# ดีไฮเดรชันของเอทานอลไปเป็นเอทิลีนด้วยมอร์ดิไนท์ที่มี Mn และ Ni
# Dehydration of Ethanol to Ethylene over Mn- and Ni-Containing Mordenites

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## บทคัดย่อ

งานวิจัยนี้ศึกษาดีไฮเดรชันของเอทานอลไปเป็นเอทิลีนด้วยมอร์ดิไนท์ที่มี Mn และ Ni ได้ทำการตรวจพิสูจน์เอกลักษณ์ของตัวเร่งปฏิกิริยาที่สังเคราะห์ด้วยการเลี้ยวเบนรังสีเอกซ์ (XRD) อินฟราเรดสเปกโทรสโคปี (FT-IR) วิธี BET และการคายแอมโมเนียแบบตั้งโปรแกรมอุณหภูมิ เปรียบเทียบผลของดีไฮเดรชันของเอทานอลไปเป็นเอทิลีนสำหรับตัวเร่งปฏิกิริยาเหล่านี้ในช่วงอุณหภูมิ 250-450 องศาเซลเซียส ความเร็วเชิงสเปซต่อน้ำหนักชั่วโมง เท่ากับ 1 เวลาการไหลของสาร 30-240 นาที และน้ำหนักของตัวเร่งปฏิกิริยา 1.0 กรัม ผลการทดลองแสดงให้เห็นว่า การเปลี่ยนรูปของเอทานอลเมื่อใช้ตัวเร่งปฏิกิริยา Mn-MOR และ Ni-MOR คล้ายคลึงกัน แต่ความเลือกจำเพาะต่อการเกิดเอทิลีนของตัวเร่งปฏิกิริยา Mn-MOR สูงกว่ามาก Ni-MOR แสดงความเลือกจำเพาะต่อการเกิดอีเทนเนื่องจากความสามารถในการเร่งปฏิกิริยาไฮโดรจิเนชัน

## Abstract

Dehydration of ethanol to ethylene was investigated over Mn- and Ni-containing mordenites. The synthesized catalysts were characterized by X-ray powder diffraction (XRD), infrared spectroscopy (FT-IR), BET method, and temperature programmed desorption of ammonia. The performances on dehydration of ethanol to ethylene for these catalysts were compared at temperature range 250-450°C, WHSV (weight hourly space velocity) of 1 h$^{-1}$, time on stream of 30-240 min and catalyst weight of 1.0 g. The results showed that conversion of ethanol of the Mn-MOR and Ni MOR was quite similar but selectivity to ethylene of the Mn-MOR catalyst was much higher. The Ni-MOR showed high selectivity to ethane due to its hydrogenation ability.

**คำสำคัญ** : เอทานอล เอทิลีน มอร์ดิไนท์ แมงกานีส นิกเกิล

**Keywords** : Ethanol, Ethylene, Mordenite, Manganese, Nickel

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## 1. Introduction

Ethylene is an important material for the organic chemistry industry used in the preparation of polyethylene, ethylene oxide, etc. Conventionally, it has been commercially produced by the thermal cracking of liquefied petroleum gas (LPG) or naphtha (Okagami, 1970). Compared to the conventional route, catalytic dehydration of ethanol to ethylene is proving attractive as it requires lower temperature and offers higher ethylene yield (Zaki, 2005). Moreover, ethanol can be produced from renewable sources. Several catalysts were developed for bioethanol-to-olefins process (Mao, 1987; Nguyen, 1990). One of the catalysts employed, □-alumina (Winter, 1976) required higher reaction temperature (450°C) and offered lower ethylene yield (80%). Zeolites have also been widely studied, the concentration and strength of acid sites are important factors in the catalytic activity (Phillips, 1997; Moser, 1989). Reaction parameters such as temperature, space velocity, and feed composition have significant effects on product distribution. With HZSM-5 catalyst at 300°C, 95% of ethylene was produced at a conversion level of 98% of ethanol. The catalyst was deactivated by coke due to its high acidity. A study to compare catalyst size showed that the nanoscale HZSM-5 zeolite catalyst exhibited better coke-resistance and stability than the microscale catalyst (Bi, 2010). Presence of heteroatoms (Ni, Mn, Fe, etc.) are among the many factors that play major roles in determining activity and selectivity of the zeolites (Cartlidge, 1989). Microporous silicoaluminophosphate molecular sieve, SAPO-34 showed high catalytic performance in dehydration of ethanol to yield C2-C4 olefins, however, it also suffered from fast deactivation (Travalloni, 2008). Catalytic activity order in dehydration of ethanol to ethylene was reported to be HZSM-5 > NiAPSO-34 > SAPO-34 > $Al_2O_3$. (Zhang, 2008).

Mordenite (MOR) zeolite is not effective as industrial catalysts in the methanol to olefin reaction, because of low selectivity for the lower olefins and rapid deactivation. However, the MOR zeolite with a lower acid site density, prepared by careful removal of aluminum atoms from its framework, the obtained dealuminated mordenite shows slow deactivation and high selectivity for the lower olefins (Aramendia, 2002; Bjorgen, 2002; Sawa, 1989). Transformation of ethanol on Fe ion-exchanged mordenite was reported to yield ethane and methane as major products, with small amount of diethyl ether, acetaldehyde and acetone (Mohamed, 2003).

Our previously reported results showed that transition metal substituted mordenite catalysts exhibited better performance for ethanol dehydration to ethylene than the original mordenite (Arenamnart, 2006).Among many metal studied: Rh, Cu, Fe, Ag, Ni, Co, Mn and Zn, Ni/dealuminated mordenite gave higher selectivity to ethane. Therefore in this work, more extensive study of ethanol dehydration over Ni- and Mn-mordenite was done including effects of temperature and time on stream on catalyst performance and hydrogenation ability of the Ni-MOR catalyst.

## 2. Research Methodology

### 2.1 Preparation of Mn and Ni-containing Mordenites

Mn- and Ni-containing mordenites were synthesized according to our reported procedure (Arenamnart, 2006). The Na-mordenite ($SiO_2/Al_2O_3$ = 5.6) was converted into the ammonium and H-form, respectively. It was then dealuminated with acid and wet impregnated with metal nitrate (1 wt%) and air-calcined at $550^oC$ for 5 h.

### 2.2 Catalyst Characterization

Mn- and Ni-containing mordenites were characterized using Powder X-ray diffractometer (Rigaku, DMAX 2002/Ultima Plus), $N_2$ physisorption (BELSORP-mini), X-ray fluorescence (SISONS instrument ARL 8410 X-ray fluorescence spectrometer) and thermogravimetric (TG) analyser. In this work we also performed temperature programmed desorption of ammonia ($NH_3$-TPD) analyses using Micromeritics Pulse Chemisorb-2705 to identify the acid site of the catalyst.

### 2.3 Catalytic Activity Measurements

Experimental setup used for this study is similar to that in ref., shown in Fig. 1. Catalyst (1.0 g) was packed between quartz wool plugs inside a fixed bed downstream quartz tubular reactor (1 cm ID, 40 cm length) and heated in a tubular furnace. The temperature was monitored by a thermocouple wrapped around the external surface of the quartz tube at the catalyst bed location. The catalyst was activated under flowing $N_2$ at $500^oC$ for 1 h and then reduced with flowing $H_2$ at $500^oC$ for 1 h. Ethanol was fed using a Milton Roy syringe pump into nitrogen stream (carrier gas) with 10 vol.%, passed from the top through the catalyst at a fixed WHSV (weight hourly space velocity), 1.0 h$^{-1}$. Reactions were performed at atmospheric pressure in the temperature range 250–450$^oC$. The products were passed through a cooling system to separate condensable

components from light gaseous products. The gaseous products were collected and analyzed by gas chromatography (Hewlett Packard-6890) by means of detectors based on thermal conductivity (TCD) and flame ionization (FID). The separation of products was carried out by means of a system made up of following columns: Carbowax Porasite column, Chromosorb column, Carbowax column, Carbopak B column, Haysep Q, Haysep T column, Molecular Sieve 5A column, Haysep Q column and Molecular Sieve 13X column. The liquid products were analyzed by using a PONA capillary column. Retention times and response factors were calibrated by using a standard gas mixture. The components of gaseous products were ethylene, methane, ethane, higher aliphatic hydrocarbon (C3–C5), diethyl ether. The components of the liquid were water, unreacted ethanol and small amount of acetaldehyde.

The activity data are reported in terms of conversion of ethanol and selectivity to ethylene. The conversion of ethanol was defined as [molar amount of converted ethanol]/[molar amount of ethanol in the feedstock]. The selectivity to ethylene was defined as [molar amount of ethanol converted to ethylene]/[molar amount of converted ethanol]. Three replications of each test were performed and the average was reported.

## 2.4 Catalyst Regeneration

Catalyst regeneration was performed by oxidizing the coke deposited onto the catalyst in air flow for 2 h at 550$^{\circ}$C. The regenerated catalyst was reused in the reaction.
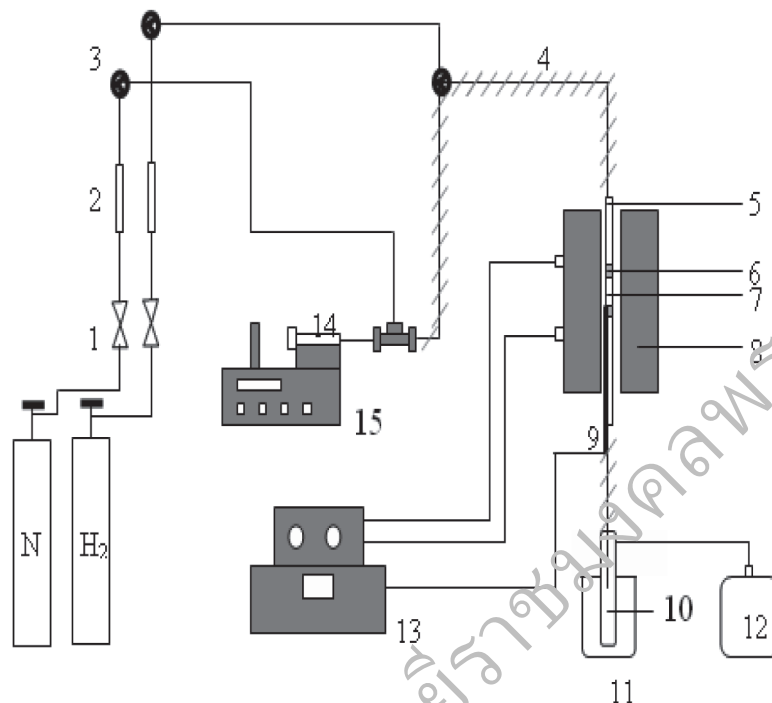
**Fig. 1** Reaction apparatus

1 = needle valve, 2 = flow controller, 3 = three-way valve, 4 = heater cable, 5 = tubular reactor, 6 = quartz wool, 7 = catalyst, 8 = electric furnace, 9 = thermocouple, 10 = cold trap, 11 = dry ice-acetone bath, 12 = tedlar bag, 13 = temperature programmed controller, 14 = syringe, 15 = syringe pump.

## 3. Results and Discussion

### 3.1 Catalyst Characterization

Fig. 2 shows typical powder diffraction patterns recorded on De-MOR, Mn-MOR and Ni-MOR. The XRD patterns of the metal impregnated mordenites essentially show the same diffraction patterns confirming the mordenite structure (Breck, 1974). The intensity of diffraction peaks of the Mn-MOR was higher than that of the Ni-MOR, indicating higher crystallinity of the former. No extra peaks due to metal incorporation were observed due to too small amount of metal (1 wt.%) or high dispersion of metal.
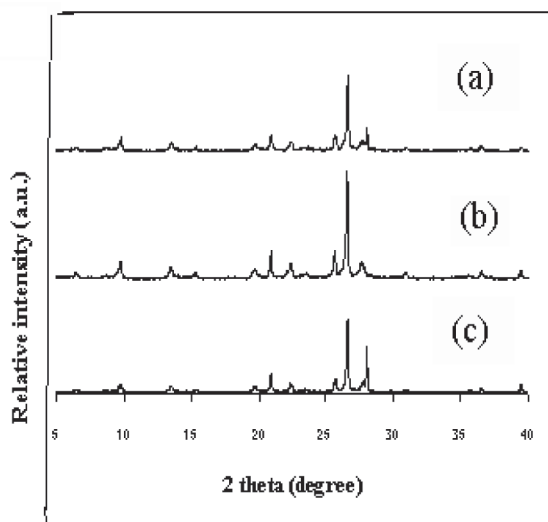
**Fig. 2** XRD patterns of (a) De-MOR, (b) Mn-MOR and (c) Ni-MOR

Table 1 presents the Si/Al molar ratio of the catalysts, provided by XRF and surface areas from BET technique. As previously reported, after dealumination, the Si/Al mole ratio of dealuminated mordenite was increased from 5.66 to 26.9 due to the leaching of aluminium from the framework of mordenite when refluxed with hydrochloric acid.

The dealuminated mordenite has a higher surface area than the original sodium mordenite as the dealumination removes the extra-framework alumina, leading to an enlargement of the effective pore size and to the uncovering of the Bronsted acid sites located in the ring channels. The surface areas of the Mn-MOR (316 $m^2/g$) and Ni-MOR (320 $m^2/g$)

were lower than the De-MOR (364 $m^2/g$), the decrease might be due to metal oxide deposition into the mordenite pores.

**Table 1** Si/Al molar ratio and surface area of the catalysts

| catalyst | Si/Al molar ratio | BET surface area ($m^2/g$) |
|---|---|---|
| Na-MOR | 5.66 | 244 |
| De-MOR | 26.90 | 364 |
| Ni-MOR | 25.78 | 320 |
| Mn-MOR | 25.92 | 316 |

Acidity of the catalyst was estimated by TPD profiles of pre-adsorbed $NH_3$. $NH_3$ desorption profiles of the catalysts are shown in Fig. 3. There were two peaks correspond to the desorption of $NH_3$ on weak and strong acid sites (Bronsted acid and Lewis acid), respectively. The amount of $NH_3$ desorbed and the desorption temperature were usually considered as a measure of total acidity and acid strength of catalysts, respectively. The amount of $NH_3$ adsorbed at lower temperature (weak acidity) is always found to be greater than that adsorbed at higher temperature (strong acidity). The weak and strong acidity of the Ni-MOR and Mn-MOR were observed at 250-255°C and 420-450°C, respectively, which was slightly higher than those of the De-MOR (235°C and

410°C). This indicated higher acid strength in the metal-MOR. The acidic strength of Ni-MOR was stronger than that of the Mn-MOR.

The area of desorption peak, that is the number of acid site of the metal-mordenites was lower than those of the De-MOR. The numbers of weak acid site and strong acid site of the Ni-MOR and Mn-MOR were 0.65, 0.32 and 0.53, 0.27 mmol/g, respectively, compared to 0.70 and 0.36 mmol/g, respectively of the De-MOR. In general, the number of acid site was important as well as the acid strength to catalytic activity for dehydration of ethanol to ethylene.
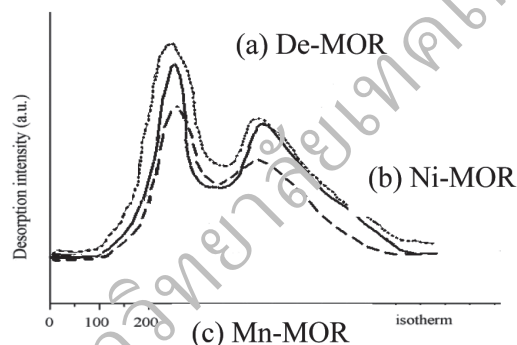


Fig. 3 NH$_3$ desorption profiles of (a) De-MOR (b) Ni-MOR and (c) Mn-MOR.

## 3.2 Catalytic Performance

From our previous results (Arenamnart, 2006), dehydration of 10 vol.% ethanol over Mn-MOR and Ni-MOR compared to the De-MOR under the same conditions

(1.0g catalyst, temperature at 350°C, WHSV of 1.0 h$^{-1}$, time on stream 60 min) showed 100% conversion. The selectivity to ethylene was 45.5% for De-MOR, 94.3% for Mn-MOR and 35.4% for Ni-MOR. The Ni-MOR also gave high selectivity to ethane (62.5%). In this work, effect of reaction temperature and time on stream on catalyst performance were investigated.

The reaction was performed at different temperatures (250, 300, 350, 400 and 450°C). The results obtained are graphically illustrated in Fig. 4 and Fig. 5, respectively. In Fig. 4, at low temperature (250C), ethanol conversion over Mn-MOR and Ni-MOR was 76.2% and 74.0%, respectively. At high temperature (400-450°C) conversion of ethanol was 95-97%. Therefore the optimum temperature was 350°C (100% conversion).

As for the selectivity, Fig. 5 shows that at lower temperatures (250-300°C), selectivity to ethylene was low due to formation of diethyl ether from intermolecular dehydration of ethanol. At 250°C, selectivity to diethyl ether is 19.3% and 24.0% for the Ni-MOR and the Mn-MOR, respectively. The selectivity to diethyl ether is catalyzed by Lewis acid sites, as indicated by others [Sayed, 1982]. When temperature was increased, small hydrocarbons were detected. At 450°C, methane (13.1% and

10.5% selectivity) and ethane (2.3% and 60.0% selectivity) for the Mn-MOR and the Ni-MOR, respectively were obtained together with small amount of acetaldehyde (1.1% selectivity). Ethanol dehydrogenation to produce acetaldehyde can occur as a side reaction at the higher temperature. It should be mentioned that our results were different from that reported in the literature (Mohamed, 2003). Over Fe ion-exchanged mordenite in the temperature range of 200-400°C ethane and methane were found as major products.

At all temperatures studied in this work, the Ni-MOR showed high selectivity to ethane: 34.1%, 45.7%, 62.5%, 64.2% and 60.0% at 250, 300, 350, 400 and 450°C respectively. Dominance of the ethane product in the absence of hydrogen in the feed might be due to chemisorbed hydrogen that was retained on the Ni surface during reduction step. This chemisorbed hydrogen can be used by hydrogenation of ethylene to produce ethane. However, the selectivity to ethane would be gradually declined with time on stream since the chemisorbed hydrogen would be virtually consumed. This will be shown later.

In addition, the high selectivity of ethane could be due to rapid conversion of ethylene on strong acid sites of the

Ni-MOR and thus favoring hydride transfer (Marchi, 1993). A similar result was reported for NiSAPO-34 sample with extra-framework nickel which caused formation of methane in the methanol to olefins reaction (Dubois, 2003). However dehydration of ethanol over NiSAPO-34 catalyst was also reported to yield 96.5% conversion and 98.3% selectivity to ethylene (Zhang, 2008). The difference might be due to different acid site or the acid strength or metal content of the catalyst.
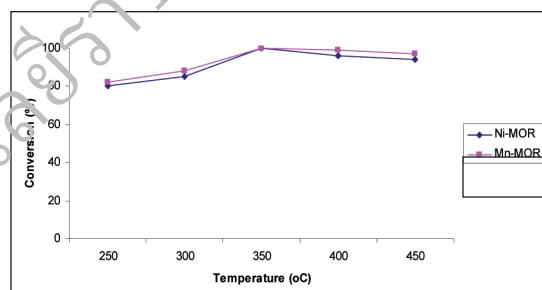


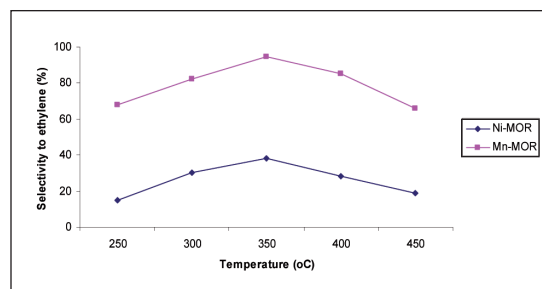Fig. 4 Ethanol conversion on Ni-MOR and Mn-MOR catalysts at various temperatures



Fig. 5 Selectivity to ethylene on Ni-MOR and Mn-MOR catalysts at various temperatures

Effect of time on stream on product selectivity at 350°C is shown in Fig. 6. Both Ni-MOR and Mn-MOR catalysts still show 100% conversion in first period of time, 30-90 min time on stream. Then the conversion was gradually dropped. At 240 min the conversion was 82.9% and 73.5% for the Mn-MOR and Ni-MOR, respectively.

Fig. 7 shows the selectivity to ethylene at 350°C with time on stream. It decreased from 92.1% at 30 min to 83.0% at 240 min time on stream for the Mn-MOR and from 34.3% at 30 min to 28.0% at 240 min for the Ni-MOR.
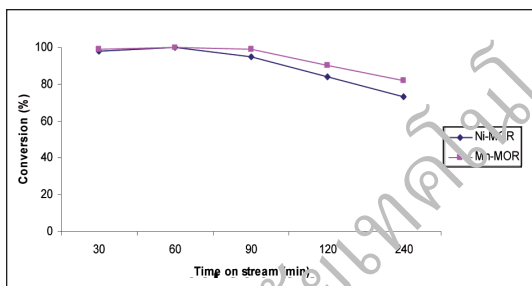


**Fig. 6** Ethanol conversion on Ni-MOR and Mn-MOR catalysts at various time on streams
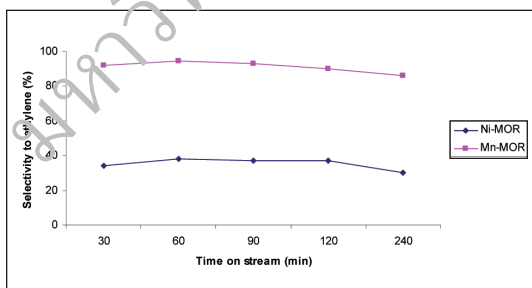


**Fig. 7** Selectivity to ethylene on Ni-MOR and Mn-MOR catalysts at various time on streams

As mentioned above that the formation of ethane might be due the chemisorbed hydrogen on the Ni-MOR catalyst surface, therefore the selectivity to ethane with the time on stream was investigated at 350°C. Result is shown in Fig. 8. It was found that selectivity to ethane decreased with time on stream, from 62.5% at 60 min to 45.0% at 240 min. This demonstrated that some of ethane was formed from reduction of ethylene by chemisorbed hydrogen. In addition, hydrogen transfer from the coke deposit might also be responsible for the hydrogenation of ethylene even though amount of coke formed was quite low (~ 2 wt%).
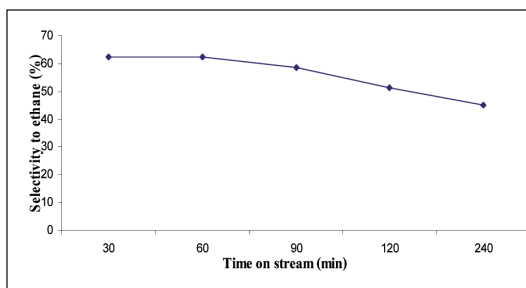


**Fig. 8** Selectivity to ethane on Ni-MOR catalyst at various time on streams

### 3.3 Catalyst Regeneration

Generally, coke forms on the strong acidic sites. After use, coke content in both catalysts was determined, it is 1.2-2.6%. Therefore the catalysts were calcined to remove coke and was reused

at the same conditions as for fresh catalyst. The result showed a decrease of ethanol conversion from 100% to 95% after three times use.

## 4. Conclusions

The Ni-MOR and Mn-MOR catalysts were synthesized, characterized, and studied for their performance in dehydration of ethanol to ethylene. Difference in product selectivity over two catalysts was due to difference in acidity as well as hydrogenation ability. The Mn-MOR gave high selectivity to ethylene while the Ni-MOR produced a large amount of ethane due to finally dispersed Ni particle formed in the reduction step of catalyst activation. In temperature range of 250-450°C, the ethanol conversion and selectivity to ethylene were found maximum at 350°C. Small hydrocarbons were detected when temperature was increased.

## 5. Acknowledgements

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