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Chapter

Partial Oxidation of Methane to Methanol on Cobalt Oxide-Modified Hierarchical ZSM-5

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Abstract

Conversion of methane to more reactive compounds such as methanol has drawn attention for many years. Hierarchical ZSM-5 zeolite has been used as support of metal oxide catalyst to facilitate the partial oxidation of methane to methanol. The NaZSM-5 zeolite was synthesized hydrothermally using double-template techniques, in which tetrapropylammonium hydroxide (TPAOH) and polydiallyldiammonium chloride (PDDA) were used as primary and secondary templates, respectively. HZSM-5 was prepared through multiple $NH4^+$ exchange of NaZSM-5 followed by calcination. Co oxide-modified ZSM-5 (Co/NaZSM-5 and Co/HZSM-5) were prepared through impregnation method. Then, the zeolites were extensively characterized using scanning electron microscope (SEM), X-ray diffraction (XRD), AAS, Fourier transform infrared (FTIR), ^{27}Al solid-state NMR, microbalance, and surface area analysis. The catalytic test was performed in batch reactor, and the product was analyzed with GC-FID. Reaction condition and acidity of ZSM-5 as support catalyst were studied. As a result, when using Co/HZSM-5 as catalyst, percentage (%) yield of methanol was increased with longer reaction time. On the other hand, the percentage (%) yield decreased when Co/NaZSM-5 was employed. Introduction of trace amount of oxygen to the gas mixture showed different results. Furthermore, the prospect of synthesis of ZSM-5 using natural resources and using biogas are also explored.

Keywords: hierarchical zeolite, ZSM-5, partial oxidation, methane, methanol

1. Introduction

Methane is a greenhouse gas considered as the second largest amount after carbon dioxide. Methane is released during the production and transport of coal, natural gas, and petroleum. In addition, methane is also produced by the farms and from the decay of organic waste in landfills [1].

Methane is a principal component of natural gas that has the potential to be converted into valuable oxygenated products such as formaldehyde, formic acid,

and especially methanol [2–4]. Methanol is one of bulk chemical that has numerous applications in chemical industries. It is used as solvent, gasoline additive, or chemical feedstock for the production of biodiesel and hundreds of other chemicals [5]. Thus, direct oxidation of methane to methanol has gained interest since conventional methods consume more energy as high temperature or pressure is required [6].

Many heterogeneous catalysts have been investigated for direct selective oxidation of methane to methanol. The main types of metal catalysts active for methane oxidation to C1-oxygenates have a degree of oxidation exceeding $^{3+}$. They include Pd, Mn, Co, Fe, V, Mo, and Ga [7]. Fe/ZSM-5 has been reported to be active for this conversion with the use of expensive N2O as oxidant [4, 8, 9]. Therefore, the use of O2 or air as oxidant is more attractive. In 2005, selective oxidation of methane into methanol using Cu/ZSM-5 was reported [10]. In 2010, Co/ZSM-5, prepared from cobalt impregnation on alkali-treated ZSM-5 zeolite aggregates, was reported to have catalytic activity in partial oxidation of methane, and selectivity and activity of catalyst depend on cobalt speciation [11].

Since 2012, our research group has conducted work on partial oxidation of methane to methanol using Co/ZSM-5 zeolite as heterogeneous catalyst. Three types of Co/ZSM-5 zeolite catalysts, i.e., cobalt-impregnated microporous ZSM-5, cobalt-impregnated hierarchical ZSM-5, and cobalt ion-exchanged hierarchical ZSM-5, have been prepared, and their catalytic activities were tested [12]. It is shown that both mesoporous properties and the type of Co species play an important role in the use of Co/ZSM-5 as heterogeneous catalyst in this reaction.

It is interesting to study further on the role of hierarchical ZSM-5 as catalyst support, especially its acidity, both Brønsted and Lewis sites. Therefore, further work has been carried out to compare the activity of hierarchical Co/ZSM-5 catalysts using the as-synthesized NaZSM-5 and H-exchanged ZSM-5 (HZSM-5) as support. The work on Co/HZSM-5 h has been explained previously, including the effect of additional trace of oxygen in the gas mixture to the yield of methanol [13]. This chapter will discuss the results from the above work, followed by exploration on the future prospect of utilize natural resources as alumina and silica precursors in ZSM-5 synthesis as well as bio-methane conversion.

2. Synthesis and characterization studies on ZSM-5 zeolites

2.1 Synthesis of hierarchical NaZSM-5 and HZSM-5 zeolites

Synthesis of hierarchical NaZSM-5 zeolite was carried out following the procedure reported by Wang et al. [14] with some modification. The gel of ZSM-5 zeolite was prepared from a homogeneous mixture with molar composition of 1 Al_2O_3: 64 SiO_2: 10 $(TPA)_2O$: 3572 H_2O. The mixture was stirred and aged at 373 K for 3 h. About 1 g PDDA was added slowly to the mixture at room temperature and stirred for 24 h. Then, the mixture was transferred into a 200 mL teflon-lined autoclave for hydrothermal process at 423 K for 144 h. Afterward, the as-synthesized zeolite was dried at room temperature followed by calcination at 823 K and labeled as as-synthesized hierarchical NaZSM-5 (NaZSM-5 h).

Hierarchical HZSM-5 zeolite was prepared through multiple ammonium exchanges (1 g of NaZSM-5 in 50 mL 1 MNH_4^+ solution). Afterward, the zeolite was dried at room temperature followed by calcination at 823 K for 3 h to obtain the HZSM-5 zeolite (labeled as HZSM-5 h).

2.2 Characterization of ZSM-5 zeolites

X-ray powder diffraction patterns were obtained with a PANalytical X-Pert Pro powder diffractometer in 5–60° 2θ with Cu Kα radiation and scanning step of 0.013° s^{-1}. Scanning electron microscope images were undertaken on a FE-SEM FEI INSPECT F50 instrument. Si, Al, and Co content was determined by using atomic absorption spectroscopy technique with the use of Shimadzu AA600 instrument. Infrared spectra were collected from pressed disks of sample mounted in a high-vacuum cell allowing in situ outgassing, using a Thermo Nicolet Nexus 470 Fourier transform infrared (FTIR) instrument at 4 cm^{-1} resolution. The surface area was calculated by using the Brunauer–Emmett–Teller (BET) method based on the adsorption data in the relative pressure (p/p$_o$) range 0.05–0.35. The pore-size distribution was determined by using the Barrett–Joyner–Halenda (BJH) desorption model. Micropore volume was obtained by t-plot analysis. Total pore volume was obtained from the amount of nitrogen adsorbed at p/p$_o$ = ca. 0.99. Mesopore volume was calculated by subtracting micropore volume from total volume. The water adsorption capacity of ZSM-5 zeolites was investigated in the experiments performed using a CI microbalance. The nitrogen adsorption and desorption isotherms at 77 K were measured using a QuadraSorb Station 2 version 5.13. The samples were outgassed for 3 h at 573 K before being measured.

2.2.1 X-ray diffraction (XRD)

Figure 1 shows X-ray diffraction (XRD) patterns of various hierarchical ZSM-5 samples. As-synthesized NaZSM-5 exhibited the characteristic peaks associated with MFI framework [15]. It indicates that MFI-structured zeolites were successfully synthesized. XRD pattern of HZSM-5 shows that ZSM-5 h zeolite structure was preserved after post-synthesis treatment on NaZSM-5 h through NH$_4^+$ exchange process followed by calcination at 823 K.

2.2.2 Scanning electron microscope

SEM image of NaZSM-5 h (**Figure 2**) shows that NaZSM-5 particles have uniform size in coffin-like shape and the surface of particles is rough. This surface damage indicating mesoporosity were introduced, after the PDDA template was removed by calcinations [14]. Since the XRD pattern for HZSM-5 h that is prepared through ammonium
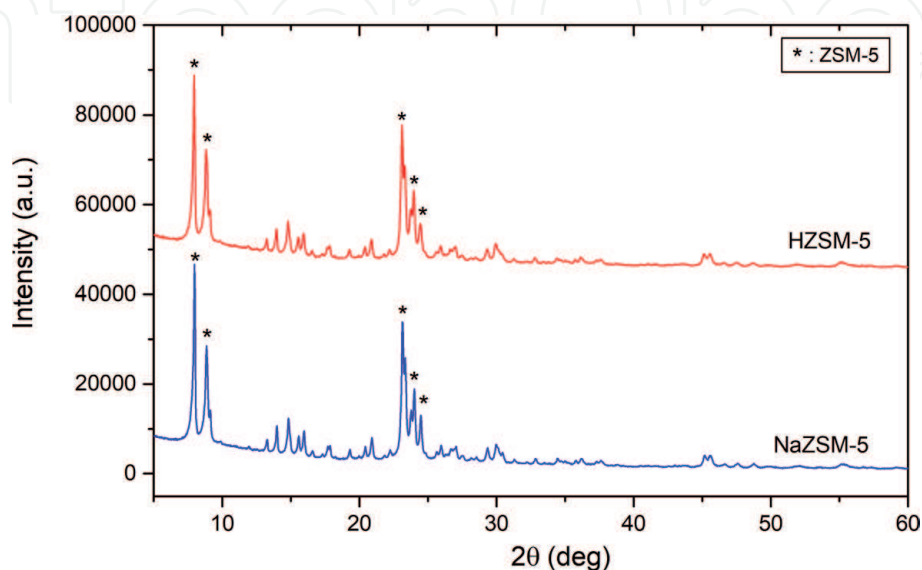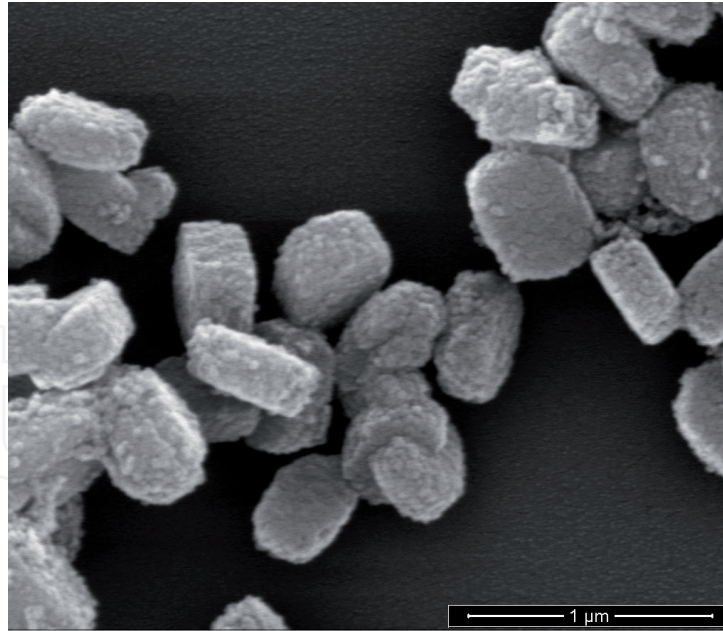

Figure 1.
XRD pattern of ZSM-5 h zeolites.

Figure 2.
SEM image of NaZSM-5 h zeolite with 100.000 magnification.

exchange and calcination at high temperature is similar to the pattern of NaZSM-5 h, it is presumed that the morphology of the crystals is also unchanged significantly.

2.2.3 Surface area analysis

Figure 3 shows N_2 adsorption and desorption isotherms of NaZSM-5 h and HZSM-5 h. The adsorption–desorption isotherms for all samples were found to belong to type IV isotherm according to BET classification, showing broad hysteresis loops indicating the presence of mesopores (ø > 2.0 nm) [16].

Figure 3.
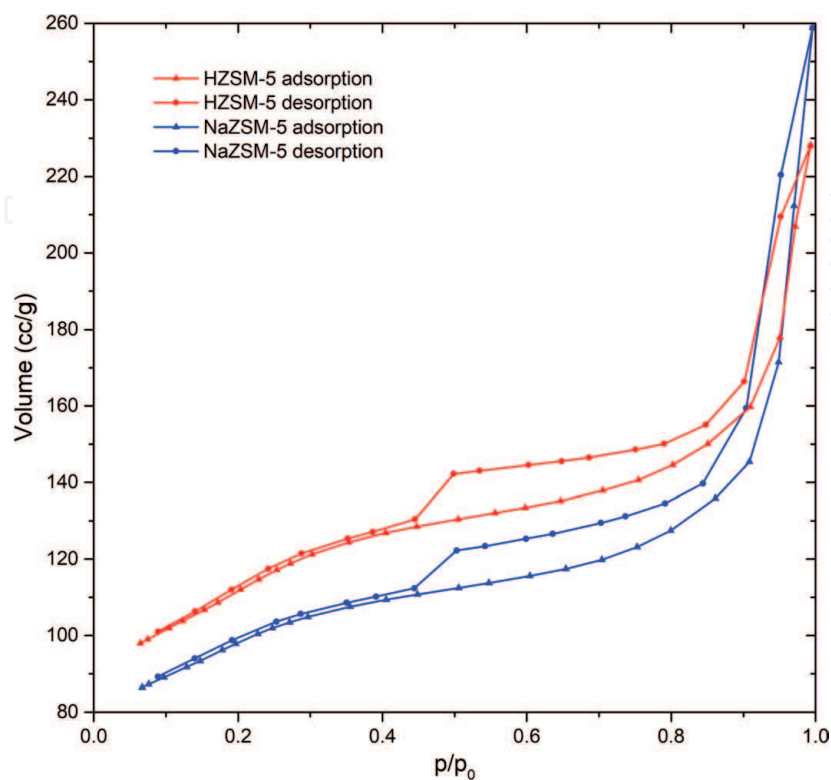*Isotherm adsorption–desorption curve of ZSM-5 zeolites.*

2.2.4 Physicochemical properties

Table 1 shows the physicochemical properties of the prepared ZSM-5 materials. Elemental analysis using AAS showed that Si-to-Al ratio of synthesized NaZSM-5 zeolite was 33.19. This makes ZSM-5 classified as high-silica zeolites (Si/Al ratio = ~10–100), which has played an important role as hydrocracking catalysis in petrochemistry due to its hydrophobic surfaces [17].

2.2.5 Fourier transform infrared

Figure 4 shows the infrared absorption spectra of ZSM-5 zeolites. The band at 820–650 cm^{-1} can be assigned to symmetric stretching vibration mode of

Properties	NaZSM-5	Co/NaZSM-5	HZSM-5	Co/HZSM-5
[1]Si/Al ratio	33.19	—	35.40	—
[1]Co-loading [wt.%]	—	2.485	—	2.498
[2]S_{BET} [m^2/g]	353.8	298.7	368.3	329.6
[2]V_{total}[cc/g]	0.4004	0.3213	0.3528	0.3150
[2]V_{micro}[cc/g]	0.1099	0.1020	0.1183	0.0990
[2]V_{meso}[cc/g]	0.2905	0.2193	0.2345	0.2160
[2]Pore radius [nm]	1.907	1.918	1.899	1.914
[3]% (w/w) adsorbed H_2O	17.97	—	27.78	—

[1]AAS, [2]BET, [3]microbalance experiment.

Table 1.
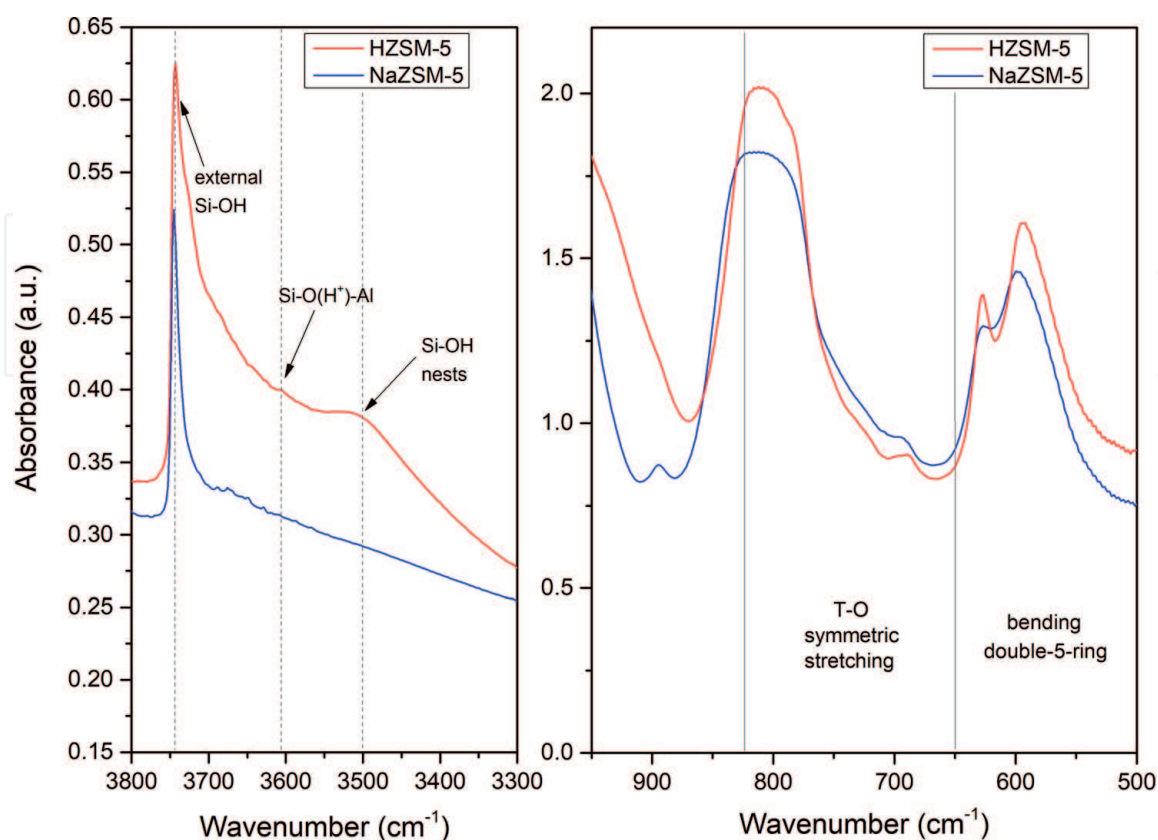*Physicochemical properties of ZSM-5 zeolites.*

Figure 4.
FTIR absorption spectra of ZSM-5 h zeolites.

T – O (T = Si or Al) and the band at 650–500 cm^{-1} that can be attributed to the pentasil double-5-ring bending vibration [18]. Absorption bands at 3745, 3605, and 3500 cm^{-1} were observed in the infrared spectra of ZSM-5 zeolites, which are assigned for the stretching vibration of terminal Si-OH, Si-O(H^{+})-Al, and Si–OH nests, respectively [19].

2.2.6 Microbalance experiments

The water adsorption capacity of NaZSM-5 h and HZSM-5 h samples, calculated from microbalance experiments, is shown in **Table 1**. After the measurement is completed, the samples were evacuated at room temperature. It is observed that the weight of the samples is decreased, close to weight before adsorption. This indicates that at room temperature, water adsorption is a reversible process as a result of water being weakly adsorbed (physisorbed) in both NaZSM-5 h and HZSM-5 h pores. The water adsorption capacity in HZSM-5 h at room temperature is higher than NaZSM-5 h. This result is consistent with the FTIR results (**Figure 4**); that is, HZSM-5 h has more silanol groups that can interact with water than NaZSM-5 h.

3. Preparation and characterization of the Co/ZSM-5 and Co/HZSM-5 catalysts

3.1 Preparation of Co/NaZSM-5 and Co/HZSM-5 zeolite catalyst

Co/NaZSM-5 h was prepared by incipient wetness impregnation method, in which 1 g of NaZSM-5 h was treated by 1.7 mL 0.2495 M Co^{2+} solution, stirred for 24 h at room temperature, and then calcined at 823 K for 3 h. Co/HZSM-5 h was prepared in a similar manner, using HZSM-5 h as starting material.

3.2 Characterization of hierarchical Co/ZSM-5 and Co/HZSM-5 zeolites

XRD, FTIR, BET, AAS, and SEM measurements were carried out on hierarchical Co/ZSM-5 and Co/HZSM-5 zeolites using similar methods as explained in 2.2, while ^{27}Al NMR spectra were recorded with a Varian Infinity Plus 400 solid-state NMR spectrometer using 90° pulses of 5 μs, a 5 s pulse delay, and a spinning rate of 4 kHz. To determine all ^{27}Al chemical shifts, kaolin was used as secondary standard. Transmission electron microscope (TEM) images were obtained using field emission TEM (300 kV) Tecnai F30 ST.

3.2.1 X-ray diffraction (XRD)

XRD pattern of Co/NaZSM-5 h and Co/HZSM-5 h in **Figure 5** shows that the ZSM-5 zeolite structure was retained after cobalt impregnation followed by calcination at 823 K on each NaZSM-5 h and HZSM-5 h, but they showed decrease in peak intensity. It is suggested that loading of Co on ZSM-5 h zeolite has caused lowering of its crystallinity. New diffraction peaks of Co$_3$O$_4$ phase (2θ = 38.6° and 47.8°) and Co$_2$SiO$_4$ phase (2θ = 56.07°) [20] are observed in XRD patterns of Co/NaZSM-5 h and Co/HZSM-5 h. This is an evidence of the presence of cobalt oxide species in the NaZSM-5 h and HZSM-5 h, respectively.

3.2.2 Surface area analysis

Figure 6 shows a decrease in surface area and total pore volume of Co/NaZSM-5 h and Co/HZSM-5 h compared to NaZSM-5 h and HZSM-5 h. More
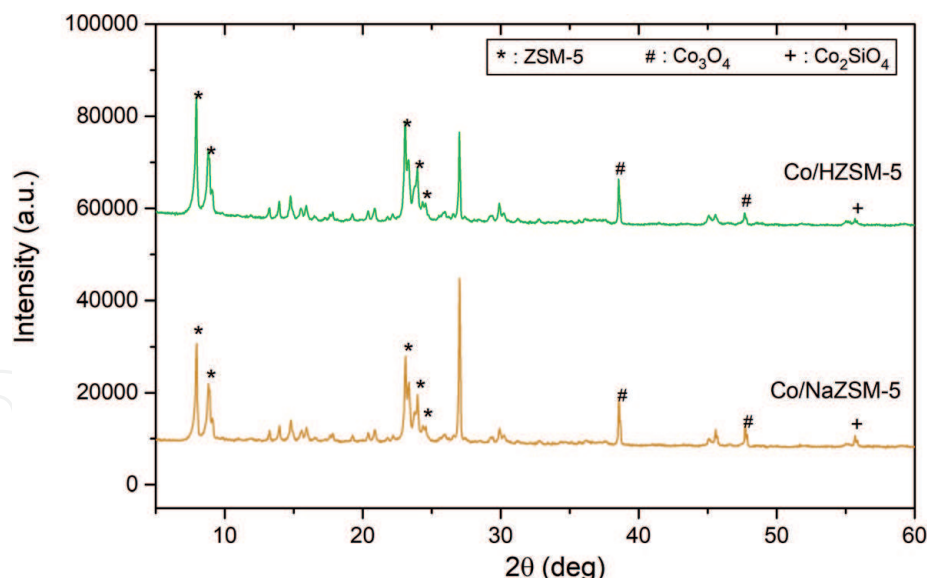
Figure 5.
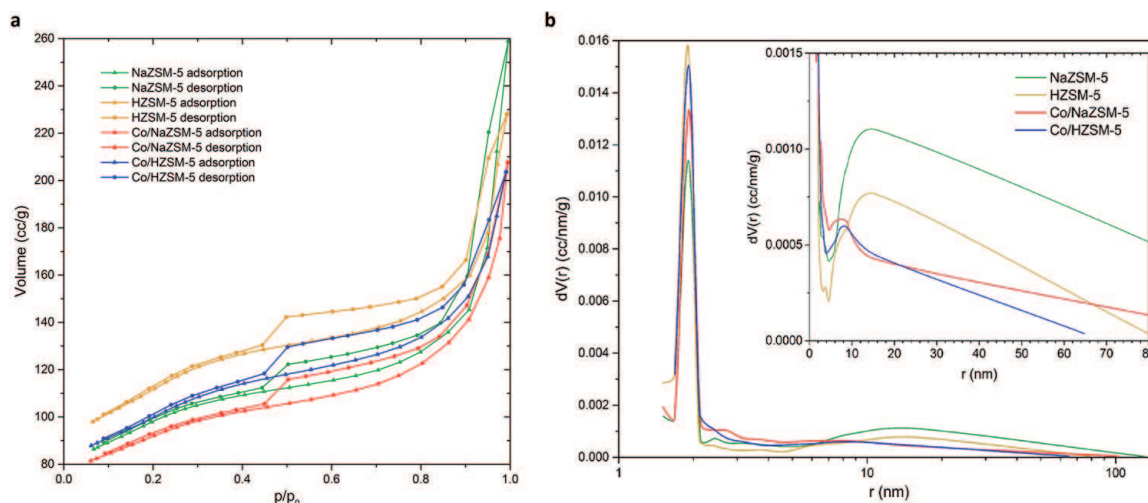*XRD pattern of Co oxide-modified ZSM-5 h zeolites.*

Figure 6.
(a) Isotherm adsorption–desorption and (b) pore-size distribution of Co/ZSM-5 h zeolites.

detailed information is summarized in **Table 1**. This proves that the cobalt species has penetrated into the pores and surface of ZSM-5 structure. Decrease of the mesopore volume was more significant than the micropore volume. It is assumed that due to less available spaces in micropore as they were already occupied by Na + ions, the counter ions, the Co^{2+} resides in the mesopore area. This reduction was more notable in NaZSM-5 h than HZSM-5 h, which is in accordance with the amount of Co loading shown in **Table 1**. It is suggested that zeolite acidity affects the amount of impregnated cobalt as the lower the acidity of zeolite, the higher the Co loading in zeolite.

3.2.3 TEM

Figure 7 shows the transmission electron microscope images from NaZSM-5 h to Co/NaZSM-5 h. It can be seen that the surface of NaZSM-5 consists of pores (lighter spots) that is in accordance with the rough morphology on the crystal surface observed by SEM. After being modified by cobalt oxide in Co/NaZSM-5 h, some area on the surface of the crystal became darker. This is indicative of the dispersion
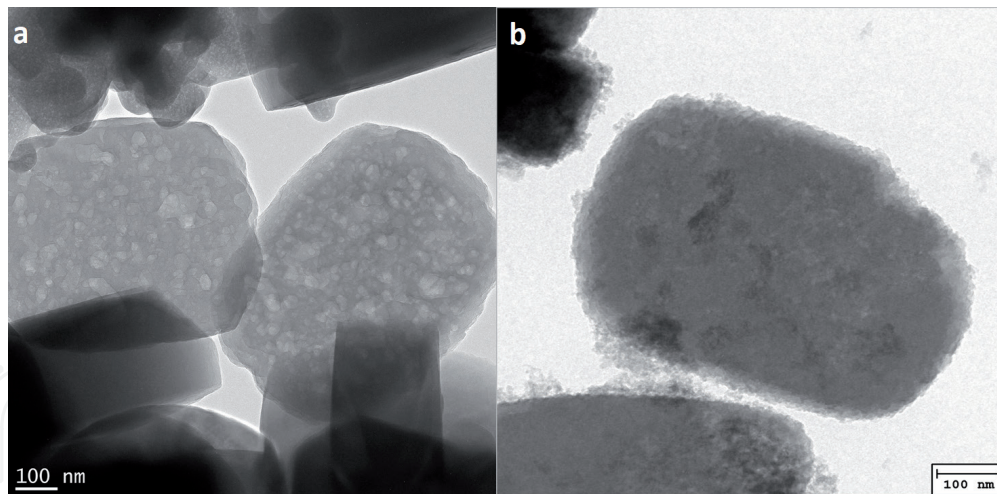
Figure 7.
TEM images of (a) NaZSM-5 h and (b) Co/NaZSM5-h.

of Co species into the pores on the surface and not creating a pool or island of cobalt oxide on the surface. This also supports the results on BET measurement that cobalt oxide prefers to reside in the mesopore.

3.2.4 Fourier transform infrared

Figure 8 shows the infrared spectra of Co/NaZSM-5 h and Co/HZSM-5 h. It can be observed that by comparing their spectra to the parent NaZSM-5 h and HZSM-5 h, respectively, it was found that cobalt impregnation decreased silanol absorption band intensity in the Si-O(H$^+$)-Al and Si-OH nests but not the terminal Si-OH, as deposited cobalt was covering silanol groups on the surfaces.
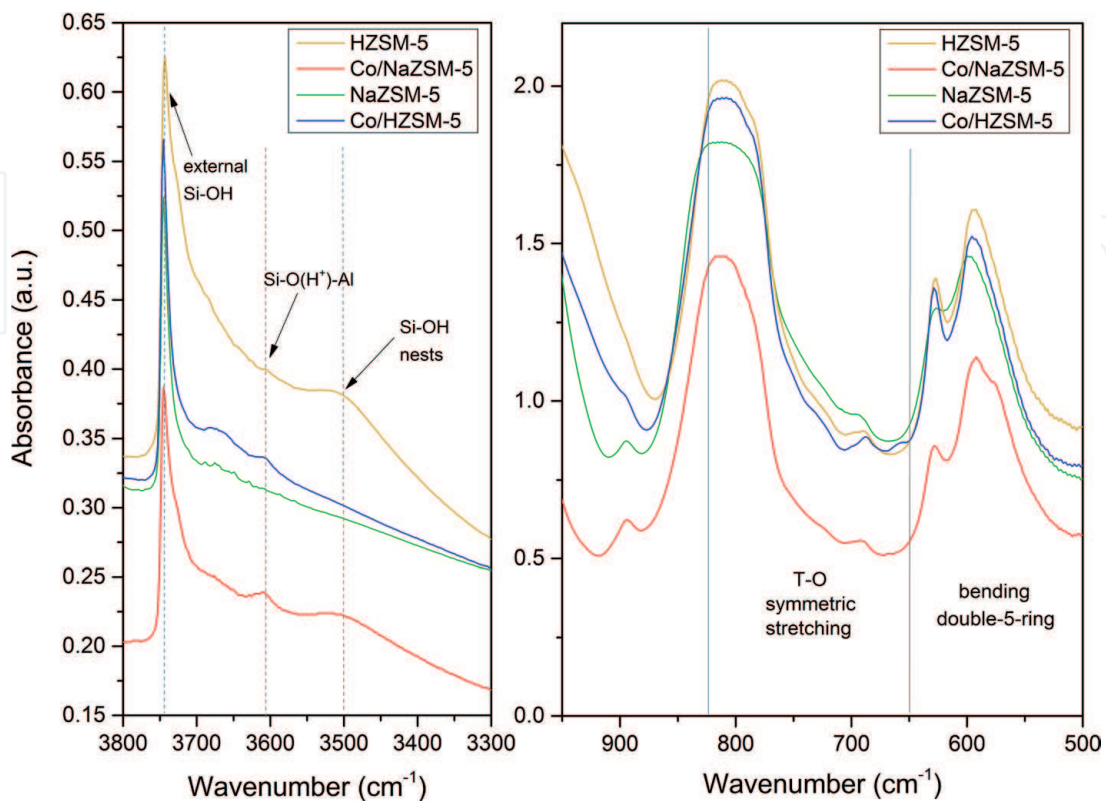

Figure 8.
FTIR absorption spectra of ZSM-5 h and Co/ZSM5-h zeolites.

3.2.5 ^{27}Al MAS NMR

Figure 9 shows ^{27}Al solid-state NMR spectra for ZSM-5 h before and after modification with acid and metal oxide. There is one main peak at 52 ppm in all ZSM-5 h zeolites, which can be assigned to the tetrahedral framework Al [16, 18]. Furthermore, ^{27}Al NMR spectra of HZSM-5 h, Co/NaZSM-5 h, and Co/HZSM-5 h were more noisy than the parent NaZSM-5 h, as a result of minor damages on zeolite framework due to acidity modification and cobalt impregnation. Furthermore, another peak at vicinity near 0 ppm, that is, attributed to octahedral non-framework Al species [21, 22], also appeared in ^{27}Al NMR spectra of Co/NaZSM-5 h and Co/HZSM-5 h.
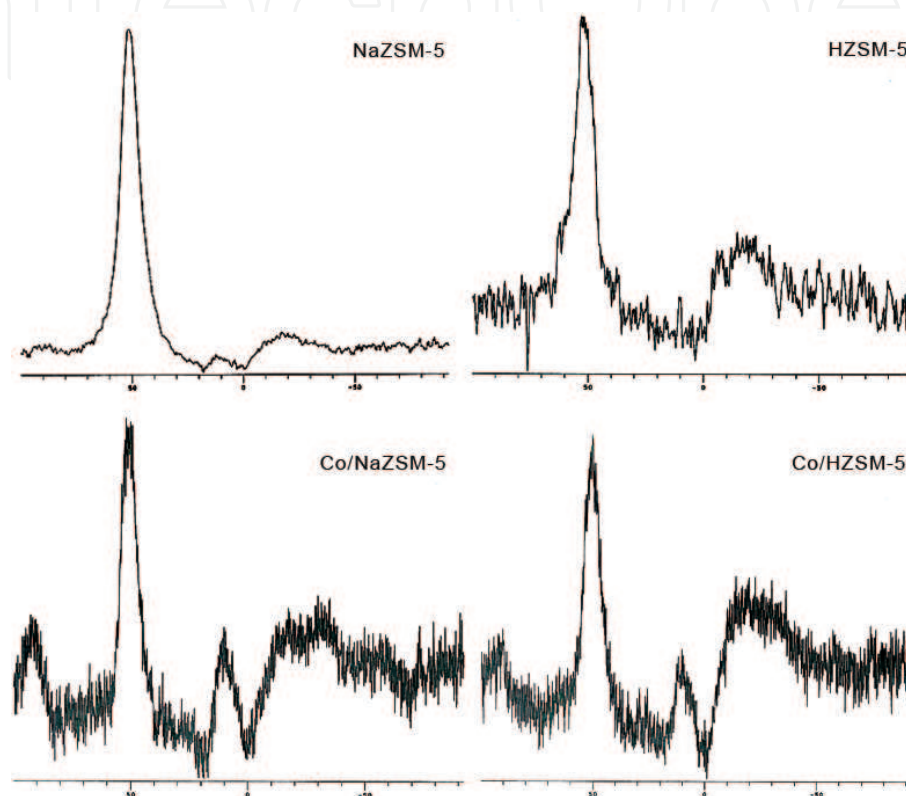

Figure 9.
^{27}Al NMR spectra of ZSM-5 h and Co/ZSM-5 h zeolites.

4. Application for partial oxidation of methane to methanol

Catalytic test on partial oxidation of methane to methanol was carried out in a stainless steel vessel as a batch reactor, following the procedure reported previously [8]. The reactor schematic diagram is shown in **Figure 10**. The catalyst used for each reaction was 0.5 g, which was activated at 773 K prior to its use. The reaction was performed at 423 K with methane pressure of 0.75 bar and a nitrogen pressure of 2 bar with a variety of reaction time of 30 minutes and 60 minutes. After the vessel was cooled down to room temperature, the product was then extracted with ethanol and characterized with GC-FID using Carbowax column. Typical chromatogram of the extracted product is shown in **Figure 11**. Methanol was determined and quantized using additional standard method. In order to observe the effect of additional O2 gas to the reaction, similar experiment was carried out using gas mixture of methane: oxygen: nitrogen (0.75: 0.1: 1.9). After the amount of methanol produced was determined, the yield of methanol was calculated as follows:

$$\% \text{ Methanol Yield} = \frac{\text{mole methanol in reaction mixture}}{\text{mole methane in the input}} \times 100\% \qquad (1)$$
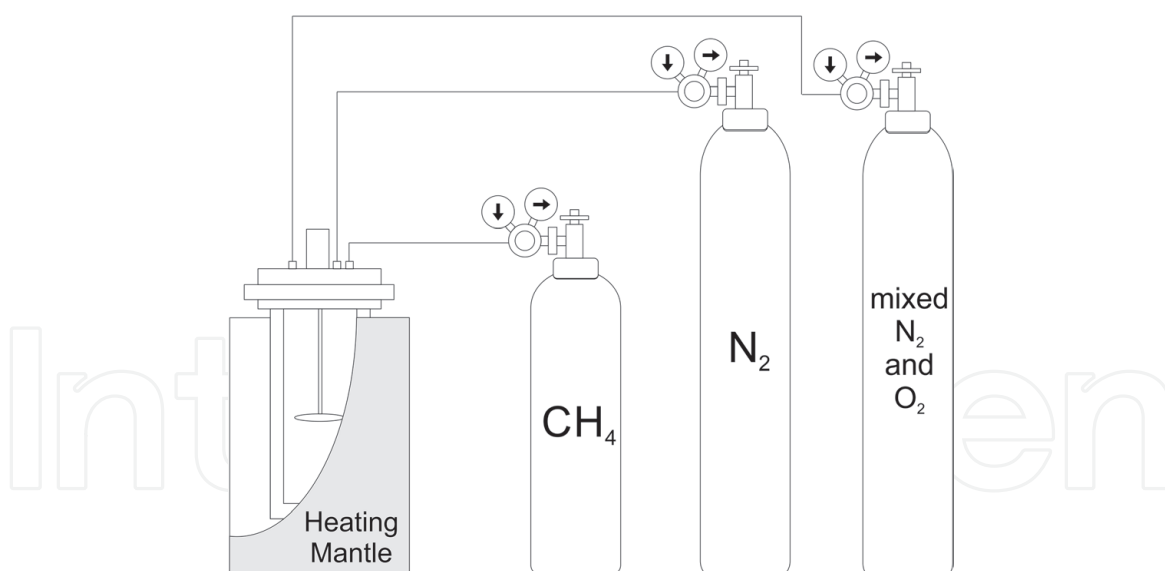
Figure 10.
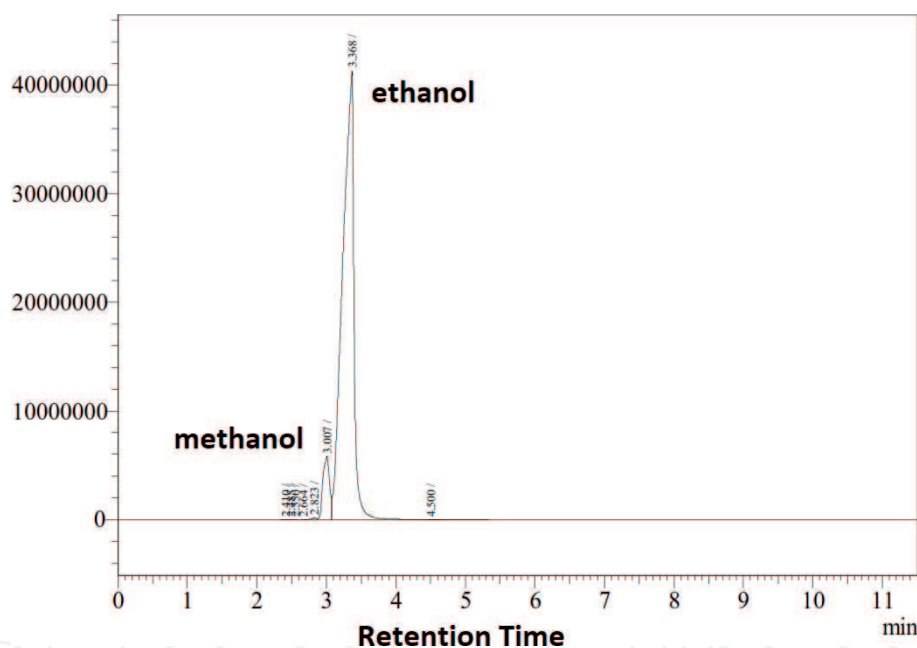*Schematic for reactor of partial oxidation of methane.*

Figure 11.
Example of chromatogram from the product mixture. [Reaction condition, 0.75 bar CH4, 2 bar N2 contains 0.5% O2; catalyst, 0.5 g Co/NaZSM-5 h; T, 150°C; t, 30 minutes].

4.1 Activity of ZSM-5 h catalysts without gas O2

The first work carried out in this partial oxidation of methane to methanol was carried out using Co/NaZSM-5 h catalysts without the presence of gas O_2 [12], based on work reported in [11]. It is shown that the partial oxidation of methane to methanol could occur without the presence of molecular oxygen, suggested that the superoxide (O^{2-}) from cobalt oxide (Co_3O_4) or surface of ZSM5 framework could act as oxidation agent at 423 K. This phenomenon has been also studied computationally in [23]. **Table 2** summarizes the results in the reaction of various ZSM-5 h without additional molecular oxygen. It can be seen that using any ZSM-5 h catalysts, the percentage (%) yield of methanol increased when the reaction time was longer and Co/HZSM-5 h is more

Reaction time (minute)	Percentage (%) yield of methanol		
	NaZSM-5 h	Co/NaZSM-5 h[5]	Co/HZSM-5 h[6]
30	3.10	8.935	N/A
60	8.40	42.56	51.55

[4]*Reaction condition: 0.75 bar CH4, 2 bar N2, 423 K, 0.5 g catalyst,* [5]*[12],* [6]*[13].*

Table 2.
Percentage (%) yield of methanol from partial oxidation of methane[4].

Reaction time (minute)	Percentage (%) yield of methanol	
	Co/NaZSM-5 h	Co/HZSM-5 h[6]
30	42.00	33.22
60	N/A	79.27
120	3.70	48.70

[7]*Reaction condition: 0.75 bar CH4, 2 bar N2 (with trace of 0.5% O2), 423 K, 0.5 g catalyst,* [6]*[13].*

Table 3.
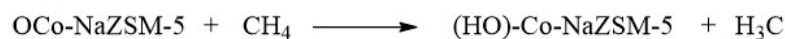*Conversion of methane to methanol in the presence of oxygen*[7].

active than Co/NaZSM-5 h catalyst. This could be indicative of contribution of Bronsted sites (-Si-OH, silanol groups) existing more significantly in HZSM-5 h than in NaZSM-5 h, as shown by FTIR spectra. The silanol groups would interact with produced methanol through hydrogen bond.

Furthermore, the effect of certain amount of molecular oxygen in the reaction was also studied. ZSM-5 h modified with Co oxide is able to catalyze the partial oxidation of methane with O2 as the oxidant [24]. The reaction results were tabulated in **Table 3**. It shows that the presence of molecular oxygen in the reaction system could increase the yield of methanol, so that the reaction could occur in shorter reaction time. For example, when Co/NaZSM-5 h was used in reaction time of 30 min, the percentage (%) yield of methanol for condition with additional oxygen is 42%, which is 4.7 times more than the reaction without oxygen. Similar results were also obtained using Co/HZSM-5 h as catalyst in 60 minute reaction time; the percentage (%) yield of methanol is 1.5 times higher in the presence of molecular oxygen. The effect of oxygen is more apparent when using Co/NaZSM-5 in 30 minute reaction time. Moreover, using Co/HZSM-5 h as catalyst and in the presence of oxygen, the percentage (%) yield of methanol reached the highest when the reaction took place for 60 min and then decreased after 120 minutes of reaction. The percentage (%) yield of methanol even significantly decreased when Co/NaZSM-5 h was employed for 120 min. It is suggested that the additional oxygen, in short reaction time, could regenerate the Co oxide species after their superoxides (O^{2-}) are being used to oxidize methane. However, in longer reaction time, the additional oxygen could also oxidize further the produced methanol to CO_2. As a result, complete oxidation takes place.
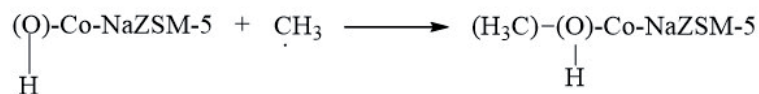
4.2 Reaction mechanism

Plausible reaction mechanism of partial oxidation of methane to methanol is proposed as shown in **Figure 12**. It is a modification from the mechanism reported in [23].
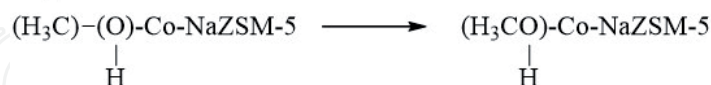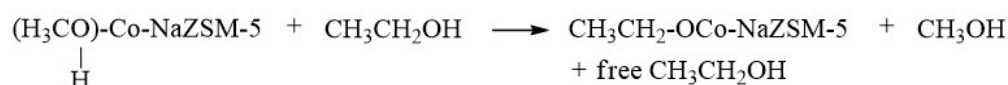
Step 1. Activation of C-H

OCo-NaZSM-5 + CH$_4$ ⟶ (HO)-Co-NaZSM-5 + H$_3$C·

Step 2. Formation of hydroxyl complex

(O)-Co-NaZSM-5 + CH$_3$· ⟶ (H$_3$C)-(O)-Co-NaZSM-5
| |
H   H

Step 3. Formation of methanol

(H$_3$C)-(O)-Co-NaZSM-5 ⟶ (H$_3$CO)-Co-NaZSM-5
| |
H   H

Step 4. Desorption of methanol (extraction with ethanol)

(H$_3$CO)-Co-NaZSM-5 + CH$_3$CH$_2$OH ⟶ CH$_3$CH$_2$-OCo-NaZSM-5 + CH$_3$OH
| + free CH$_3$CH$_2$OH
H

Step 5. Reactivation of active site (during calcination in the presence of O$_2$)

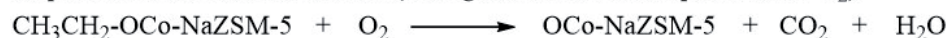CH$_3$CH$_2$-OCo-NaZSM-5 + O$_2$ ⟶ OCo-NaZSM-5 + CO$_2$ + H$_2$O

Figure 12.
Schematic diagram of plausible mechanism reaction of partial oxidation of methane on Co/NaZSM-5.

5. Future prospect

5.1 Utilization of synthesis of hierarchical NaZSM-5

Synthesis of zeolites using natural resources such as kaolin, natural zeolites, coal fly ash, and rice husk has drawn many researchers since decades ago [25]. Especially in developing countries, this work by Chareonpanich et al. [26] has been a success to the synthesis of ZSM-5 zeolite from lignite coal fly ash and rice husk to produce microporous ZSM-5. Our group has reported the synthesis of hierarchical ZSM-5 using similar procedure, with addition of secondary template (labeled as nZSM-5) [27] as the synthesis mentioned earlier in this chapter. The zeolite from this work has MFI structure although the crystallinity was lower than the pro-analysis sourced-synthetic ZSM-5. Nevertheless, the activity of Co/nZSM-5 was comparable to that of Co/cZSM-5 (prepared from commercially available NaZSM-5 with Si/Al 6.82). Synthesis of ZSM-5 using kaolin and natural zeolite and its activity as catalyst for methane oxidation is also carried out, and it is still an undergoing work.

5.2 Bio-methane as feed

Biogas is one of environmentally friendly renewable energy sources, and its utilization is very economically profitable [28]. Biogas is generally produced from anaerobic organic waste derived from the environment such as livestock manure, containing methane and carbon dioxide as the largest component and a small amount of nitrogen compounds, oxygen, hydrogen sulfide, halogen compounds, and aromatics [29]. In general, biogas can be used in combustion engines [28]; however, direct use of biogas on combustion engines can produce toxic emissions with low efficiency of biogas utilization. In our work [29], utilization of biogas as feed to be partially oxidized to methanol has been studied. Since biogas, obtained from the local biogas farm industry, consists mainly of methane (83.7%) and oxygen (16%), it is directly used without purification. The challenge faced was to compress the biogas in order to feed the reactor as much as the ultrahigh purity (UHP) methane

gas. This is due to the relatively high oxygen content. Thus, the concentration of biogas (0.17 bar) fed to the reactor was much lesser than the previous UHP methane gas (0.75 bar). Nevertheless, the partial oxidation reaction of methane without additional oxygen gave 10.99% of percentage (%) yield of methanol compared to 40.56% when UHP methane was used.

6. Conclusion

Here are some remarks that could be drawn from this chapter:

1. NaZSM-5 h, HZSM-5 h, Co/NaZSM-5 h, and Co/HZSM-5 h zeolites have been characterized extensively. NaZSM-5 that is converted to HZSM-5 has more silanol functional groups and Bronsted acid sites. After impregnation with cobalt oxides, NaZSM-5 shows more decreasing pore volume and surface area than HZSM-5.

2. Acidity of ZSM-5 zeolite as support catalyst influences the percentage (%) yield of methanol, and further oxidation of methanol is decreased when acidity of zeolite is higher.

3. There is a prospect for hierarchical ZSM-5 synthesized from natural source and waste to be utilized as catalyst or support catalyst, as for partial oxidation of methane.

4. There is room for research on utilization of biogas to be partially oxidized to methanol. This also leads to other heterogeneous catalytic reactions of methane.

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Conflict of interest

There are no conflicts of interest to declare.

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