanadium loading on a silica support, to the level that polynuclear vanadium and microcrystalline V_2O_5 form, enhances the production of total oxidation process, whereas a lower loading, with well-defined structure in the form of vanadium tetrahedrally bound by three oxygen atoms to the support, enhances dehydrogenation selectivity [20-21]. It is believed that the decreased availability of the oxygen lattice to react with propane leads to more selectivity than the V_2O_5 phase where the vanadium is in octahedral coordination. It was proved that dispersed vanadium is more easily reduced by hydrogen and ethane compared to crystalline V_2O_5 [22]. This is consistent with our observation that as-synthesized VS-1 containing extrinsic vanadium, probably present in the form of polynuclear vanadium, is not only less selective in propylene formation, but also responsible for total oxidation, as indicated by the higher selectivity in carbon monoxide and carbon dioxide species.

Tetrahedral vanadium generally contributes to alkane hydrogenation, which normally occurs at low vanadium content. Oligomeric species like pyrovanadate, V_2O_7, contain bridge oxygen atoms between vanadium, which easily react and promote oxygenated product. This contrasts with isolated VO_4, which have no bridging oxygen, and are responsible for dehydrogenation process [2].

It is well known that the behavior of the catalyst depends not only on the catalyst preparation method, but also on the conditions and methodology used to determine the catalytic effect. In this work, several factors related to the experimental operation were investigated as follows:

Reaction temperature effect

It was found that, with increasing temperature, the propane conversion remarkedly increases, and more possibility for cracking consequently occurs, via radical reaction, which normally occurs in the homogeneous pyrolysis and thermal cracking of propane [23]. The latter observations are therefore consistent with our experimental results that conversion of propane increases but propylene selectivity decreases at higher temperature due to the increase of carbon monoxide, as shown in figures 7.3 and 7.4.

Space velocity effect

Several studies show that control of the contact time is key to obtain good selectivity or high conversion in the oxidative dehydrogenation reaction. It is generally known that decreasing contact time in oxidative reaction increases selectivity due to a decrease of over-oxidation to give carbon dioxide, especially for auto-thermal reaction [24]. With increasing alkane conversion, studies show that the selectivity to carbon dioxide increases and is compensated by decreasing selectivity of alkene, indicating the existence of subsequent oxidation reactions of the alkene product at longer resident times [2]. Such effects are also indicated in our results, presented in figure 7.5, which show the effect of space velocity on the catalytic activity of VS-1 (Si/V=477, NaOH/Si=0.3) at the reaction temperature of 450°C. The conversions of both oxygen and propane increase with decreasing space velocity. Propylene selectivity is lowest at the lowest space velocity of $8.4\text{x}E^4$ $cm^3/g/hr$, increases significantly at $1.02\text{x}E^5$ $cm^3/g/hr$, and again increases slightly at $1.20\text{x}E^5$ $cm^3/g/hr$; in contrast, carbon monoxide selectivity increases at space velocity $8.4\text{x}E^4$ $cm^3/g/hr$ reflecting the fact that oxygen conversion is higher than the conversion of propane.

7.5 Conclusions

The influence of synthesis conditions on the catalytic properties in oxidative dehydrogenation of VS-1 zeolite, synthesized using the silatrane precursor, shows that propane conversion increases with increasing vanadium content in the zeolite structure while selectivity slightly decreases. However, the temperature has a more dramatic effect on both conversion and selectivity. Product selectivity decreases with increasing temperature due to the dominant radical mechanism or non-catalytic reaction at high temperature, causing more production of carbon monoxide. High sodium hydroxide concentration generate less vanadium in the VS-1 zeolite structure, but results in higher conversion and selectivity of carbon monoxide, probably owing to the reaction at defect sites. The nature of the active site of vanadium in VS-1 zeolite was studied by comparing the reaction of as-synthesized versus ammonium acetate treated VS-1. Our observations are consistent with the expectation that tetrahedral vanadium within zeolite is responsible for the selective oxidative dehydrogenation of propane, while extrinsic vanadium or polymeric species are responsible for over-oxidation to give higher carbon monoxide and carbon dioxide selectivity. The space velocity and the propane/oxygen ratio are important parameters influencing the catalytic behavior. By adjusting the balance between the space velocity and the propane/oxygen ratio it is possible to obtain good selectivity with compromise of conversion. A shorter contact time gives higher product yield and conversion though lower in selectivity.

7.6 Acknowledgements

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7.7 References

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Caption of Figures

Figure 7.1 Relationship between vanadium loading concentration and vanadium content in a) as-synthesized and b) 1 N ammonium acetate treated VS-1 zeolite

Figure 7.2 Propane conversion and propylene selectivity using VS-1 zeolites with varying vanadium contents at different reaction temperatures.

Figure 7.3 Conversion of propane (●) and oxygen (■), and product selectivity, at a C_3H_8 to O_2 feed ratio of 2, is plotted as a function of temperature, for VS-1 zeolites synthesized using two different sodium hydroxide concentrations (Low sodium hydroxide concentration ≡ NaOH/V = 3 (Si/V=477) and high sodium hydroxide concentration ≡ NaOH/V = 5 (Si/V=880)).

Figure 7.4 Conversion of propane (●) and oxygen (■), and product selectivity, at a C_3H_8 to O_2 feed ratio of 2, is plotted as a function of temperature, for as-synthesized (Si/V=281) and ammonium acetate-treated (Si/V=477) VS-1.

Figure 7.5 Conversion of propane (●) and oxygen (■), and product selectivity, at a C_3H_8 to O_2 feed ratio of 2, and a reaction temperature of 450°C, is plotted as a function of space velocity for VS-1 zeolite synthesized using the formula Si/V/TPA/NaOH/H_2O = 40/1/4/12/2800.

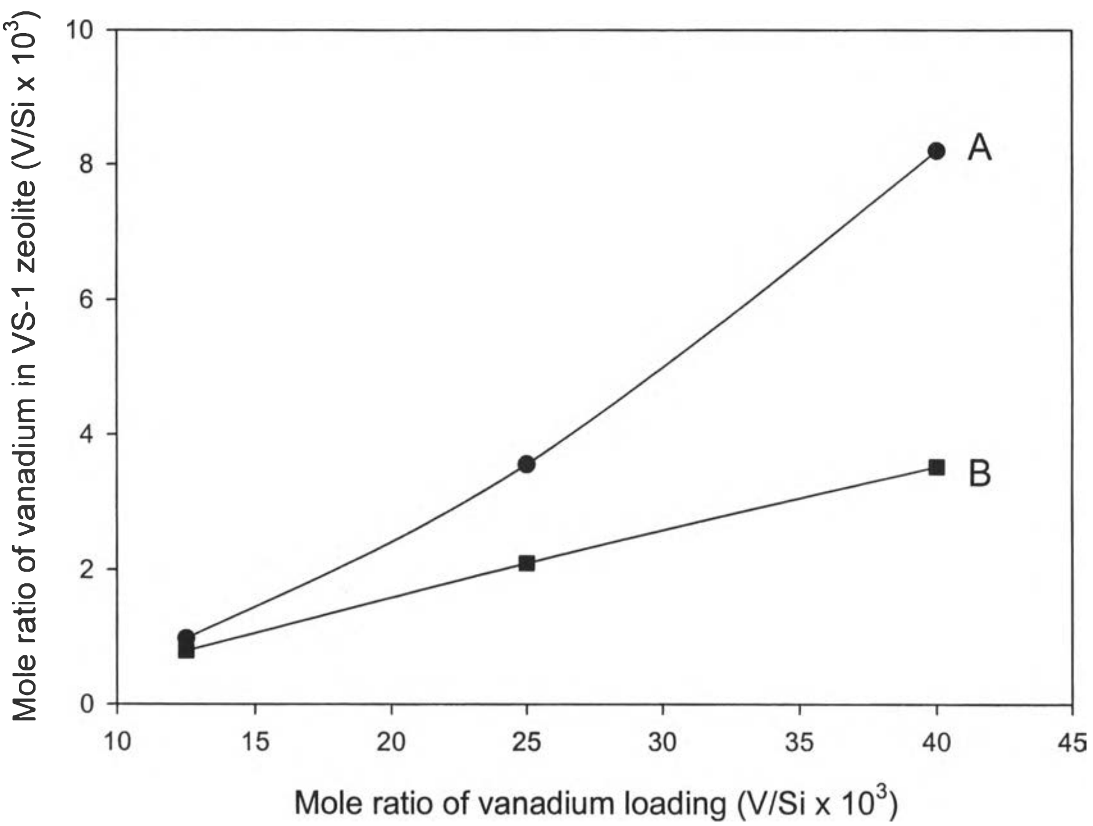
Mole ratio of vanadium in VS-1 zeolite (V/Si x 10^3)
0
2
4
6
8
10
10
15
20
25
30
35
40
45
Mole ratio of vanadium loading (V/Si x 10^3)
A
B

Figure 7.1

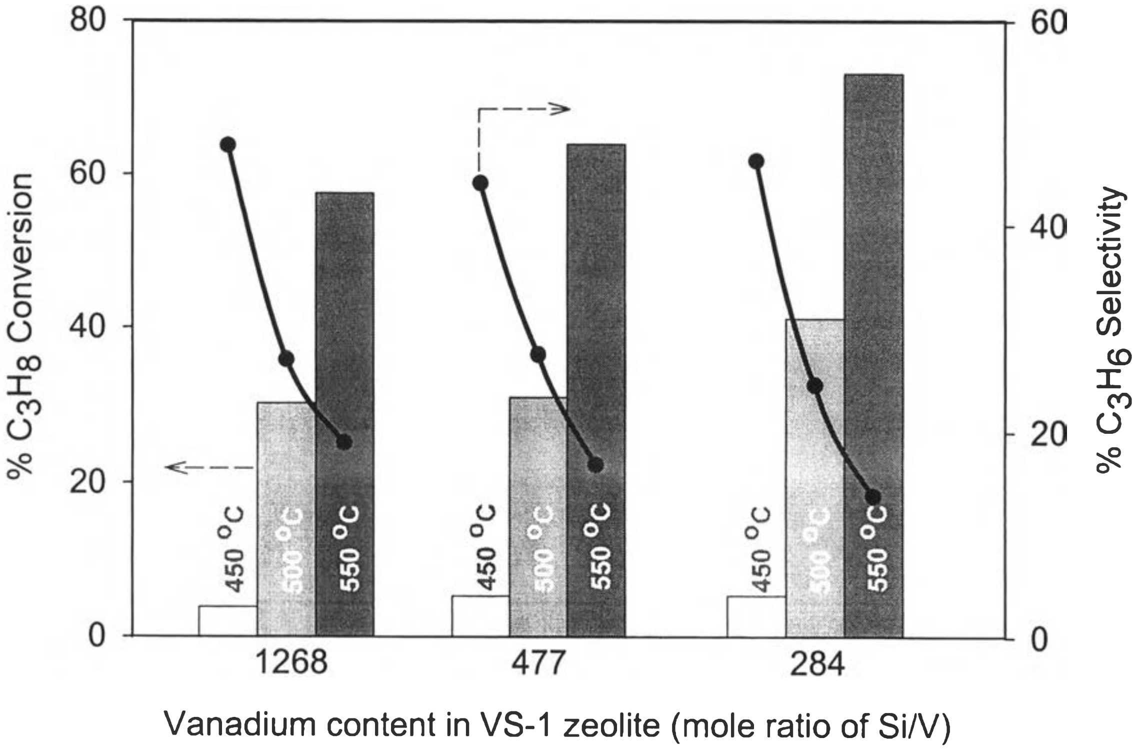
80
60
40
20
0
% C_3H_8 Conversion
60
40
20
0
% C_3H_6 Selectivity
450 °C
500 °C
550 °C
450 °C
500 °C
550 °C
450 °C
500 °C
550 °C
1268
477
284
Vanadium content in VS-1 zeolite (mole ratio of Si/V)

Figure 7.2

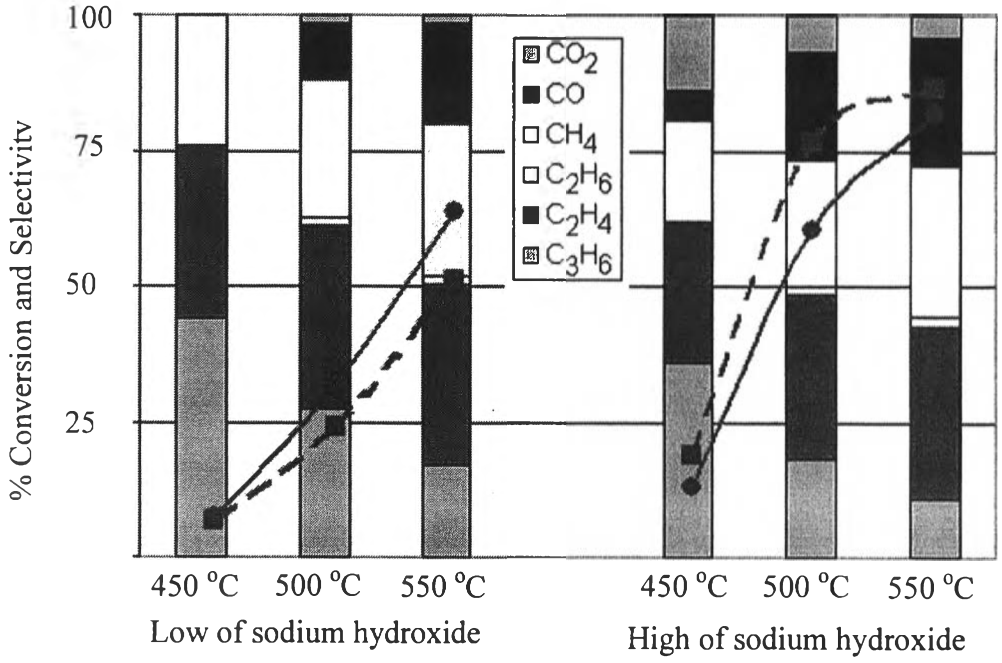
% Conversion and Selectivity
100
75
50
25
CO2
CO
CH4
C2H6
C2H4
C3H6
450 °C
500 °C
550 °C
Low of sodium hydroxide
450 °C
500 °C
550 °C
High of sodium hydroxide

Figure 7.3

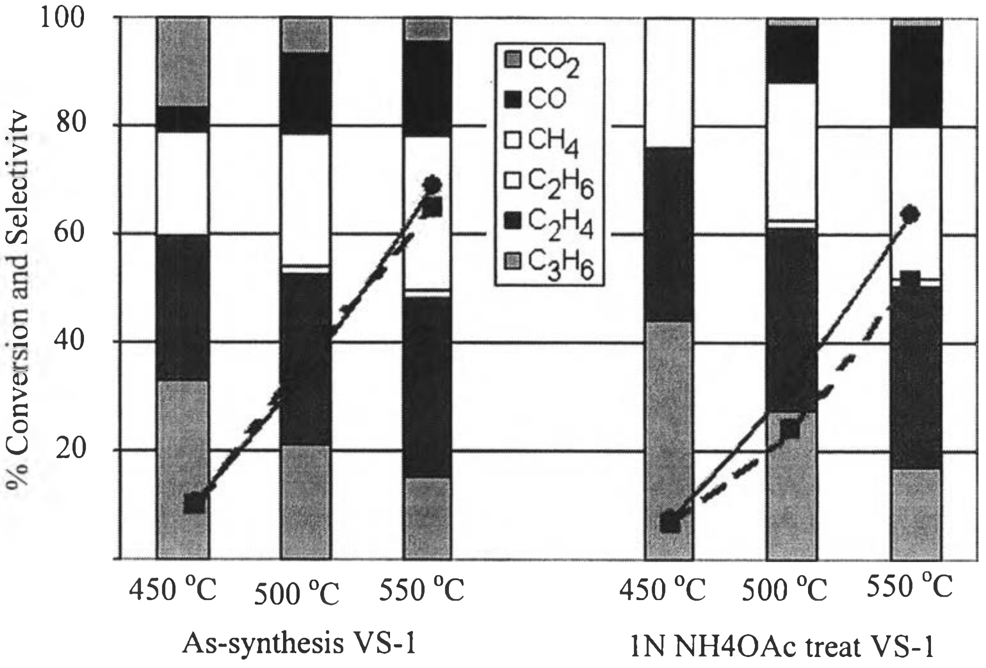
100
80
60
40
20
% Conversion and Selectivity
CO2
CO
CH4
C2H6
C2H4
C3H6
450 °C
500 °C
550 °C
As-synthesis VS-1
450 °C
500 °C
550 °C
1N NH4OAc treat VS-1

Figure 7.4

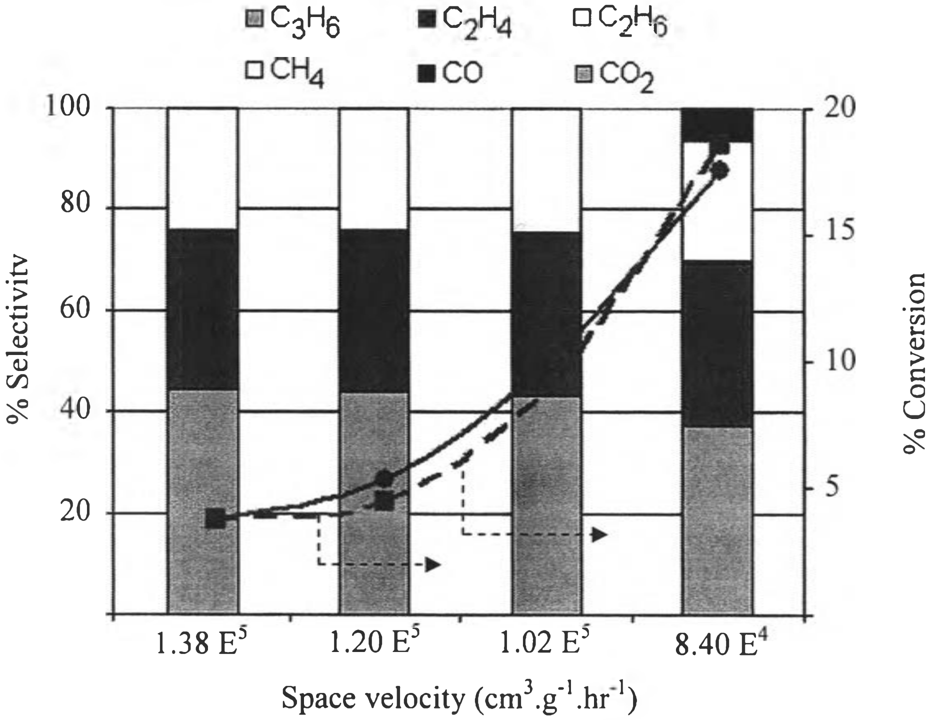
C3H6
C2H4
C2H6
CH4
CO
CO2
100
80
60
40
20
% Selectivity
20
15
10
5
% Conversion
1.38 E5
1.20 E5
1.02 E5
8.40 E4
Space velocity (cm3.g-1.hr-1)

Figure 7.5