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by Teh Lee Peng

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Catalytic CO Methanation over Mesoporous ZSM5 with Different Metal Promoters

Teh Lee Peng [1] *, Sugeng Triwahyono [2], Aishah Abdul Jalil [3,4], Herma Dina Setiabudi [5,6], Muhammad Arif Ab Aziz [3,7]

Abstract

The carbon monoxide methanation has possessed huge potential as an effective method to produce synthetic natural gas (SNG). The basic requirements such as high catalytic activity at low temperatures (<500 °C) and high stability throughout all temperatures is needed for an ideal methanation catalysts. The ultimate goal of the study is to examine the influential of different metal promoters towards catalytic properties and catalytic CO methanation performance. A series of metal promoters (Rh, Co, Pd and Zn) mesoporous ZSM5 were synthesized using an incipient-wetness impregnation method and evaluated for catalytic CO methanation. XRD analysis showed that only metal oxides and no metallic phase of Rh, Co, Pd and Zn were observed. The nitrogen physisorption analysis showed that mZSM5 possessed high surface area and micro-mesoporosity with intra- and interparticle pores. FESEM analysis illustrated that mZSM5 had typical coffin-type morphology and Rh metal dispersed on the surface of the support was confirmed by EDX analysis. Moreover, Rh (CO conversion = 95%, CH_4 yield = 82%) and Co (CO conversion = 91%, CH_4 yield = 71%) promoters showed significant improvement in CO methanation. On the other hand, Pd (CO conversion = 18%, CH_4 yield = 12%) and Zn (CO conversion = 10%, CH_4 yield = 9%) promoters had only low benefit to the CO methanation. This study affirmed that the catalytic activity of CO methanation was influenced by the variation in the type of metal loading due to different nature of metallic phases and their synergistic interaction with the supporting material.

Keywords: Synthetic Natural Gas, CO Methanation, Mesoporous ZSM5, Metal Promoters, Rh

1. Introduction

Recent years, CO methanation has gained widespread attention in the production of synthetic natural gas (SNG) and appeared to be a promising approach due to growing demand for natural gas as an important future energy carrier [1-2]. The CO methanation reaction occurs as follows [3-4]:

$$3H_2 + CO \rightarrow CH_4 + H_2O \qquad \Delta H_{298K} = -206.1\ \text{kJ mol}^{-1} \tag{1}$$

In CO methanation, nickel-based catalysts [5-7] are undeniably known as the reference for methanation benchmark. Unfortunately, the highly exothermic nature of the methanation reaction have resulted in Ni sintering and carbon formation. Therefore, it is urgent need to design and develop new material for CO methanation as the alternative for the well-established Ni-based catalysts. It is noteworthy that supporting material played a significant role on the catalytic performance. Mesoporous zeolite is a type of material, which is the combination of microporous structure with additional intracrystalline or intercrystalline mesoporous. It demonstrated excellent catalytic activity in alkylation and cracking [8], methanol-to-olefins (MTO) [9-10], adsorption reaction [11] and CO_2 capture [12]. Gua et al. studied CO_2 methanation over mesoporous Ni/ZSM5, Ni/SBA-15, Ni/MCM-41, Ni/Al_2O_3 and Ni/SiO_2. The presence of basic property and the metal-support synergistic effect is the main reason of Ni/ZSM-5 as the most active methanation catalyst among all the mesoporous supports. Moreover, it also presented superb anti-coking and anti-sintering properties [13]. Therefore, mesoporous ZSM5 (mZSM5) can be a better alternative for CO methanation.

Besides, it is well known that different metal promoters exhibited different catalytic properties and performance. In literatures, the effective and convenient way to improve the catalytic methanation activity is by addition of metal promoters. Furthermore, it should be noted that the rate controlling step in CO methanation is believed to be CO dissociation in which this dissociation step is structure-sensitive dependent and happen on metallic phase [14]. Panagiotopoulou [15] studied hydrogenation of CO_2 over Rh/TiO_2, Ru/TiO_2, Pt/TiO_2 and Pd/TiO_2 catalysts. They reported that catalytic methanation activity of Rh catalyst is more active than Ru catalyst. On the contrary, Pd and Pt catalyst are practically inactive. The results significantly depend on the nature of the metallic phase. Zhang et al. [16] studied the promotional effect of cobalt on MoS_2 catalyst for CO methanation using a density functional study. It is noted that cobalt metal demonstrated promoting effects on the MoS_2 and provided easiness of OH species removal for continuous vacant of active sites which can be always available for further adsorption and interaction. Martin et al. [17] examined the structure-function relationship of Rh/Al_2O_3 and Rh/SiO_2 towards CO_2 methanation. They found that the dissociation of CO_2 led to minor formation of RhO_x is the reason for the enhanced activity in Rh/Al_2O_3 catalyst. But, it is noteworthy that the existing metal promoters still suffered from deactivation because of low surface area of support material and low dispersion of loaded metal, which can be avoidable by choosing a suitable supported metal material [18].

In the contemporary work, we examined the comparative study for CO methanation over a series of metals (Rh, Co, Pd and Zn) supported on mesoporous ZSM5 (mZSM5). The selection of the metals was based on the potential basis to replace the existing Ni-based catalysts. Rhodium and palladium were proposed as the noble metal's candidates. On the other hand, cobalt and zinc are representative of non-noble metals. Although these metals have been studied over a variety of supports, but to the best of our knowledge, the approach to introduce these metals onto mZSM5 have not been reported before. In the current work, the influence of the different metals in the physicochemical properties of mZSM5 and their catalytic performance are presented and discussed. Various techniques including XRD, N_2 physisorption, FTIR, FESEM were used to characterize the structural, textural and morphology 3 of the catalysts. The CO conversion and the products yield (CH_4 and CO_2) were investigated. Among all the promoted catalyst, Rh/mZSM5 exhibited the best catalytic performance, which was viewed as a promising candidate for CO methanation. Furthermore, we found that the modification with different type of metals on mesoporous ZSM5 demonstrated different catalytic activity. The metal-support synergistic effects are necessary for superior catalytic performance.

3. Results and Discussion

3.1. Physicochemical Properties of Catalysts

Figure 1 shows the XRD diffraction analysis of all the catalysts. The XRD results show the typical diffraction peaks at 2θ = 7-10° and 22-25°, which also presented in typical MFI type zeolite [19]. The introduction of the metals did not shift the peaks position, but the intensities of the peaks were slightly decreased as compared to the bare mZSM5. However, the characteristic diffraction peaks of ZSM-5 still remained.

The broad peak at 2θ = 34.5° was observed on Rh/mZSM5, which is assigned to (114) peak for Rh_2O_3 particles in an orthorhombic structure [20]. The high dispersion of Rh species was confirmed by the absence of other Rh-containing crystal phases. Vita et al. [21] reported that no evidence for the existence of rhodium phase (elemental rhodium and/or Rh oxides) on CeO_2 was observed because of low loading amount and well-dispersed Rh metal on the support. A peak at 2θ = 37° was observed on Co/mZSM5, which is a characteristic peak of crystalline Co_3O_4, as reported by Li et al. [22] and Díez-Ramírez et al. [23]. Some of the peak for Co oxides may be overlapped with the peak of mZSM5, and thus, no peak of metallic Co was observed. For Pd/mZSM5, a sharp diffraction peak which assigned to PdO was observed at 2θ = 34°. But, no diffraction peak at 2θ = 40° and 46°, which attributed to metallic Pd was observed [24-25]. Similar result was reported by Adams et al. [26] whereby no diffraction peaks assigned to Pd species were detected on the TiO_2, SiO_2 and Al_2O_3 supports due to the small amount and well distribution Pd species on the surface of the support. Furthermore, several peaks at 2θ = 34.5° (002), 36.3° (101), 47.6° (102) and 56.7° (110), which are characteristic peaks of ZnO wurtzite structure were observed on Zn/mZSM5 [27]. In brief, the XRD results indicated that no significance structural degradation was observed after metal introduction and the impregnated metals (Rh, Co, Pd and Zn) are mainly exists as metal oxides form.

The nitrogen physisorption was employed to depict the porosity of the material. Figure 2 demonstrated the nitrogen physisorption isotherms of the metal-promoted mZSM5 catalysts. The presence of micropores was affirmed by nitrogen uptake at low relative pressure. According to IUPAC classification, all catalysts exhibited isotherms with type IV pattern and H1 hysteresis loops, signifying the characteristic of mesoporous materials. It showed co-existence of micro-mesoporosity properties in the material. Moreover, 2 pronounced steps occurred at P/P_0 = 0.2-0.4 and 0.9-1.0, which attributed to capillary condensation of the intraparticles pores and interparticles pores, respectively [28]. The results revealed a significantly increased in mesopores in Rh/mZSM5, as demonstrated by the adsorption behavior in N_2 adsorption-desorption isotherm. It is probably due to the presence of external surface Rh particles which may causing blockage of the original pores structure and created bigger pores. This also have led to the increased in intraparticle pores and total pore volume in Rh/mZSM5. The same phenomenon was also observed in metal loaded onto aluminophosphate, which led to an increased in the adsorption-desorption volume probably due to the formation of mesoporous structure [29]. Besides, Bautista et al. [30] claimed that the behavior in dissimilarity of the mesopore size is attributed to the continuous pores restructuring of the material.

Figure 3 demonstrated NLDFT pore size distribution of the catalysts. All catalysts demonstrated pore size distribution in the range of < 20 Å and 35-70Å. It can be observed that the introduction of metals altered the pore size distribution of the catalysts. The high number of pores at ~35Å was observed for Pd/mZSM5, might be due to the pore blockage by Pd metal loading. Besides, Zn/mZSM5 showed an obviously decreased in the pores at ~40Å, with the simultaneously increased the pores at ~12Å.

Table 1 summarizes the textural properties of the catalysts. The surface area of mZSM5, Rh/mZSM5, Co/mZSM5, Pd/mZSM5 and Zn/mZSM5 are 857, 642, 594, 520 and 674 $m^2\ g^{-1}$, respectively. In addition, the total pore volume of mZSM5, Rh/mZSM5, Co/mZSM5, Pd/mZSM5 and Zn/mZSM5 are 0.2303, 0.2580, 0.2610, 0.2090 and 0.2530 $cm^3\ g^{-1}$, respectively. It can be concluded that introduction of the metals led to the decrease in surface area. In addition, two different trends of total pore volumes were observed: total pore volume increased after introduction of Rh, Co and Zn. While, it is decreased with Pd loading. It can be postulated that the location of loaded Rh, Co, and Zn is on the exterior part of the mZSM5. On the other hand, Pd located in the inner of the mZSM5 pores. It is noteworthy that suitable textural properties are believed 25 to be one of the factors for excellent catalytic activity by providing higher exposure of the active metal-reactant gases interactions and improved the reactant-product diffusion efficiency.

The examination of the functional groups in the catalyst was done by FTIR analysis. Figure 4 displays the FTIR spectra 6 in the range of 4000-400 cm^{-1} for fresh metal-promoted mZSM5 catalysts. The stretching vibration of hydroxyl group and bending vibration of water molecules were presented in the band at 3460 cm^{-1} and 1680 cm^{-1}, respectively. The absorption region of zeolite is shown in the region of 1300-400 cm^{-1}, due to the presence of SiO_4 and AlO_4 tetrahedron units. The characteristic band of the external and internal asymmetric stretching vibration were located at 1280 24 cm^{-1} and 1150 cm^{-1}, respectively. Moreover, the presence of external symmetric stretching was showed in a small band at 800 cm^{-1}. Two sharp bands were observed at 580 cm^{-1} and 450 cm^{-1} can be ascribed to the framework double four membered ring vibration and T-O bending vibration (Si-O and Al-O) of MFI type zeolites [31-32]. The FTIR results showed no shifting in the peak positions for metal-loaded mZSM5 catalysts as compared with the bare mZSM5 (not shown), indicating there is no structural framework difference present in the catalysts.

Figure 5 illustrates FESEM images and EDX analysis of mZSM5 and Rh/mZSM5. Both mZSM5 and Rh/mZSM5 demonstrated coffin-shaped morphology. The mZSM5 showed a smooth surface morphology while some of Rh particles were dispersed on the mZSM5 surface was observed for Rh/mZSM5. 23 To confirm the presence of Rh on the surface of the support, EDX analysis was carried out. From the analysis, it confirmed the approximately 5 wt% of Rh loading on mZSM5 support.

3.2. CO Methanation Performance

Figure 6 shows the catalytic performance results for all the catalyst in 150-450 °C. 22 At 450 °C, the

CO conversion and CH_4 yield followed order of: Rh/mZSM-5 > Co/mZSM-5 > Pd/mZSM-5 > Zn/mZSM-5. Only low CO conversion was obtained for bare mZSM5 (not shown). It should be noted that the presence of small amount CO_2 as the side product of the methanation reaction. This is due to the co-occurrence of methanation reaction with the accompanying of water-gas shift reaction (WGSR). Overall, the most active catalyst was Rh/mZSM-5, while the poorest catalyst was Zn/mZSM-5. The results presented the variation of metals loaded on mZSM-5 will demonstrated different physicochemical properties and lastly affected the CO methanation activity of the catalysts. We correlated the relationship of catalytic activity with properties of the catalyst (crystal structure, textural properties and structural properties), but no obvious trends were seen. The Rh promotional effect towards catalytic performance could be combination results of all the properties and formation of more available active sites (Rh metal for H_2 dissociation and mZSM5 for CO adsorption and interactions). Moreover, the synergistic effect of both Rh metal and ZSM5 support could be responsible for this enhancement [13, 33-34]. The good performance of Rh/mZSM5 in CO methanation could be attributed to a synergy between well dispersed Rh metal, large surface area and suitable micro-mesoporosity of mZSM5 support. However, this synergistic effect needs to be further clarification in the future work. In the recent study of Kim et al. [35], the high methanation activity of Ru/TiO_2 catalyst have been reported, which simply governed by "synergy" interaction of Ru and TiO_2 support (in anatase and rutile phase), and further led to formation of more dispersed and active Ru species.

The improvement of the catalyst in term of catalytic activity with the introduction of metals onto supporting material was also reported in the previous literatures [36-42]. Panagiotopoulou et al. [36] reported the apparent activation energy and products selectivity in the solo- or co-methanation of CO/CO_2 were depended on the nature of the Ru, Rh, Pt, Pd metallic phase. Besides, Tada et al. [37] evaluated the effect of CO conversion activity and products selectivity with the introduction of secondary metals (Ni, Co, Fe, La, K, Ni-La) onto Ru/TiO_2. They found that CO methanation activity was significantly affected with the addition of La as secondary metal on Ru species for improving the electron density and further facilitated CO bond dissociation. Aziz et al. [38] studied a series of 12 metal-based mesostructured silica nanoparticles (MSN) catalysts on CO_2 methanation. The active sites that are responsible for this methanation reaction are basic metallic surface centers and/or oxygen vacancy sites. Miyao et al. [39] reported that the enhancement in CO methanation activity was observed after the addition of vanadium to the Ni/Al_2O_3 catalyst with inhibition of water-gas shift reaction activity. Bacariza et al. [40] investigated the study of magnesium-promoted on Ni-based USY zeolites in CO_2 methanation. The results showed that lower content of Mg improved the methanation activity by enhanced Ni particles dispersion and CO_2 activation. Cao et al. [41] favored CO methanation of KIT-6 zeolite at low reaction temperature by Ni and V surface modification. They stated that the CO dissociation was improved by electron transferring from V species to Ni^0 and the enhancement in H_2 uptake and Ni dispersion is attributed to the presence of suitable V amount. The enhancement of La promoted Ni supported on Y- and Beta- zeolites towards CO_2 methanation activity was study by Quindimil et al. [42]. The introduction of La promoter increased the surface basicity, Ni dispersion and CO_2 adsorption capacity of the zeolites. Based on previous literatures, the enhancement in activity was dependent on the intrinsic essence of the metallic phase, which affected the activation and dissociation of CO/CO_2, and further accelerate the methanation activity accompanied with inhibiting the side reactions.

4. Conclusions

A series of metal-based mesoporous ZSM5 catalysts (Rh/mZSM5, Co/mZSM5, Pd/mZSM5 and Zn/mZSM5) prepared using dual templating and conventional incipient wetness impregnation method were tested towards CO methanation. The XRD results confirmed the successfully synthesized of ZSM5 support and the loaded metals were in the form of metal oxides. The nitrogen physisorption results showed that all metal-promoted mZSM5 possessed both micropores and mesopores. Co-existing of both micro-mesoporosity in ZSM5 gave an impact on the catalytic activity of CO methanation. At 450 °C, the catalytic performance of CO methanation arranged in the sequence of Rh/mZSM-5 > Co/mZSM-5 > Pd/mZSM-5 > Zn/mZSM-5. Rh/mZSM5 showed the best performance with CO conversion = 95% and CH_4 yield = 82%. While, Zn/mZSM5 is the poorest catalyst with CO conversion = 10% and CH_4 yield = 9%. This study clearly showed the improvement in the CO methanation activity was significantly governed by the effect of metal promoters on mZSM5. The good activity in Rh/mZSM5 probably due to the synergistic effect of both Rh metal and mZSM5 support.

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Figure 1

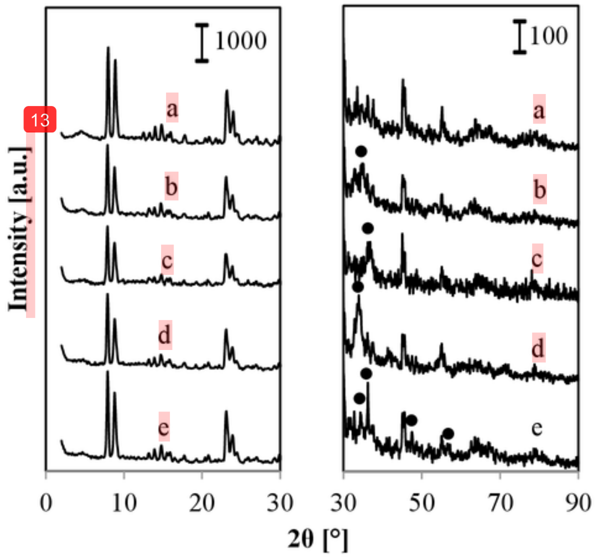


Figure 1. X-ray diffraction patterns of (a) mZSM5, (b) Rh/mZSM5, (c) Co/mZSM5, (d) Pd/mZSM5 and (e) Zn/mZSM5. (●) = metal oxides.

Figure 2

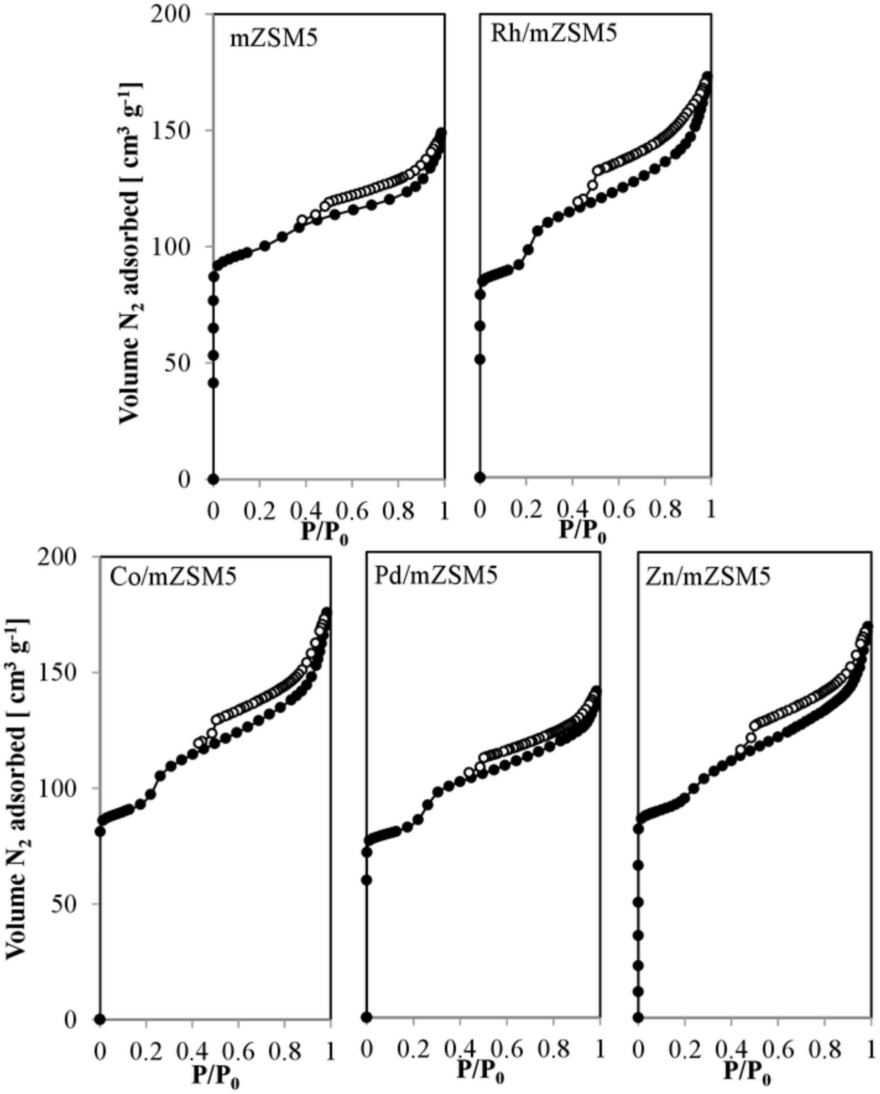


Figure 2. Nitrogen physisorption isotherms of the catalysts.

Figure 3

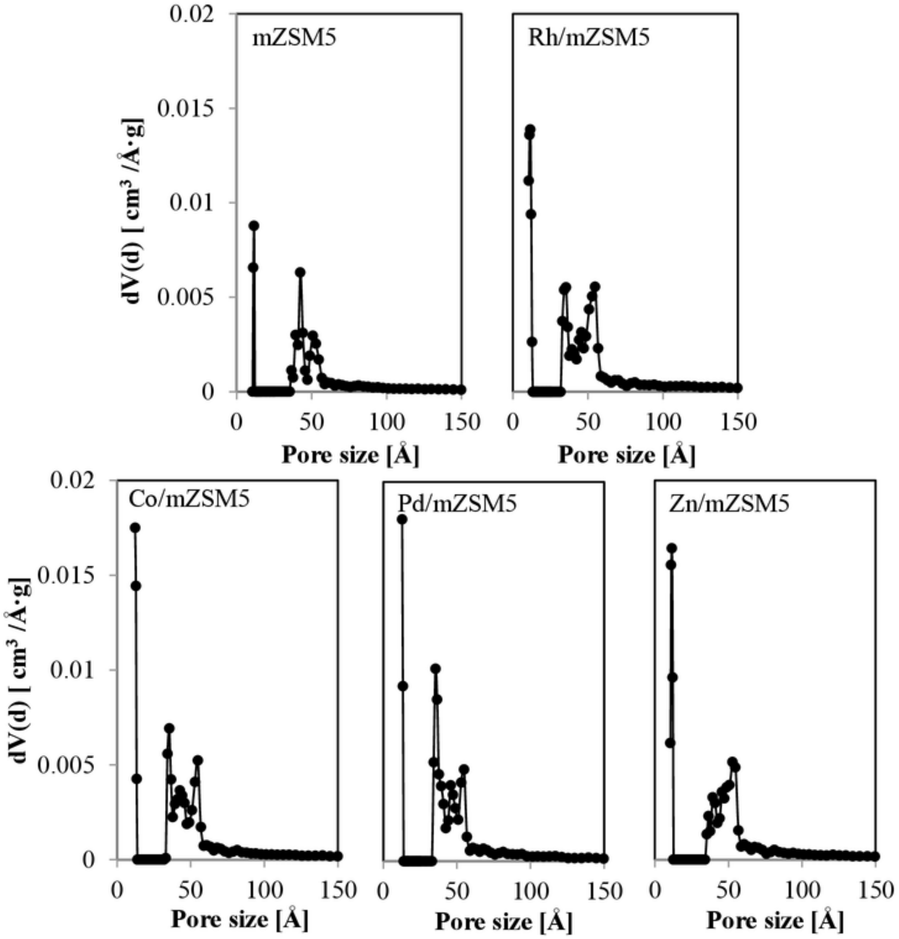


Figure 3. NLDFT Pore size distribution of the catalysts.

Figure 4

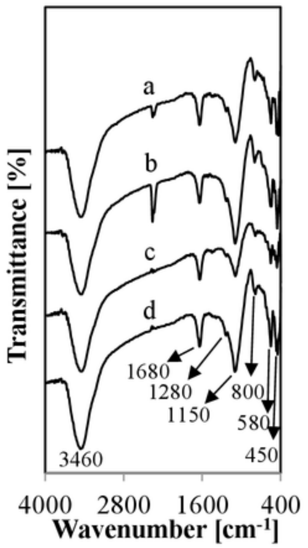
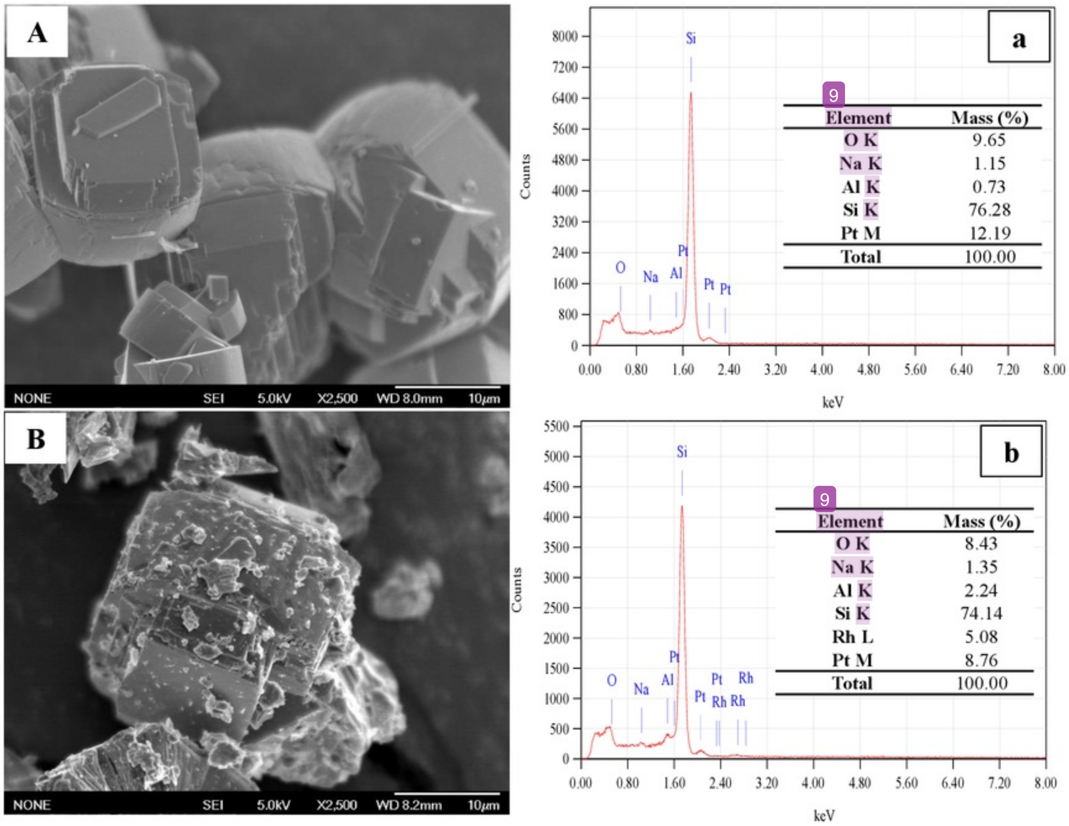


Figure 4. FTIR spectra of (a) Rh/mZSM5, (b) Co/mZSM5, (c) Pd/mZSM5 and (d) Zn/mZSM5 fresh catalysts in the region of 4000-400 cm^{-1}.

Figure 5



Element	Mass (%)
O K	9.65
Na K	1.15
Al K	0.73
Si K	76.28
Pt M	12.19
Total	100.00

Element	Mass (%)
O K	8.43
Na K	1.35
Al K	2.24
Si K	74.14
Rh L	5.08
Pt M	8.76
Total	100.00

Figure 5. FESEM images and EDX analysis of (A,a) mZSM5 and (B,b) Rh/mZSM5.

Figure 6

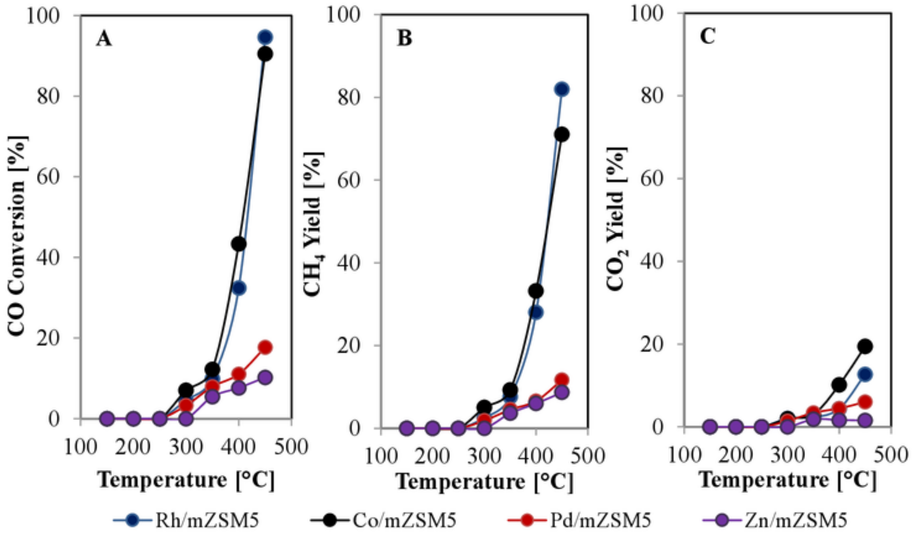


Figure 6 The catalytic performance of the catalysts. (A) CO conversion, (B) CH_4 yield and (C) CO_2 yield.

Table 1

Table 1 Physicochemical properties of the mZSM5-based catalysts.

Adsorbents	**Surface area (m^2/g)**	**Total pore volume (cm^3/g)**
mZSM5	857	0.2303
Rh/mZSM5	642	0.2580
Co/mZSM5	594	0.2610
Pd/mZSM5	520	0.2090
Zn/mZSM5	674	0.2530

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