DIRECT SYNTHESIS OF METHANOL BY PARTIAL OXIDATION OF METHANE WITH OXYGEN OVER COBALT MODIFIED MESOPOROUS H-ZSM-5 CATALYST

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ABSTRACT

Partial oxidation of methane over mesoporous catalyst cobalt modified H-ZSM-5 has been carried out. Mesoporous Na-ZSM-5 (Si/Al = 35.4) was successfully synthesized using double template method which has high surface area (450 m^2/g) and average pore diameter distribution of 1.9 nm. The as-synthesized Na-ZSM-5 was converted to H-ZSM-5 through multi-exchange treatment with ammonium ion solution, causing decreased crystallinity and surface area, but increased porous diameter, due to dealumination during treatment process. Moreover, H-ZSM-5 was loaded with cobalt (Co = 2.5% w) by the incipient impregnation method and calcined at 550 °C. Partial oxidation of methane was performed in the batch reactor with 0.75 bar methane and 2 bar of nitrogen (with impurities of 0.5% oxygen) as the input at various reaction time (30, 60 and 120 min). The reaction results show that cobalt species in catalyst has an important role, because H-ZSM-5 cannot produce methanol in partial oxidation of methane. The presence of molecular oxygen increased the percentage of methanol yield. The reaction is time-dependent with the highest methanol yield (79%) was acquired using Co/H-ZSM-5 catalyst for 60 min.

Keywords: methanol; methane; partial oxidation; H-ZSM-5; cobalt

ABSTRAK

Oksidasi parsial metana pada katalis mesopori H-ZSM-5 termodifikasi kobalt telah dilakukan. Na-ZSM-5 mesopori (Si/Al = 35,4) telah berhasil disintesis dengan menggunakan metode double template dengan luas permukaan yang besar (450 m^2/g) dan dengan rata-rata distribusi ukuran pori 1,9 nm. Na-ZSM-5 yang telah disintesis dikonversi menjadi H-ZSM-5 dengan pertukaran ion beberapa kali dalam larutan ammonium nitrat yang menyebabkan berkurangnya kristanilitas dan luas permukaan, tetapi meningkatkan diameter pori, karena terjadinya dealuminasi selama proses ini. H-ZSM-5 kemudian disisipi kobalt (Co = 2,5% w) dengan menggunakan metode impregnasi dan dikalsinasi pada 550 °C. Oksidasi parsial metana dilakukan pada batch reactor dengan 0,75 bar metana dan 2 bar nitrogen (mengandung 0,5% gas oksigen) sebagai input dengan variasi waktu reaksi (30, 60 dan 120 menit). Hasil reaksi menunjukan bahwa spesi kobalt dalam katalis memiliki peranan penting, karena H-ZSM-5 tidak dapat memproduksi methanol pada reaksi oksidasi parsial metana. Dengan adanya gas oksigen, yield metanol meningkat. Reaksi ini bergantung pada waktu dengan yield metanol tertinggi (79%) didapat dari katalis Co/H-ZSM-5 selama 60 menit.

Kata Kunci: methanol; metana; oksidasi parsial; H-ZSM-5; kobal

INTRODUCTION

Due to the harmful for life, the presence of methane in atmosphere has been concerned. Methane is one of greenhouse gas which caused greenhouse effect. After water vapor and carbon dioxide, methane is most abundant greenhouse gas in atmosphere. The emission of methane to atmosphere is from human and natural activities. Major source of methane emission is petroleum industry. Methane is primary component of natural gas. The second source is natural source, which

is inevitable. Ruminants produced high number of methane from its digestive system. The high concentration of methane in atmosphere was potential for conversion methane to useful compound such as methane oxygenate compound [1].

Direct conversion of methane to oxygenate compound has been reported in several papers [2-11]. Ono et al. has reported oxidation of methane using molecular oxygen as oxidant using silicon-rich ZSM-5 which produced methanol and formaldehyde [7]. Direct conversion of methane had also reported using metal

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oxide containing ZSM-5. Michalkiewicz [8] used Fe-ZSM-5 as catalyst for partial oxidation of methane with molecular oxygen and produced methanol and formaldehyde. The yield and selectivity of methanol depend on the Si/Fe molar ratio and the highest yield was reported at 31.51% with the selectivity to methanol of 10.37% using Fe/H-ZSM-5 catalyst. Bezniz et al. [9-10] all had been reported partial oxidation of methane using Co-ZSM-5 and the effect of catalyst preparation route and ZSM-5 treatment has also reported. This work concludes that cobalt ion-exchanged ZSM-5 resulted mainly in the formation of formaldehyde, while larger Co-oxide particles prepared by impregnation led in the formation of methanol. Our previous work [11] also reported that this reaction depend on the pore size and type of Co-species in the surface of ZSM-5. This work concluded that larger pore size of ZSM-5 resulted in higher conversion percentage and impregnation method created more active Co-oxide compound than ion-exchange method.

Microporous ZSM-5 has small pores which significantly influence the mass transport and the amount of active site, which further limits the application of zeolites as catalyst [12-14]. Mesoporous ZSM-5 is one of the answers of small pores problem. Mesoporosity of zeolite has been introduced by various synthesis routes and modification methods [14-16]. Wang et al. [15] has successfully synthesized mesoporous ZSM-5 using two templates in which tetrapropylammonium hydroxide acting as MFI structure directing agent and cationic dimethyldiallyl ammonium chloride acrylamide copolymer is used as mesoporous directing agent. The hydrophilic cationic polymer is selected due to feasible dispersion into synthesis solution and to increase the interaction with the negatively-charged silica species during the crystallization of zeolites.

In our work, mesoporous ZSM-5 synthesized using similar method to Wang et al [15] and converted into acidic H-ZSM-5. Then, a cobalt modified H-ZSM-5 catalyst were prepared, characterized and employed for the partial oxidation of methane to methanol. The Co/H-ZSM-5 showed higher activity compared with non-modified H-ZSM-5. Optimum reaction time was also determined.

EXPERIMENTAL SECTION

Material and Catalyst

The procedure for mesoporous Na-ZSM-5 synthesis was adopted from Wang et al. works [15]. About 0.1 g of $NaAlO_2$ (Sigma Aldrich), 12.06 g of tetrapropylammonium hydroxide, TPAOH (1 M in water, Sigma Aldrich) and 7.88 g of tetraethyl orthosilicate, TEOS (98% in water, Sigma Aldrich) was dissolved in 28.21 g water in 250 mL of propylene bottle under stirring in 100 °C. Then the pH of solution was set to be 11 using acetic acid glacial. After 3 h under stirring, 1 g of cationic dimethyldiallyl ammonium chloride acrylamide copolymer, PDDA (35% in water, Sigma Aldrich) was added into the mixture. After 15 h stirring, the mixture was transferred into an autoclave for further crystallization at 150 °C for 144 h. The reaction mixture was collected by filtration and dried at room temperature and calcined at 550 °C for 8 h. Si/Al ratio was determined by AAS.

H-ZSM-5 was synthesized through multiple ion-exchange of Na-ZSM-5 with ammonium ions. Approximately 1 g of Na-ZSM-5 was dispersed in 1 M NH_4NO_3 solution under stirring for 18 h at 60 °C. The white crystal was collected with filtration then dried at room temperature and calcined at 550 °C for 6 h.

The catalyst was prepared by impregnation of cobalt(III) to H-ZSM-5 in incipient wetness. The impregnation process was deployed by dispersing 1 g of H-ZSM-5 in 1.7 mL of $Co(NO_3)_3$ 0.25 M solution under vigorous stirring for 24 h at room temperature. The impregnated H-ZSM-5 were dried at room temperature overnight and calcined at 550 °C for 3 h. The resulted catalyst contained 2.5% of cobalt, as confirmed by AAS, and labeled as Co/H-ZSM-5.

Characterization

To determine the Si/Al ratio and the amount of cobalt in impregnated H-ZSM-5, the sample was dissolved in HNO_3 and HF and then the corresponding metal content was determined by Shimadzu AA–6300 type AAS instrument. The X-Ray diffraction pattern of the sample was recorded with D8 Advance Bruker Co XRD type with Cu Kα ($λ$ = 1.54056 Å) in the range of 5-50°. Nitrogen Adsorption-desorption isotherms at -196 °C were measured using an Autosorb iQ system. The samples were outgassed for 6 h at 300 °C before the measurements. The surface area was calculated following typical BET procedures. Pore size distribution was obtained using BJH pore analysis. Micropore volume was obtained by t-plot analysis. Total pore volume was obtained from the amount of nitrogen adsorbed at P/P_o of ca. 0.99. Mesopore volume was calculated by subtracting micropore volume from total volume.

Reaction Procedure

Partial oxidation of methane was carried out in a batch reactor with the volume of 300 mL. Each reaction was performed with 0.5 g of catalyst, 0.75 bar of methane and 2 bar of 0.5% oxygen in nitrogen in various reaction times and temperature. After the

reaction reached desirable time and the reactor was cooled down until room temperature, 2 mL of ethanol as extractant was injected to the reactor. The reaction mixture and catalyst were separated with centrifugation method.

Product Determination

For the determination of methanol content in the reaction mixture, GC-2010 type of gas chromatography instrument with HP-Carbowax column and FID detector was used, employing isocratic mode at 30 °C. The determination of methanol was carried out using standard addition method. After the mole of methanol in reaction mixture determined, the yield of methanol could be calculated using the equation below.

$$\% \text{ Methanol Yield} = \frac{\text{mole methanol in reaction mixture}}{\text{mole methane in the input}}$$

RESULT AND DISCUSSION

Catalyst Characterization

X-ray powder diffraction

All the XRD patterns of Na-ZSM-5, H-ZSM-5 and Co/H-ZSM-5 are shown in Fig. 1. All the samples have similar XRD pattern. Synthesized Na-ZSM-5 has exhibited the characteristic of peaks associated with MFI (Mordenite Framework Inverted) structure [17], which means Na-ZSM-5 had been successfully synthesized. SEM image of single crystal of Na-ZSM-5 is shown in Fig. 2. AAS result shows that Si/Al ratio of synthesized Na-ZSM-5 is 35. H-ZSM-5 and Co/H-ZSM-5 had the MFI identical peaks in XRD pattern. This indicates that the ion exchange treatment with ammonium ion and impregnation with cobalt(III) ion has not affected the structure of ZSM-5. The decreased of intensity at 2θ 22–25° between all the samples show the decreased of the crystallinity of the sample. The decrease of crystallinity in H-ZSM-5 occurred due to dealumination process because of the acidic ammonium solution [18]. A small peak of Co_3O_4 were observed in the cobalt impregnated ZSM-5 XRD pattern, in 2θ 31.8° and 47.8° which also reported by Zhang et al. [19].

SEM images

Fig. 2 shows the SEM images of the surface of Na-ZSM-5. It is shown in Fig. 2a uniform coffin-like crystals which is typical shape for ZSM-5 crystals [20]. Fig. 2b shows a closer image of Na-ZSM-5 crystal, which has dimension of 1.9 μm x 1.1 μm and has strikingly rough surface. This occurred due to the use of cationic surfactant as a template. Wang et al reported that the rough surface of ZSM-5 is one of the characteristic of mesoporosity in ZSM-5 structure [15]. As comparison,
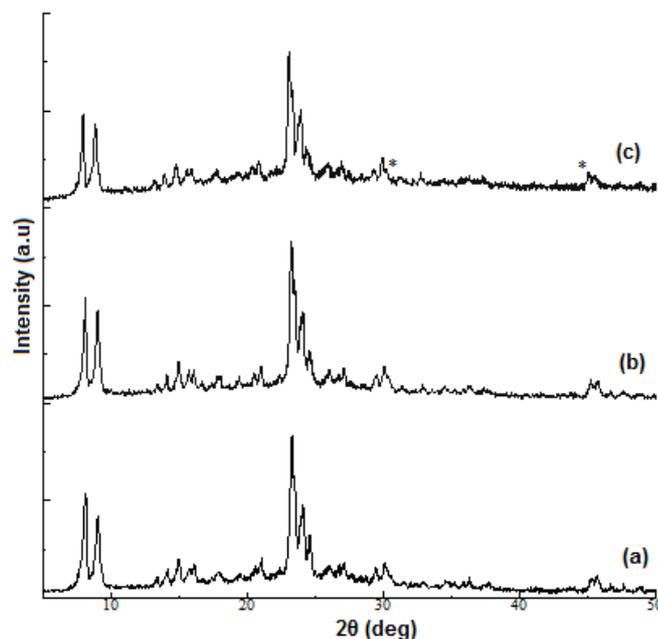
Fig 1. XRD pattern of a. Na-ZSM-5, b. H-ZSM-5 and c. Co/H-ZSM-5 (* = corresponding to Co_3O_4)
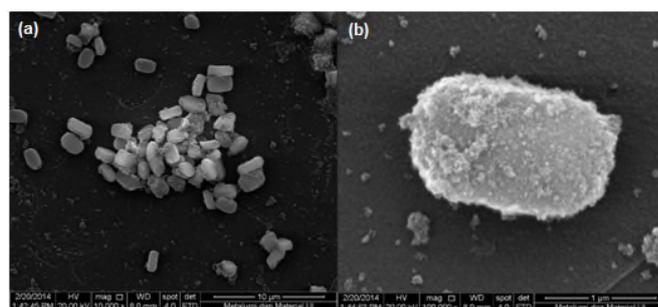
Fig 2. SEM image of Na-ZSM-5 (a) 10000x magnitude (b) 100000x magnitude

SEM images of Na-ZSM-5 show relatively smooth surface [21].

FT-IR spectra

All the infrared spectra of the sample have broad band at 3350–3650 cm^{-1} that corresponds to the stretching vibration of hydroxyl group (Fig. 3). This v-OH comes from adsorbed water and Si-OH and Al-OH groups from ZSM-5 surface. The intensity of silanol group of each sample is different in which the H-ZSM-5 gives the highest. A new peak appears at 1400 cm^{-1} after Na-ZSM-5 dispersed in ammonium ion solution (Fig. 3b), which corresponds to bending of N-H group from ammonium ion [22]. The silanol group vibration becomes broader due to the addition of hydrogen bonding, between ammonium and silanol groups on ZSM-5 surface. During calcination, the ammonia is removed and results in H-ZSM-5. The increase intensity
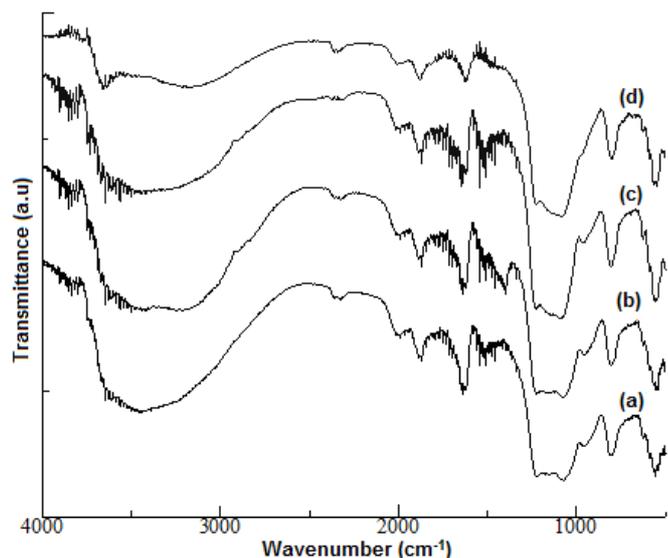
Fig 3. FTIR spectra of all ZSM-5 samples, a. Na-ZSM-5, b. NH4-ZSM-5, c. H-ZSM-5, d. Co/H-ZSM-5
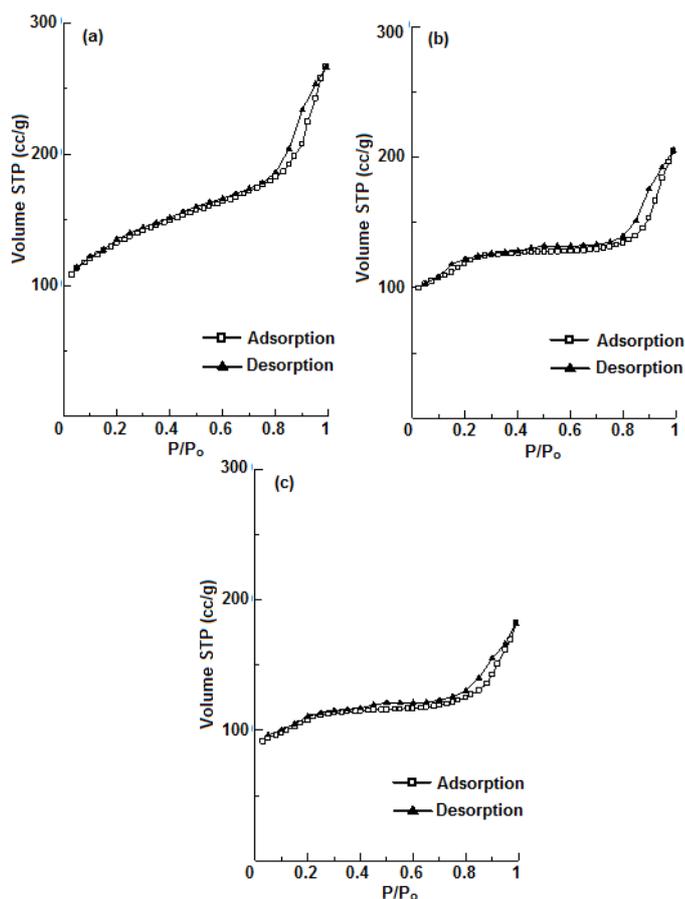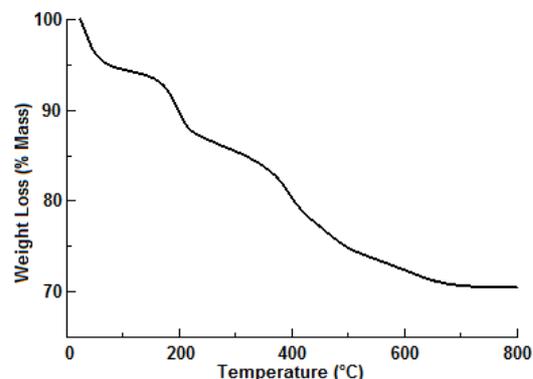
Fig 4. TG curve of uncalcinated Na-ZSM-5

Table 1. The properties of ZSM-5 catalyst determined by surface are analysis

	S_{BET} [m^2/g]	V_{total} [cc/g]	V_{meso} [cc/g]	V_{micro} [cc/g]	Pore Size [nm]
Na-ZSM-5	450.14	0.413	0.325	0.088	1.891
H-ZSM-5	408.26	0.317	0.256	0.061	1.984
Co/H-ZSM-5	364.87	0.281	0.218	0.063	1.87

of peak attributed to silanol group vibration and the disappearing of peak assigned to bending of ammonium show that H-ZSM-5 had been synthesized successfully (Fig. 3c). The impregnation of cobalt reduced the intensity of peak related to silanol group vibration (Fig. 3d). This happened because most metal loaded ZSM-5 decreased probably due to the extraction of the silanol groups into the acidic solution [23].

Thermal analysis

The Thermogravimetric (TG) curve of templated Na-ZSM-5 is shown in Fig. 4. Thermal analysis was performed to study the process that occurred during calcination. TG curve shows several declines which indicate the weight loss at certain temperature. The slight weight loss around under 150 °C is due to the removal of physisorbed water. The second weight loss within 200–440 °C corresponds to the decomposition and removal of cationic polymer. The last weight loss in the region of 440–510 °C corresponds to the decomposition of TPA, the ZSM-5 structure directing agent [15]. The wide temperature range of TG analysis explains that the cationic polymer is located inside the ZSM-5 framework. The formation of mesoporosity occurs when is removed during calcination. These results are in agreement with the hysteresis loop observed in nitrogen adsorption experiment.

N₂ adsorption-desorption

Brunauer–Emmett–Teller (BET) model equation was carried out to determine the surface area and porous nature of the samples. Nitrogen adsorption–

Fig 5. Isotherm Adsorption of a. As-synthesized Na-ZSM-5, b. H-ZSM-5 and c. Co/H-ZSM-5
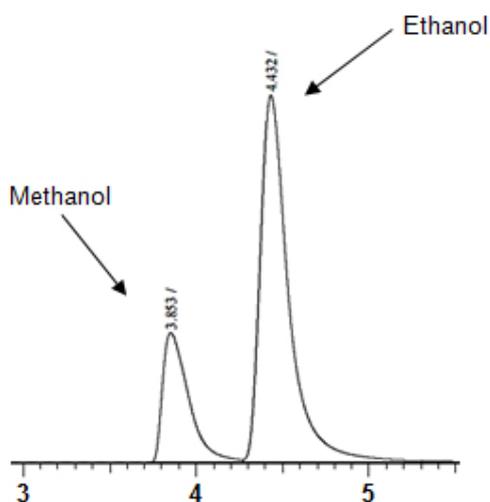
Fig 6. Example of chromatogram from the product mixture (Reaction condition: 0.75 bar CH_4, 2 bar 0.5% O_2 in N_2, temperature: 150 °C, 0.5 g Co/H-ZSM-5 as catalyst, 30 min)
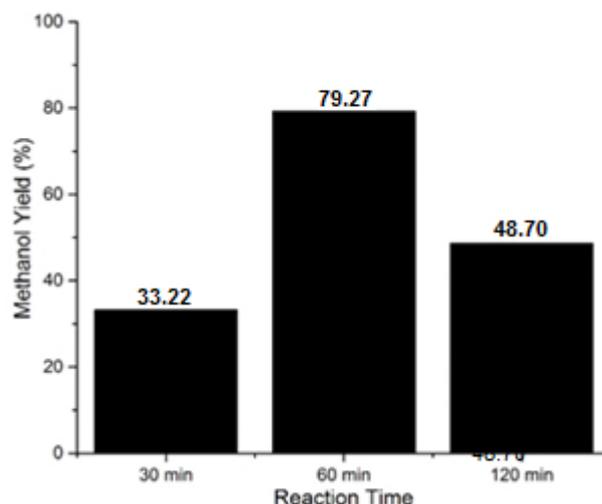
Fig 7. The reaction result of partial oxidation of methane to methanol in various time reaction (Reaction condition: 0.75 bar CH_4, 2 bar 0.5% O_2 in N_2, 150 °C, 0.5 g Co/H-ZSM-5 as catalyst)
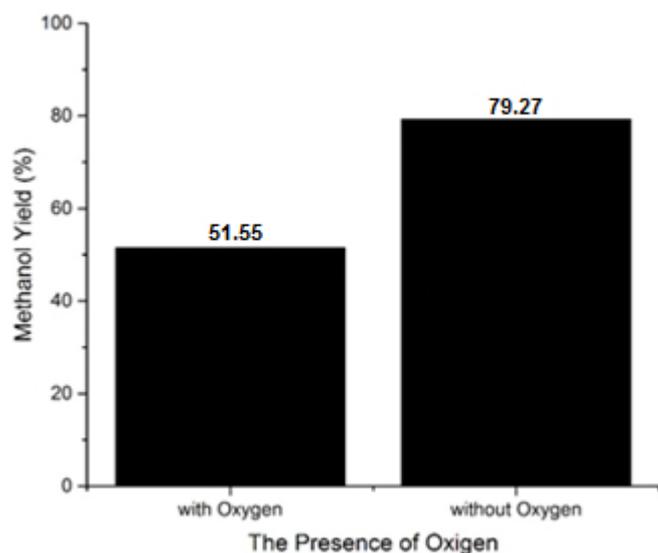
Fig 8. The effect of oxygen on the reaction result of partial oxidation of methane to methanol [Reaction condition: 0.75 bar CH_4, 2 bar 0.5% O_2 in N_2, 150 °C, 60 min, Co/H-ZSM-5 as catalyst]

desorption isotherms curves of Na-ZSM-5, H-ZSM-5, and Co/H-ZSM-5 are given in Fig. 5. According to the IUPAC classification of physisorption isotherms, all samples exhibit the typical type IV curves with shaped hysteresis loops. Type IV isotherm is a characteristic of mesoporous materials. The BET surface area, pore size and pore volume of the samples are listed in Table 1. The dealumination process occurring during ammonium-exchange treatment has increased the pore size and reduced the surface are of ZSM-5 (Fig. 5b).

Furthermore, the decrease in surface area, total volume and pore size of Co/H-ZSM-5 indicates that cobalt is inside the pores of ZSM-5. This is consistent to our previous work [11]. The significant decreased of meso volume than micro volume indicated than the position of cobalt species is likely in the mesopores.

Catalytic Activity

In order to investigate catalytic activity, 0.5 g of Co/H-ZSM-5 is exposed in 0.75 bar of methane and 2 bar 0.5% oxygen in nitrogen at 150 °C in several reaction time. Since the reaction products were strongly adsorbed on the surface of the catalyst, an extraction procedure is needed to evaluate the catalytic activity of the samples. The extraction was performed using ethanol as extractant. GC analyses were performed to determine the amount of methanol.

Fig. 6 showed the typical chromatogram of reaction mixture which contain methanol in ethanol.

Fig. 7 summarized the result of reactions carried out in various reaction times. The experimental result shows that the methanol yield was significantly increased for the first 60 min, which double the methanol produced in 30 min reaction. After 60 min reaction, the methanol yield is gradually decreased. In longer reaction time, it is possible that complete oxidation occurs, producing carbon dioxide and water [24].

Non-modified H-ZSM-5 was also used as catalyst in similar reaction, but methanol was not produced [not shown in this paper]. This result indicates that cobalt oxide species in the surface of ZSM-5 has important

role in the reaction, as the active sites of the catalyst. Fellah et al. described the role of this cobalt oxide species is to activate the C-H bond and produce unstable methyl radical [25]. Furthermore, the effect of certain amount of molecular oxygen in the reaction was also studied. The reaction result (Fig. 8) shows that the presence of oxygen in the reaction system could increase the yield of methanol. In other word, it could assist for reaction to take place in shorter reaction time. When reaction took place without oxygen, it is suggested the oxygen (in form of O^{2-}) from cobalt oxide or ZSM-5 surface act as oxidation agent [25].

CONCLUSION

Partial oxidation of methane in the presence of oxygen over cobalt modified mesoporous H-ZSM-5 catalyst has been successfully carried out at mild condition. The presence of cobalt oxide species in the surface of H-ZSM-5 is shown to be crucial, because non-modified H-ZSM-5 has no catalytic activity for this reaction. Finally, this mesoporous catalyst is promising to be used as catalyst to directly convert methane to methanol.

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