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Manganese Oxide Doped Noble Metals Supported Catalyst for Carbon Dioxide Methanation Reaction

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Abstract. *Manganese oxide supported on alumina was prepared for methanation reaction by doping the manganese oxide based catalyst with noble metals, namely ruthenium, Ru and palladium, and Pd, via an impregnation method. The potential catalyst was calcined at 400° C, 700° C and 1000° C for 5 hours separately. An in-house-built micro reactor with an FTIR detector and GC was used to study the percentage of* CO_2 *conversion and also the percentage of* CH_4 *formation. Ru/Mn (30:70)-*Al_2O_3 *calcined at 1000° C was the potential catalyst, which gave 86.82%* CO_2 *conversion and 61.94%* CH_4 *yield at a reaction temperature of 200° C. XRD analysis showed that the catalyst is of a crystalline phase, while FESEM illustrated the catalyst surface was covered with small and dispersed particles with an undefined shape. EDX analysis revealed that there was 21.15% reduction of Ru in the spent catalyst compared to the fresh catalyst due to the migration of Ru particles into the porous support during the reaction. There was 5.39% reduction of surface area over the spent Ru/Mn (30:70)-*Al_2O_3 *catalyst, characterized by Nitrogen Adsorption analysis. FTIR analysis revealed that the catalyst surface is hydrated.*

Keywords: *Manganese oxide; Methanation; Ruthenium; Palladium; Catalyst.*

INTRODUCTION

Natural gas consists of light, volatile hydrocarbons, mostly methane (70-90%), ethane, propane, butane and pentane (0-20%), and of non-hydrocarbon gases, such as carbon dioxide (0-8%), nitrogen (0-5%) and hydrogen sulfide (0-5%). Carbon dioxide is referred to as "acid gas" because it forms corrosive compounds such as carbonic acid in the presence of water [1]. The presence of this impurity will make the natural gas fall under "sour natural gas", thus resulting in lowering the price of natural gas in the worldwide market, as well as causing difficulties for its distribution to the market.

Several methods have been developed for the removal of acid gases from the natural gas composition, such as amine treating and membrane separation [2]. Since amine treating and the membrane separation system have several drawbacks, such as high costs and the high heat of the reaction, the focus has now shifted to a more promising method, which is the catalytic conversion system.

Manganese has been widely explored for various types of reaction including solid state chemistry, biotechnology, organic reactions and environmental management. However, manganese had not yet been widely explored for its ability as a base catalyst for the CO_2 methanation reaction, but it has received attention from researchers as a dopant material for metal oxide for CO_2 methanation.

The hydrogenation of carbon oxides was performed over promoted iron-manganese catalysts [3]. It was found that manganese containing a catalyst showed higher activity towards the formation of hydrocarbons. Then, these catalysts were promoted with copper, sodium and potassium. Carbon dioxide conversion was favored by alkaline addition, especially by potassium due to the promotion of the water-gas shift reaction. Furthermore, alkaline promotion enhanced selectivity towards long-chain products, either in CO_2 and CO hydrogenation processes.

Hydrogenation of CO_2 was studied over a Fe-Mn oxide catalyst doped with Rh and La as reported by Dziembaj and Makowski [4]. They found that the

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existence of Rh led to a much faster and more complete reduction.

Ching [5] investigated cobalt containing nickel oxide supported alumina catalyst doped Mn for a CO_2 methanation reaction. It was found that for 5% of Mn, only 17.71% of CO_2 is converted at a reaction temperature of 300°C, while, when Mn was introduced into iron containing nickel oxide, the percentage of CO_2 conversion did not differ much, as in the Co:Ni catalyst.

Lohitharn and Goodwin [6] investigated the activities of precipitated $FeCuSiO_2$ catalysts by the addition of Mn for both CO hydrogenation and the WGS reaction. They found that $FeCuSiO_2$ addition to Mn can improve the catalytic activity. In this work, the manganese oxide doped Ru or Pd catalyst should be capable of achieving both a low temperature and a high conversion of carbon dioxide gas to methane.

MATERIALS AND METHODS

Preparation of Catalysts

$MnCl_2.2H_2O$, produced by the MERCK Eurolab, was dissolved with 2 ml of triply distilled water. A mixed catalyst solution was prepared by mixing appropriate amounts of noble metal chloride salts or noble metal nitrate salts ($Pd(NO_3)_2.xH_2O$ and $RuCl_3.xH_2O$). The wetness impregnation method was used to prepare the Al_2O_3 supported catalyst by impregnating the catalyst solution on Al_2O_3 beads (MERCK Eurolab) support for 15 minutes, then, taken out and dried at ambient. The impregnation and drying were repeated three times. Then, the impregnated Al_2O_3-bead was washed-dispensed with triply distilled water to remove chloride ion. This process was repeated until no change occurred in the solution when adding the $AgNO_3$ reagent. It was then aged at 80°C for 24 hours and calcined in an oxygen atmosphere at 400°C for 12 hours. The potential catalyst was then further calcined at 700°C and 1000°C for another 12 hours.

Catalytic Performance Test

All the prepared catalysts were tested for their catalytic activity towards a carbon dioxide methanation reaction by using an in-house-built micro reactor. The analysis was conducted using simulated natural gas comprised of a continuous flow of a CO_2 and H_2 (1:4) mixture, composition 20% of CO_2 and 80% of H_2, and a flow rate of 50 mL/min. This reactor was coupled with Fourier Transform Infra Red (FTIR) Nicolet Avatar 370 DTGS. The formation of methane was detected by a Hewlett-Packard 6890 Series GC System (Ultra 1) with a 25.0 m × 200 μm × 0.11 μm nominal column, helium gas as the carrier gas with a flow rate of 20 mL/min at 75 kPa, and by using a Flame Ionization Detector (FID). The measurements were done at reaction temperatures of 100°C, 200°C, 300°C and 400°C.

Characterization of Catalysts

XRD analysis was done using a Siemens D5000 Crystalloflex X-Ray Diffractometer equipped with Cu target ($\lambda_{CuK\alpha} = 1.54\,\mathring{A}$) radiation. Using a step scan of 0.050° and a step time of a second per step, data were collected over the range of 2θ from 10° to 80°. FESEM-EDX analysis was accomplished by using a Philips XL 40 microscope with energy of 15.0 kV coupled with an EDX analyzer, and bombarded using an electron gun with a tungsten filament under 25 kV resolutions in order to get the required magnification image. N_2 adsorption-desorption isotherms for the catalysts were measured by Micromeritics ASAP 2010. All samples were evacuated at 120°C prior to the measurement. The samples were analyzed for the presence of functional groups using FTIR Nicolet Avatar 370 DTGS with a KBr pellet technique.

RESULTS AND DISCUSSION

Catalytic Performance of Alumina Supported Manganese Oxide Catalyst

From Figure 1, it can be seen that the conversion of CO_2 over a manganese oxide based catalyst was incoherent throughout the reaction. The maximum percentage of CO_2 conversion in this study was achieved at a reaction temperature of 100°C, which is only 9.40%. However, after this point, the conversion continuously decreases slightly until the end of the studied reaction temperature of 280°C. It can be suggested that at the calcination temperature of the catalyst at 400°C, the Mn species on the catalyst surface existed in both trivalent and divalent states with Mn^{3+} as the major species, accompanied by the minor Mn^{2+} species [7]. Chen et al. [8] also claimed that the predominant

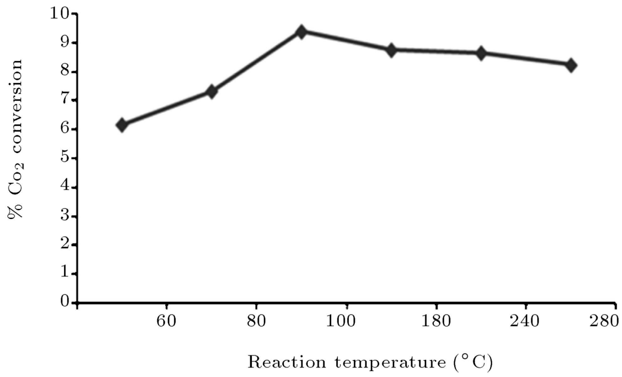


Figure 1. Catalytic performance of MnO/Al_2O_3 catalyst calcined at 400°C for CO_2 conversion reaction.

phases of MnO and Mn_3O_4 can be obtained after calcination at 400°C in air. It can be concluded that the existence of the more trivalent state of Mn does not favor the methanation reaction, attributable to the incoherent trend of CO_2 conversion.

Catalytic Activity Screening of Alumina Supported Manganese Oxide Based Catalyst with One Dopant for CO_2 Conversion in Methanation Reaction

As shown in Table 1 and Figure 2, a conclusion can be drawn from this investigation that Ru/Mn (30:70)-Al_2O_3 catalyst showed the best catalytic performance for CO_2 conversion. It can be seen that the percentage CO_2 conversion for all ratios of Ru/Mn-Al_2O_3 catalysts showed very little increase until at 240°C and, then abruptly inclines and reaches its maximum at 400°C, whereby the percentage of CO_2 conversion was the highest at 89.01%. However, the Pd/Mn- Al_2O_3 catalyst for all ratios showed no change in CO_2 conversion even until the maximum studied temperature of 400°C.

It can be suggested that the incorporation of ruthenium into the manganese oxide based catalyst system has a positive effect on the methanation reaction. This is in agreement with the results obtained by Panagiotopoulou et al. [9] who reported that CO_2 methanation is strongly favored with increasing Ru content. The combination of Mn and Ru showed maximum conversion up to 89.01% for a higher ratio of Ru in the system. This result suggests that the combination of Mn and Ru enhances the catalytic activity because H_2 and CO_2 are easily chemisorbed and activated on these surfaces. The high CO_2 conversion was probably due to the Mn species, which caused the removal of Cl atoms from the $RuCl_3$ precursor and increased the density of active Ru oxide species on the catalyst, which resulted in high catalytic activity as claimed by Murata et al. [10].

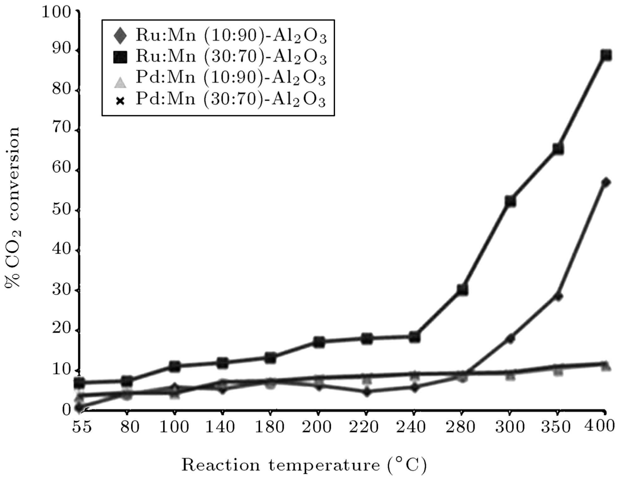


Figure 2. Catalytic screening for Al_2O_3 supported manganese oxide based catalysts with one dopant calcined at 400°C for CO_2 conversion reaction.

Murata et al. [10] studied the effect of Ru and Mn concentration on Fischer-Tropsch synthesis and claimed that when the Ru to Mn ratio was 5:10, the CO conversion is up to 42.9%, and selectivity towards CH_4 up to 9.10%. They also noted that increasing Mn content resulted in decreased CO conversion, which is in agreement with the result of the catalytic screening of Ru/Mn (10:90)-Al_2O_3, which showed lower activity compared to that of Ru/Mn (30:70)-Al_2O_3.

When Pd was used as the dopant, the percentage of CO_2 conversion was observed to be less compared to when Ru was used as the dopant. For Pd/Mn (10:90)-Al_2O_3, the maximum CO_2 conversion of 11.54% can be seen at the reaction temperature of 400°C. Moreover, when the ratio of Pd in the system is made higher, Pd/Mn (30:70), the maximum conversion at 400°C was only 11.63%. From this observation, it can be suggested that Pd and Mn is not a good combination for methanation reaction, since temperatures higher than 400°C are required to achieve more than 12% CO_2 conversion. This was also reported by Wachs [11]; the reason given being that some active basic metal oxide components, such as MnO and CeO, did not interact strongly with the different oxide functionalities present on the oxide support and, consequently, did not disperse very well to form crystalline phases.

Panagiotopoulou et al. [9] found that Pd was the least active catalyst; the CO_2 conversion being less than 5% at 450°C. The atomic radius of Pd (137 pm) is

Table 1. Percentage conversion of CO_2 catalyzed by various manganese oxide based catalysts with one dopant and calcined at 400°C for CO_2 methanation reaction.

Catalyst	**Reaction Temperature (°C)**			
	100°C	**200°C**	**300°C**	**400°C**
	% Conversion of CO_2			
Ru/Mn (10:90)-Al_2O_3	5.86	6.29	18.12	57.27
Ru/Mn (30:70)-Al_2O_3	11.23	17.18	52.42	89.01
Pd/Mn (10:90)-Al_2O_3	4.55	8.01	9.23	11.54
Pd/Mn (30:70)-Al_2O_3	4.34	8.29	9.44	11.63

much bigger than that of Mn (135 pm). This may cause pore blockage by the bigger size of Pd, thus preventing any adsorption of CO_2 gas on the catalyst surface which, as such, retarded the methanation reaction. It was also noted that Pd does not favor a CO_2 methanation reaction but favored a conversion of CO_2 to CO, possibly via a reverse water gas shift (RWGS) reaction.

Catalytic Activity Screening of Alumina Supported Manganese Oxide Based Catalyst with Two Dopants for CO_2 Conversion Methanation Reaction

Table 2 and Figure 3 revealed that the additional loading of Pd into MnO doped Ru catalyst decreases its catalytic activity as compared to the other two catalysts, with a smaller loading ratio of Pd. This is because Pd was suspected to decrease the performance of the catalyst by oxidizing the CO intermediate back to CO_2 as claimed by Panagiotopoulou et al. [9] who reported that Pd does not favor CO_2 methanation reaction but favors a conversion of the CO intermediate to CO_2.

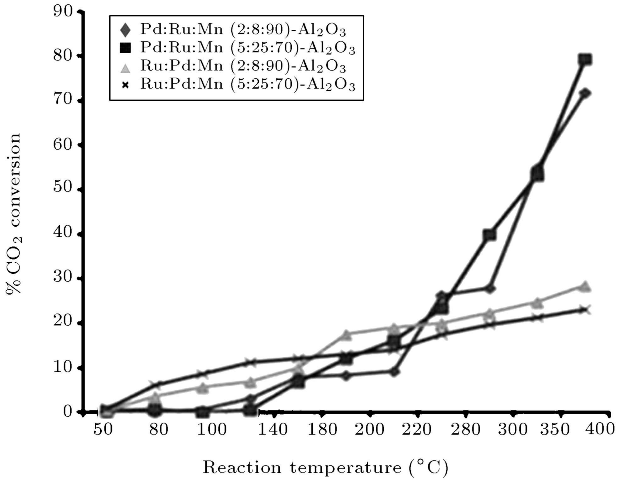


Figure 3. Catalytic screening for Al_2O_3 supported manganese oxide based catalysts with two dopants calcined at 400°C for CO_2 conversion reaction.

All the studied catalysts showed low percentage CO_2 conversion (maximum 20% conversion) from the start to 300°C of reaction temperature. However, after 300°C, the catalyst system of Pd/Ru/Mn-Al_2O_3 gave a profound increase in CO_2 conversion.

It can be suggested that Ru is strongly chemisorbed onto the surface of the support, which corresponds to the high activity, but when Pd is in higher proportion than Ru, the activity decreases. This may possibly be due to the adsorption of Pd on the surface of Ru particles, which leads to the decrease in activity. The bigger atomic size of Pd (137 pm) compared to that of Ru (134 pm) is one of the reasons why Pd is not a good dopant to Mn as compared to Ru, since Pd can deactivate the catalyst by covering the surface of the active species, thus leading to low catalytic activity.

From the catalytic screening of all prepared catalysts, Ru/Mn (30:70)-Al_2O_3 was chosen as the best catalyst for further studies. This is due to its high activity towards methanation reaction, whereby the CO_2 conversion was 89.01% at a reaction temperature of 400°C. This catalyst was then subjected to higher calcination temperatures of 700°C and 1000°C, and its catalytic activity was monitored by using FTIR.

From Table 3 and Figure 4, it can be concluded that the percentage of CO_2 conversion over the reaction temperatures increases as the calcination temperature increases, whereby the catalytic centers of the catalyst were activated, thus enhancing the activity. It can be concluded that higher calcination temperatures lead to the formation of active species such as Mn_3O_4 and RuO_2, which are responsible for the high catalytic activity towards the CO_2 methanation reaction. Furthermore, calcination temperatures higher than 400°C were assumed to have eliminated any presence of the Cl^- ion, which might poison the catalyst active site. This is in agreement with Bradford et al. [12] who found that most of the Cl^- ion was removed after reduction pretreatment at 500°C using the Ru/Al_2O_3 catalyst. The formation of the active species was confirmed by the XRD analysis.

Table 2. Percentage conversion of CO_2 catalyzed by various manganese oxide based catalysts with two dopants after calcined at 400°C for CO_2 methanation reaction.

Catalyst	**Reaction Temperature (°C)**			
	100°C	**200°C**	**300°C**	**400°C**
	% Conversion of CO_2			
Pd/Ru/Mn (2:8:90)-Al_2O_3	0.56	9.27	27.96	71.83
Pd/Ru/Mn (5:25:70)-Al_2O_3	0.02	4.74	40.00	79.48
Ru/Pd/Mn (2:8:90)-Al_2O_3	5.69	17.59	22.39	28.51
Ru/Pd/Mn (5:25:70)-Al_2O_3	8.57	9.23	19.75	23.16

Table 3. Percentage conversion of CO_2 catalyzed by alumina supported manganese oxide based catalysts doped with ruthenium with ratio of 30:70 and calcined at different temperatures.

Catalyst	**Calcination Temperature (°C)**	**Reaction Temperature (°C)**			
		100°C	**200°C**	**300°C**	**400°C**
		% Conversion of CO_2			
Ru/Mn (30:70)-Al_2O_3	400	11.23	17.18	52.42	89.01
	700	6.06	21.46	67.07	97.36
	1000	27.75	86.82	98.65	99.21

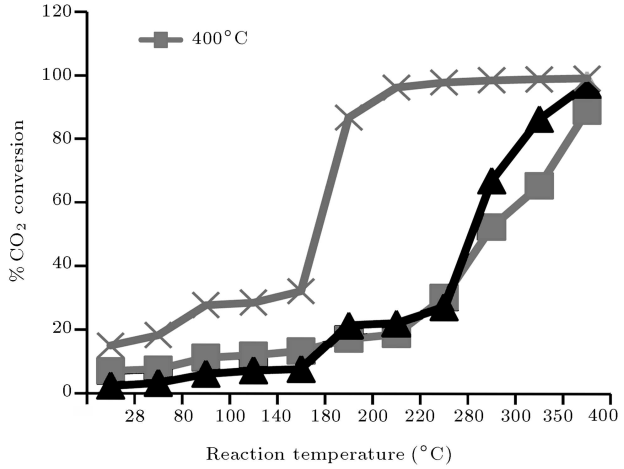


Figure 4. The trend plots of percentage of CO_2 conversion over Ru:Mn (30:70)-Al_2O_3 catalyst calcined at different temperatures.

Detection of Methane by Gas Chromatography for CO_2 Methanation Reaction

The Ru/Mn (30:70)-Al_2O_3 catalyst calcined at 1000°C was considered a potential catalyst for the CO_2 methanation reaction, since it gives 86.82% of CO_2 conversion with 61.94% CH_4 yield at an applicable low reaction temperature of 200°C (Table 4); having undergone reproducibility tests three times. This result is comparable to the result obtained by Wan Abu Bakar et al. [13] who reported only 19.19% of CO_2 conversion with 6.1% of CH_4 yield over Pr/Co/Ni (5:35:60)-Al_2O_3 at the same reaction temperature. Therefore, Ru/Mn (30:70)-Al_2O_3 catalyst, calcined at 1000°C, was selected as the best catalyst in this work. The limitation of a reaction temperature up to 200°C was applied to suit the requirements in the petroleum refinery plants.

Characterization of Catalysts

XRD Analysis

The potential catalyst, Ru/Mn (30:70), was analyzed by XRD in order to determine the active oxide phases that have contributed to the enhancement of catalytic activity. From Figure 5, it was observed that the degree of crystallinity of all the studied catalysts improved as they were calcined at higher temperatures (400°C, 700°C and 1000°C). A high crystallinity phase was only observed for catalysts calcined at 1000°C, whereby the catalyst calcined at 400°C showed an amorphous phase and those calcined at 700°C showed a weak crystalline phase.

At a calcination temperature of 400°C, the phase is highly amorphous and dominated by the alumina support and no other peak can be assigned. At higher calcination temperatures of 1000°C, the Al_2O_3 cubic phase at 2θ values of 46.04(I_{100}), 67.03(I_{93}) and

Table 4. Testing results of CO_2/H_2 methanation reaction over Ru/Mn (30:70)-Al_2O_3 catalyst calcined at different temperatures.

Catalyst	**Reaction Temperature (°C)**	**Converted CO_2 (%)**		**Unreacted CO_2 (%)**
		% Formation of CH_4	**% Formation of $CO+H_2O$**	
Ru/Mn (30:70) calcined at 700°C	100	-	6.06	93.94
	200	-	21.46	78.54
	300	50.73	16.34	32.93
	400	49.07	48.29	2.64
Ru/Mn (30:70) calcined at 1000°C	100	0.00	27.75	72.25
	200	61.94	24.88	13.18
	300	56.07	42.58	1.35
	400	51.92	47.29	0.79

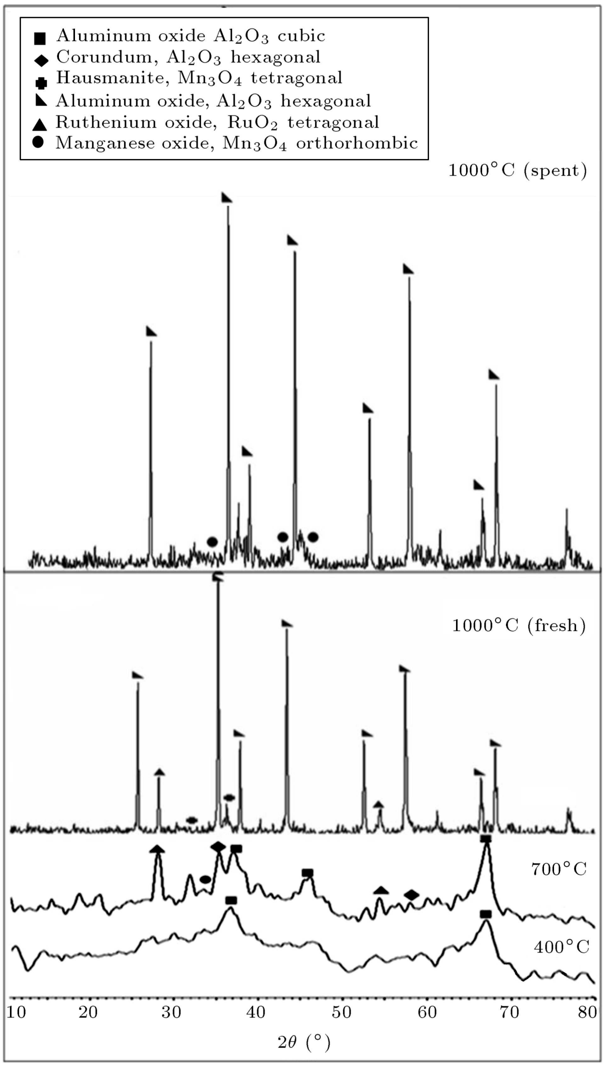


Figure 5. The XRD diffractograms of Ru/Mn (30:70)-Al_2O_3 catalyst calcined at 400°C, 700°C and 1000°C.

37.64°(I_{47}), with d_{obs} values of 1.97, 1.39 and 2.39 Å(d_{ref} values of 1.98, 1.39 and 2.38 Å), which was observed in catalysts calcined at 700°C, had transformed into a Al_2O_3 hexagonal phase that was detected at 2θ values of 35.49(I_{100}) and 58.04°(I_{36}), with d_{obs} values of 2.53 and 1.59 Å(d_{ref} values: 2.52 and 1.59 Å). Interestingly, new peaks attributable to the RuO_2 tetragonal phase species were observed at calcination temperatures of 700°C at 2θ values of 28.12(I_{100}) and 54.39°(I_{54}), with d_{obs} values of 3.17 and 1.69 Å(d_{ref} values: 3.17 and 1.69 Å). The RuO_2 tetragonal phase was more intense due to its higher sensitivity towards XRD analysis.

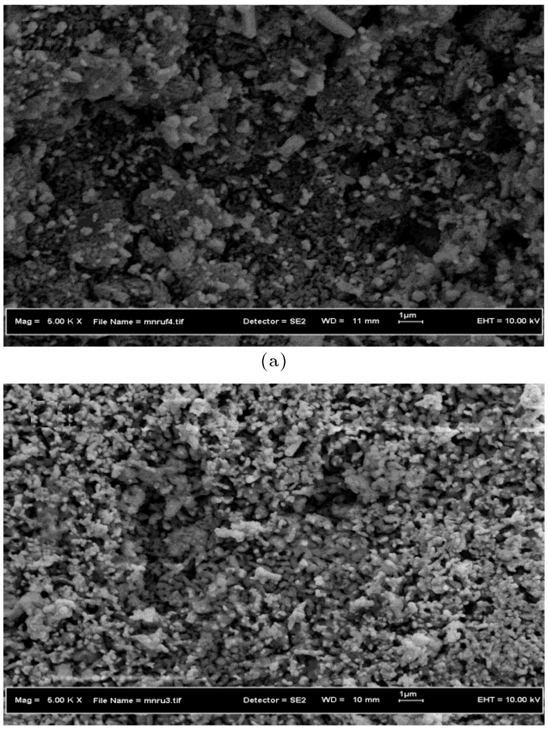
Furthermore, the peaks due to the Mn_3O_4 tetragonal phase at 2θ values of 36.13(I_{100}) and 32.49°(I_{76}) with d_{obs} values at 2.48 and 2.75 Å(d_{ref} values: 2.48 and 2.76 Å) were observed in the fresh catalyst after calcination at 1000°C, but were transformed to an orthorhombic phase in the spent catalyst, which was detected at 2θ values of 33.56(I_{100}), 41.72 (I_{52}), 44.96(I_{38}) and 36.35°(I_{30}) with d_{obs} values of 2.67, 2.16, 2.01 and 2.47 Å(d_{ref} values: 2.67, 2.16, 2.013 and 2.47 Å), which is expected to be a stable phase when the temperature is higher than 300°C, as reported by Chen et al. [8]. Vicente et al. [14] had also expected that a mixture of manganese oxides should be formed when the Mn based catalyst was subjected to calcination temperatures higher than 500°C. Overall, the peaks observed that were assigned to the existence of Mn_3O_4 species are low. This is probably because Mn_3O_4 is present in low quantities and is probably less sensitive towards XRD analysis compared to RuO_2 species.

However, after the catalytic testing, the peak of the RuO_2 tetragonal phase was no longer observed. The collapse of the RuO_2 peak may be due to the well-dispersion of RuO_2 particles into the bulk matrix of the catalyst as claimed by Safariamin et al. [15] who suggested that the Ru particles had been well-dispersed into the catalyst that contains a higher ratio of support. This may also explain the lower percentage of CO_2 conversion for the reproducibility test towards the CO_2 methanation reaction over the same catalyst without pretreatment before testing. The above statement was supported by the obtained EDX results, which revealed the percentage weight composition of Ru in the spent catalyst, 13.12%, which is much lower than Ru in the fresh catalyst, 34.27%.

Field Emission Scanning Electron Microscopy (FESEM)

Figure 6a depicts the image of an alumina supported Ru/Mn catalyst in the ratio of 30:70 before testing (fresh) in 5000 times magnification, while Figure 6b shows the image of an alumina supported Ru/Mn catalyst in the ratio of 30:70 after testing (spent) in 5000 times magnification.

From the micrograph in Figure 6a, it was clear that the surface of the fresh catalyst is covered with an agglomeration of Mn and Ru. This may be due to the heat from the calcination process subjected to the catalyst, which resulted in the agglomeration of the particles. The particles were of undefined shape. However, in Figure 6b, it can be observed that the particles on the spent catalyst surface are smaller and highly dispersed. This is probably because the Ru particles had been adsorbed into the bulk matrix of the catalyst, thus exhibiting a well-dispersed surface,



(a)

(b)

Figure 6. FESEM micrographs Ru/Mn catalyst supported alumina in the ratio of 30:70. (a) Fresh and (b) spent in 5000 × magnification at calcination temperature 1000°C.

which indicates the reduction of active species on the catalyst surface. This is in agreement with Safariamin et al. [15] who concluded that Ru particles had been well-dispersed into the pore of the support. The reduction of the active species of Ru on the catalyst surface explains the reason for the reduced catalytic activity for the reproducibility test towards the CO_2 methanation reaction over the same catalyst.

Energy Dispersive X-Ray Analysis (EDX)

The results from the EDX analysis (Table 5) show the existence of all the metal precursors used in the preparation. This result suggested that the weight percentage of Ru in the fresh catalyst is higher compared to Mn. The high weight percentage of Ru on the catalyst surface may also be attributable to the high catalytic activity towards the methanation reaction, which is highly favored in the presence of Ru [9]. It was also noted that Ru in the spent catalyst is reduced by 21.15% compared to the fresh catalyst. This may be due to the migration of Ru into the bulk matrix of the catalyst surface. This result is in agreement with the findings observed by Nurunnabi et al. [16] who claimed that the Ru may have been adsorbed into the porous support, hence a lower concentration of Ru on the surface, which can be detected by EDX as reported by Rosso et al. [17].

Table 5. Elemental composition from EDX analysis for fresh and spent Ru/Mn (30:70)-Al_2O_3 catalysts calcined at 1000°C.

Form	Element	Weight Percent (%)
Fresh Catalyst	Al	18.20
	O	31.00
	Mn	16.53
	Ru	34.27
Spent Catalyst	Al	29.21
	O	41.52
	Mn	16.16
	Ru	13.12

Nitrogen Adsorption (NA) Analysis

The surface area of the spent catalyst was 5.39% lower than the surface area of the fresh catalyst. It can be suggested that the reduction of the surface area is not a major factor for the reactivity of the catalyst. RuO_2 may also have a role as the active species. RuO_2 was present in the fresh Ru/Mn (30:70)-Al_2O_3 catalyst, but disappeared after the catalytic testing as shown in XRD and EDX analysis. The N_2 adsorption-desorption isotherms of the fresh and spent catalyst samples are also similar to that of Type IV with a hysteresis loop indicating the presence of mesopores (Figure 7).

Fourier Transform Infrared (FTIR) Analysis

There were only four significant absorption peaks to be noted as shown in Figure 8. The peaks at wavenumbers between 3000 and 3800 cm^{-1} were attributable to the stretching mode of the OH groups from the adsorbed water molecule, while the peaks at wavenumbers between 1600 and 1700 cm^{-1} correspond to the bending mode of the OH groups from the adsorbed water molecule. The strong IR absorption of the oxide support occurs below 800 cm^{-1}.

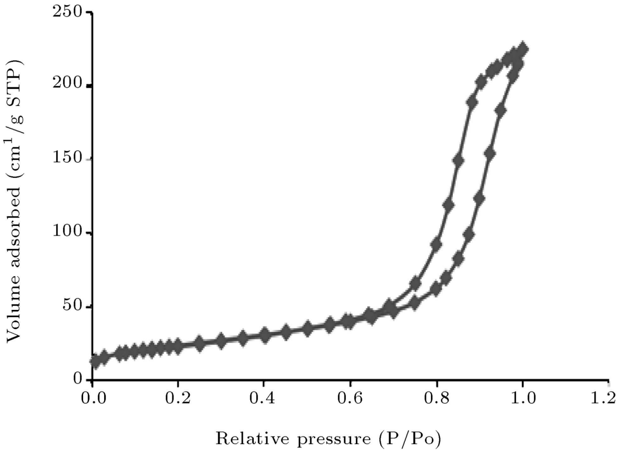


Figure 7. Isotherm plot of Ru:Mn (30:70)-Al_2O_3 catalyst calcined at 1000°C.

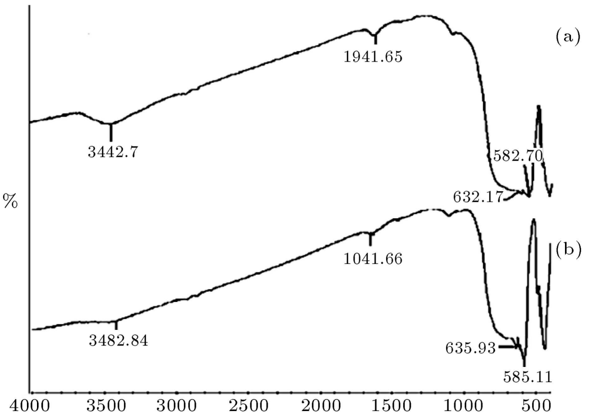


Figure 8. Comparison of FTIR spectrum for (a) fresh Ru/Mn (30:70)-Al_2O_3 and (b) spent Ru/Mn (30:70)-Al_2O_3 catalysts calcined at 1000°C.

CONCLUSIONS

The 86.82% of CO_2 conversion with 61.94% CH_4 yield was obtained at a reaction temperature of 200°C for a Ru/Mn (30:70) catalyst calcined at 1000°C. Maximum CO_2 conversion was obtained at a higher reaction temperature of 400°C, which is 99.21%, but a slightly lower CH_4 yield of 51.92%. RuO_2 in a tetragonal phase and hausmanite, Mn_3O_4 in a tetragonal phase, was proposed as the active species of Ru/Mn (30:70)-Al_2O_3 catalyst. It was also noted that the Al_2O_3 phase should be hexagonal for the catalyst to achieve high catalytic activity towards a CO_2 methanation reaction.

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