

Preferential methanation of CO in a syngas involving CO₂ at lower temperature range

Muhamad B.I. Choudhury^a, Shakeel Ahmed^{b,*}, Mazen A. Shalabi^c, Tomoyuki Inui^c

^a Center for Petroleum & Minerals, Research Institute, King Fahd University of petroleum & Minerals, Dhahran 31261, Saudi Arabia

^b Center for Refining & Petrochemicals, Research Institute, King Fahd University of petroleum & Minerals, P.O. Box 907, Dhahran 31261, Saudi Arabia

^c Chemical Engineering Department, King Fahd University of petroleum & Minerals, Dhahran 31261, Saudi Arabia

Received 16 March 2006; received in revised form 31 July 2006; accepted 3 August 2006

Available online 18 September 2006

Abstract

Preferential elimination of CO in a model syngas involving CO₂ at a low temperature range was studied on a series of Ni-based multi-component composite catalysts supported on θ -alumina spheres. The catalysts were characterized by TPR to evaluate the change of reduction temperature with the catalyst composition, which corresponded to the catalytic performance. Performance of CO methanation on these catalysts was compared in a continuous flow reactor under atmospheric pressure. The Rh-modification onto the known highly active three-component methanation catalyst Ni-La₂O₃-Ru exhibited an evident enhancement in the activity. Complete conversion of CO to methane preferentially occurred on this four-component catalyst, Ni-La₂O₃-Ru-Rh, as low as 230 °C. As long as CO remained in the syngas, methanation of CO₂ was completely retarded. It was reconfirmed that La₂O₃ increases Ni dispersion, and Rh and Ru enhance H₂ adsorption, and induce the reduction of main catalyst component NiO_x at a low temperature range by hydrogen spillover. These are the causes of the very high performance of this catalyst. © 2006 Elsevier B.V. All rights reserved.

Keywords: Preferential methanation of CO; Rh-modified Ni-based composite catalyst; Hydrogen spillover; TPR measurements

1. Introduction

Preferential methanation of CO from a syngas involving CO₂ is an intriguing issue from the view point of purification of hydrogen to be provided to the consecutive catalytic reactors and/or pressure swing adsorption (PSA) processes. For example, in case of polymer electrolyte fuel cell (PEFC), since the operating temperature is as low as 80 °C, Pt catalyst in the cathode is sensitively deactivated by even a very low concentration of CO and sulfur compounds. The conversion of hydrocarbon fuels to hydrogen may be achieved by reforming or partial oxidation [1]. Both systems produce carbon monoxide associated with hydrogen. The carbon monoxide concentration is preferably reduced catalytically to less than 10 ppm to avoid deactivating fuel cell electrodes [2]. The most preferable approach to reduce CO in the hydrogen-rich feed gas is preferential catalytic oxidation of CO to CO₂. However, in

this case part of hydrogen is likely to combust to form water, and result in loss of energy.

The rate of CO₂ hydrogenation on a Ni catalyst, even with the co-existence of promoters is less than that of CO. This had been confirmed by comparative studies on the kinetics of CO and CO₂ methanation over a commercial supported Ni catalyst [3], Inui et al., prepared Ni-La₂O₃-Ru catalyst to investigate co-methanation of CO and CO₂ [4], and found CO₂ methanation was completely retarded until CO has been converted to methane. This kind of distinct reaction behaviors could not be observed by the use of lower active catalysts, i.e., both parts of CO and CO₂ were converted into methane at higher temperature region [4]. These facts have strongly indicated that when one can use more highly active catalyst the preferential methanation of CO could be achieved prior to CO₂ methanation at lower temperature range.

In order to develop such a super active catalyst, very low concentration of Rh as the catalyst ingredient was designed and adopted in the present study based on the distinct enhancing effects for hydrogenation [5]. In this study the temperature-programmed-reduction (TPR) method was adopted as the most

* Corresponding author. Tel.: +966 3 860 3428; fax: +966 3 860 4509.

E-mail address: shakeel@kfupm.edu.sa (S. Ahmed).

effective tool for measuring the reduction behavior, which is induced by the effect of hydrogen spillover. Hossain et al. [6] and Al-Saleh et al. [7] studied catalysts activity using TPR method by measuring hydrogen consumption and shifting of reduction temperature. They confirmed that activity of hydrocracking for heavy oil by supported Co catalyst was enhanced remarkably by addition of precious metals Pd-Rh. They concluded that the increased reducibility was due to the hydrogen spillover effect as evidenced by the TPR measurements.

Numerous supported precious metal catalysts were investigated for CO removal by preferential methanation in literature:

Gorke et al. investigated Ru supported on silica or alumina in a microchannel reactor to reduce CO content. The methanation allowed removing CO almost completely from the gas flow at a temperature of 300 °C using Ru/SiO₂ catalyst. Although, oxygen was added to the feed, the CH₄-selectivity was still 95% at temperatures of 350 °C using the Ru/SiO₂ catalyst [12].

Aksoylu et al. [13] prepared Ni/Al₂O₃ catalysts that showed CO conversions of more than 90% at a longer residence time. Although Xavier et al. [14] were able to increase the activity of Ni/Al₂O₃ catalysts by doping Al₂O₃ with 1.5 wt% CeO₂.

Fujita et al. [15] examined the competitive methanation without oxygen co-feed (10 vol% CO and 10 vol% CO₂ in balance H₂) over Ru/SiO₂ catalyst and other catalysts. They observed that CO₂ methanation rate at 200 °C is 4.6 times faster than the CO methanation rate.

Over et al. [16] pointed out that changing the CO/CO₂ ratio in the gas feed to higher values than 2:1 will deteriorate the overall activity due to blocking the surface by CO molecules.

In the present study the results of preferential methanation will be presented using novel Rh-modified high activity Ni-La₂O₃-Ru catalyst for the preferential methanation of CO in H₂- and CO₂-rich syngas mixture.

2. Experimental

2.1. Preparation of catalysts

The Al₂O₃ support (Daviact AL-2750) was supplied by Davison Catalysts. The support was in the form of spheres of 3 mm average diameter with BET surface area of 135 m²/g and pore volume of 0.65 ml/g. Before impregnation, it was calcined at 1060 °C at a rate of 10 °C per minute that converted γ -alumina to θ -alumina. This calcinations temperature 1060 °C has been known as the optimum temperature to give the highest performance of methanation catalysts [8].

Incipient wetness impregnation method [9] was adopted for the catalyst preparation. Weight percent of Ni and La₂O₃ were taken 5.0 and 2.7, respectively. These weight percents were shown as the optimum amounts for methanation catalysts for multi-component catalyst by Inui et al. [9]. The composition for that catalyst was 5.0% Ni-2.7% La₂O₃-0.5% Ru/SiO₂. For Ru the weight percent was varied in this study from 0.20 to 1.0, and Rh was 0.10 or 0.20 wt%. For the metal salt solution, distilled water of 115 vol% of pore volume of the θ -alumina (BET surface area 128 m²/g and pore volume 0.62 ml/g) was used for impregnations. After impregnation, the sample was dried at

60 °C by increasing the temperature from room temperature to 60 °C in 2 h. The sample was then placed in a closed beaker for NH₃-H₂O treatment. The ammoniacal treatment converts metal salt anion to ammonium salt, and increases the activity of methanation of carbon oxides as found by Inui et al. [10]. The NH₃-H₂O vapor treated catalysts were then dried from 60 to 120 °C for 2 h and then temperature was elevated up to 250 °C for 1.5 h. In this step the most of the ammonium salts removed by sublimation of nitrate. Hydrogen reduction and thermal treatment was done afterwards. In this step salt-removed catalysts were shifted to a tubular electric furnace, and was heated up to 430 °C for 2 h, in a stream of 10 vol% H₂ diluted with N₂ with a flow rate of 6 l/h. In the case of Ni-La₂O₃ the thermal treatment temperature was 530 °C. Fig. 1 shows the block diagram of the catalysts preparation.

For the multi-component catalysts, precious metals were loaded first. In a typical sample preparation, for the preparation of four-component catalyst (5.0 wt%Ni-2.7 wt%La₂O₃-0.50 wt%Ru-0.10 wt%Rh) (designated as Cat.11), the order of impregnation was as follows:

- (i) Rh was impregnated onto θ -alumina that was followed by drying, the ammoniacal treatment, drying, thermal/reduction treatment.
- (ii) Ru was impregnated onto the Rh impregnated θ -alumina and followed by drying, ammoniacal treatment, drying, thermal/reduction treatment.
- (iii) Ni-La₂O₃ were loaded onto the Rh and Ru loaded θ -alumina following same procedures.

2.2. Characterization of catalysts

The BET surface area, pore volume and pore size distribution were obtained from nitrogen adsorption-desorption isotherms measured at 77 K by a Quantachrome, NOVA-1200 porosimeter, using the BJH method. All samples were

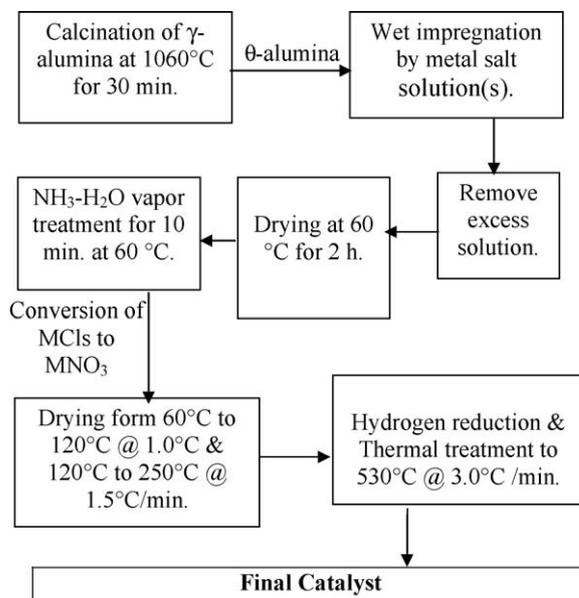


Fig. 1. Block diagram of catalyst preparation procedures.

pretreated under nitrogen flow at 350 °C for 1 h prior to nitrogen adsorption.

TPR measurements were carried out in a system supplied by Ohkura Riken Co., Ltd. (Model TP-2000). The procedure for pretreatment and subsequent TPR experiments was as follows. At first, a 150 mg portion of catalyst sample (particle size: 600–212 μm) was placed in a quartz tube (8.0 mm o.d.) reactor and was held in the center by quartz wool plugs. The samples were pretreated in a flow of dry air. The temperature was raised to 400 °C at a constant heating rate of 10 °C/min and held at 400 °C for 2 h, and then cooled to ambient temperature. The air was purged by flowing dry Ar (30 ml/min) for 30 min at ambient temperature.

For the TPR measurement the gas mixture used for reduction was 5% H_2 in Ar at a flow rate of 20 ml/min. The temperature of the reactor was increased linearly from room temperature to 1030 °C at a heating rate of 10 °C/min and then retained isothermally for 15 min. The moisture produced due to reduction or dehydration was trapped by a 5 Å molecular sieve. The hydrogen concentration was determined with a thermal conductivity detector (TCD). The TCD and molecular sieve trap were thermostated at 50 ± 0.1 °C. The temperature of the catalyst and the TCD current response were continuously monitored and recorded on a dedicated personal computer (NEC Model PC9821-Xe10).

2.3. Performance test of catalysts for methanation

To test the performance of the catalysts a continuous flow packed bed micro-reactor was used. The reactor was a quartz tubular reactor with an inside diameter of 1.5 cm. The length of the tube was 48 cm. Catalyst was placed in-between the supporters (calcium carbide) in the middle of the reactor. A mixture of 6.0 vol% CO , 6.0 vol% CO_2 , 44.0 vol% H_2 , 44.0 vol% N_2 was used as a model syngas composition. The space velocity of the mixed gas was $10,000 \text{ h}^{-1}$. Temperature of the reactor was raised from room temperature until CO fully converted to methane. To get the composition of gas mixture a gas chromatograph (Shimadzu GC 17A, TCD) was used with an activated charcoal packed into 3 m Column.

3. Results and discussion

3.1. Characterization of catalysts

BET surface area and pore volume measurements have been carried out on the prepared and commercial catalysts. The results of BET surface area and pore volume measured by nitrogen adsorption for the selected methanation catalysts are given in Table 1.

From this table it is evident that the surface area of commercial catalyst (Cat.2) is substantially lower than the rest of the catalysts prepared in this study. This difference is due to high nickel loading and also the alumina used for making this commercial catalyst. On the other hand, the prepared two-, three- and four-component catalysts showed a narrow range of surface area and pore volume. Maximum 8% reduction of

Table 1
Surface area and pore volume of methanation catalysts

Catalyst/support	BET surface area (m^2/g)	Pore volume (ml/g)
γ -Alumina*	135	0.65
θ -Alumina	128	0.62
Cat.2	82.3	0.52
Cat.5	118	0.59
Cat.7	120	0.58
Cat.9	119	0.61
Cat.11	121	0.59

* Davicat AL 2750.

surface area was observed for Cat.5 in comparison with the θ -alumina support. This indicates that 5% Ni and other small amount of precious metals may not have caused significant pore blocking and reduction of surface area.

3.2. TPR profiles for commercial methanation catalysts

TPR profiles for two kinds of commercial methanation catalysts, Cat.1 and Cat.2 composed of 21.0 wt%Ni and 5.0 wt%Ni supported on γ - Al_2O_3 and θ - Al_2O_3 , respectively, are shown in Fig. 2.

The reduction temperature profile for the low Ni loading catalyst; 5.0 wt%Ni on θ - Al_2O_3 (Cat.2), was very broad and the peak appeared at around 499 °C. This high temperature indicates the lower methanation activity. On the other hand a TPR profile for the high Ni loading catalyst, 21.0 wt%Ni on γ - Al_2O_3 (Cat.1), shows major peak temperature at 478 °C. The small peak at lower temperature is due to bulk NiO loosely bounded to the support and higher temperature major peak is due to strong NiO supported with alumina. This peak temperature roughly coincides with that of the former one, and is identical to the result observed with the same method by Ahmed et al. [11].

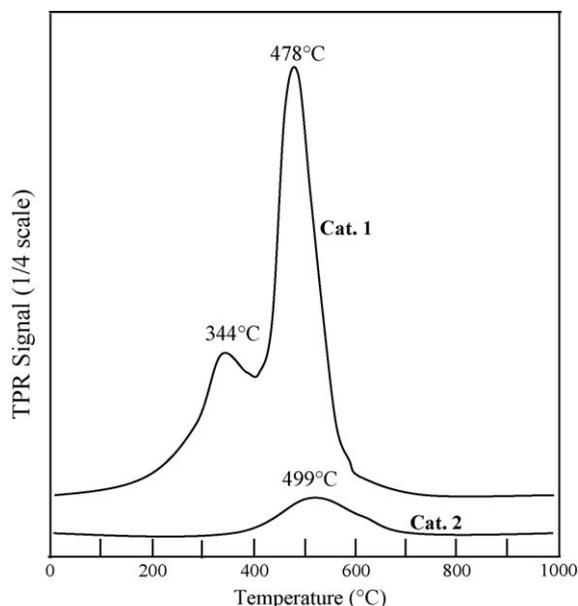


Fig. 2. TPR profiles of 21.0 wt%Ni on γ -alumina (Cat.1); 5.0 wt%Ni on θ -alumina (Cat.2).

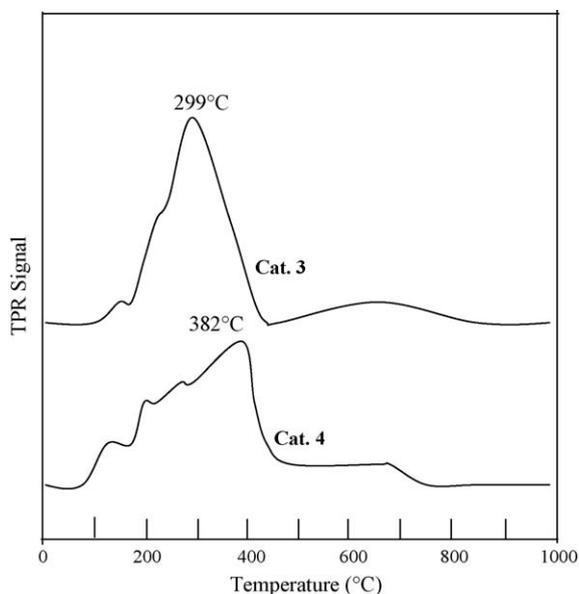


Fig. 3. TPR profiles of 5.0 wt%Ni-2.7 wt%La₂O₃-0.20 wt%Ru on θ -alumina (Cat.3); 5.0 wt%Ni-2.7 wt%La₂O₃-0.20 wt%Rh on θ -alumina (Cat.4).

3.3. TPR profiles for methanation catalysts changing kinds of precious metal

The properties of two kinds of prepared catalysts, 5.0 wt%Ni-2.7 wt%La₂O₃-0.20 wt%Ru (Cat.3) and 5.0 wt%Ni-2.7 wt%La₂O₃-0.20 wt%Rh (Cat.4) supported on the θ -alumina are shown in Fig. 3. As for the composition of these catalysts the loading of Ni-La₂O₃ parts are same as the optimum composition concluded by the former study (designated as Cat.13) [9]. However, Ru and Rh content was decreased from 0.50 to 0.20 wt%.

Both TPR profiles evidently shifted to lower temperature ranges with monotonous peaks compared with those for commercial catalysts shown in Fig. 2.

To demonstrate the role of La₂O₃ with precious metals, catalysts were prepared without La₂O₃ while keeping the loading of precious metal as same as the three-component catalysts. i.e., 5.0 wt%Ni-0.20 wt%Ru (Cat.5) and 5.0 wt%Ni-0.20 wt%Rh (Cat.6). For comparison two-component catalyst without the precious metals was also prepared, i.e., 5.0 wt%Ni-2.7 wt%La₂O₃ (Cat.7).

These TPR profiles were shown in Fig. 4. In those profiles although reduction temperatures were shifted to lower temperature sides, the profiles with precious metals composed of multiple peaks, especially in the case of Ni-Rh catalyst. In case of Cat.7 (Ni-La₂O₃), La₂O₃ has insignificant role on reducing reduction temperature.

In cases of the bi-metallic catalysts, Ni-Ru and Ni-Rh, dispersion of Ni on the support was not enough and the effect of hydrogen spillover by the existence of Ru and Rh could not progress smoothly.

Comparing the difference in TPR profiles in Figs. 3 and 4, it can be said that the lowering of the reduction temperature of nickel oxides is caused by both existence of La₂O₃ and precious metals. The former has a role of increasing Ni dispersion and

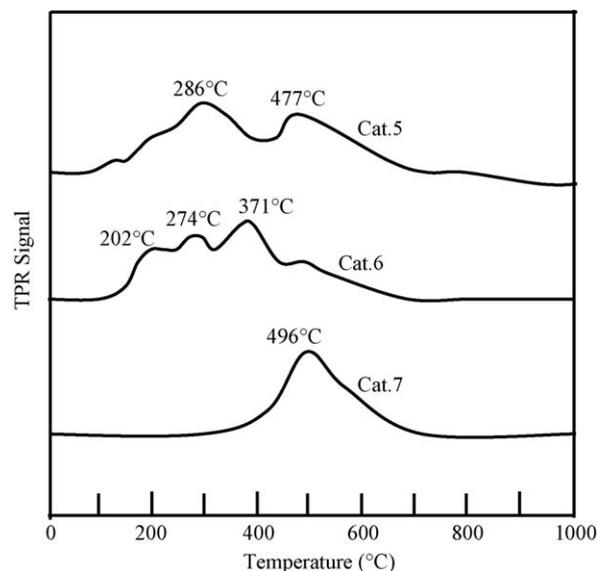


Fig. 4. TPR profiles for 5.0 wt%Ni-0.20 wt%Ru on θ -alumina (Cat.5); 5.0 wt%-0.20 wt%Rh on θ -alumina (Cat.6); 5.0 wt%Ni-2.7 wt%La₂O₃ (Cat.7).

the latter has a role of the porthole of the hydrogen spillover as concluded in the former works [4,9].

3.4. TPR profiles for methanation catalysts changing the Ru loading onto Ni-La₂O₃ catalyst

The effect of Ru loading on the performance of multi-component composite catalysts was investigated. In the case of known catalyst (Cat.13) [9] the Ru loading was 0.50 wt%, and then in this study the loading of Ru was varied in the range of 0.20–1.0 wt% for Cat.3 and Cat.8, respectively. TPR profiles for these three kinds of catalyst are shown in Fig. 5. As shown in this figure, the peak temperatures of TPR profiles shifted to lower temperature to 299, 284, and 233 °C correspondingly to 0.20 (Cat.3), 0.50 (Cat.9), and 1.0 wt% (Cat.8), respectively, with increasing Ru loading. The shape of TPR profiles, however, changed from broad one to sharper peak. In case of the lowest Ru loading (0.20 wt%) high temperature satellite peak remained. This indicates incomplete reduction of Ni oxides. On the other hand, in the case of the highest Ru loading (1.0 wt%) a sharp lower temperature satellite peak became prominent. This indicates excess Ru exists separately from the bulk of NiO_x-La₂O₃ parts and this isolated Ru oxide can be easily reduced by hydrogen at low temperature around 147 °C. In case of the middle Ru loading (0.50 wt%) (Cat.9), it has the same composition of the previously studied methanation catalyst (Cat.13) [9] the low temperature satellite peak is very small, and the most uniform and monotonous single peak was observed. These results indicate that the most proper loading of Ru to exert the uniform reduction is confirmed 0.50 wt% as concluded by the former study.

Though the known three-component catalyst (5.0 wt%Ni-2.7 wt%La₂O₃-0.50 wt%Ru) [10] was not characterized by TPR method before this study but it was recognized that combination of three types of metals supported on θ -alumina are optimized for maximum performance.

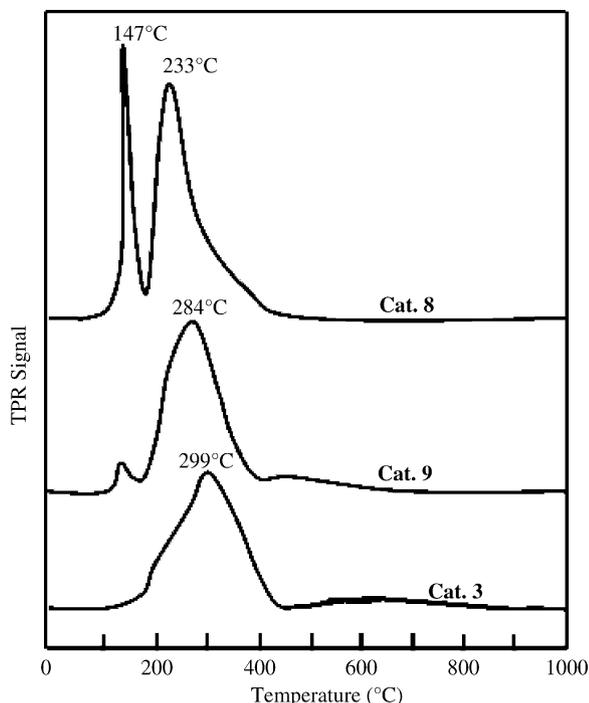


Fig. 5. TPR profiles for 5.0 wt%Ni-2.7 wt%La₂O₃-1.0 wt%Ru (Cat.8); 5.0 wt%Ni-2.7 wt%La₂O₃-0.50 wt%Ru (Cat.9); 5.0 wt%Ni-2.7 wt%La₂O₃-0.20 wt%Ru on θ -alumina (Cat.3).

3.5. TPR profiles for the methanation catalysts with Rh-modification onto the known three-component catalyst

The same composition of the known three-component catalyst; 5.0 wt%Ni-2.7 wt%La₂O₃-0.50 wt%Ru (Cat.9), was then modified by a very low loading Rh to enhance the hydrogen reduction and the methanation activity with anticipating the promotion of hydrogen spillover as mentioned above. The loading of precious metal should be used as low as possible from the view point of the preparation cost from the former study [7] the optimum composition for three-component catalysts had been found as: 5.0 wt%Ni, 2.7 wt%La₂O₃ and 0.50 wt%Ru (Cat.13). Combination of Ru and Rh could act as a super active catalyst [10].

In order to make sure the good loading balance of the ingredients in the four-component catalyst of Ni-La₂O₃-Ru-Rh, loadings of Ru and Rh were varied, from 0.20 to 1.0 wt% and 0.10 to 0.20%, respectively while keeping the constant composition of 5.0 wt%Ni-2.7 wt%La₂O₃. The results of TPR profiles are shown in Fig. 6. Evidently, in case of the catalyst modified by Rh with 0.10 wt% (Cat.11) on to the known three-component catalyst, i.e., content of Ru is 0.50 wt%, the most monotonous and sharp reduction profile was observed. On the other hand, in cases of too low concentration Ru (i.e., 0.20 wt%) (Cat.10) and too high concentration Ru (i.e., 1.0 wt%) (Cat.12), the TPR profiles were broad and two peaks appeared, respectively. However, a decrease in the peak temperature could be observed with increasing Ru loading.

Thus the optimum composition of the four-component catalyst from the view point of TPR profile was concluded as

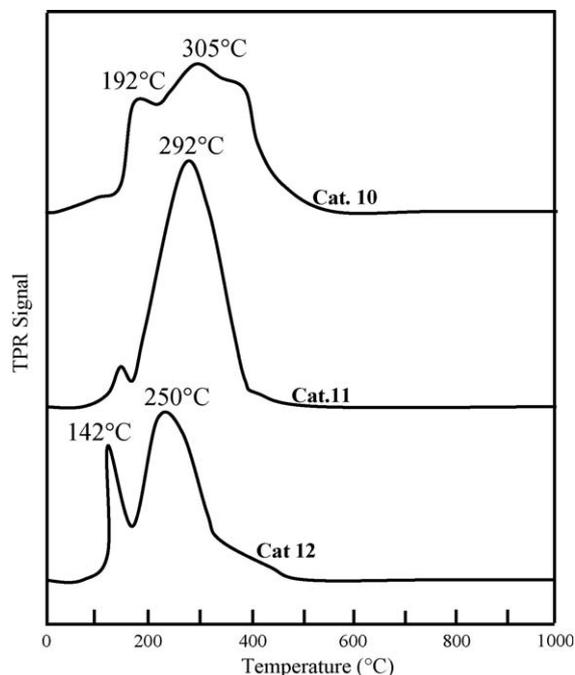


Fig. 6. TPR profiles for 5.0 wt%Ni-2.7 wt%La₂O₃-0.20 wt%Ru-0.10 wt%Rh (Cat.10); 5.0 wt%Ni-2.7 wt%La₂O₃-0.50 wt%Ru-0.10 wt%Rh (Cat.11); 5.0 wt%Ni-2.7 wt%La₂O₃-1.0 wt%Ru-0.20 wt%Rh on θ -alumina (Cat.12).

0.10 wt%Rh-modified catalyst (Cat.11) onto the known three-component 5.0 wt%Ni-2.7 wt%La₂O₃-0.50 wt%Ru.

3.6. Performance of catalysts for methanation

The temperature dependence of CO and CO₂ conversion in methanation reaction on four types of representative catalysts is shown in Fig. 7. Catalysts tested were as follows: the commercial 21.0 wt%Ni/ γ -Al₂O₃ catalyst (Cat.1), the two-component supported 5.0 wt%Ni-2.7 wt%La₂O₃ catalyst (Cat.7), 5.0 wt%Ni-0.20 wt%Ru (Cat.5) the three-component

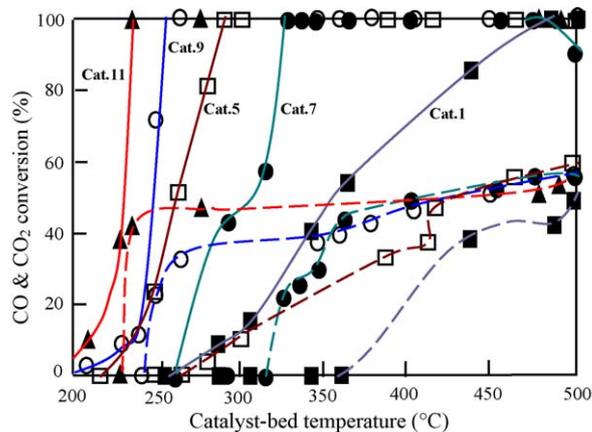


Fig. 7. Temperature dependence of CO and CO₂ conversion; (▲) Cat.11 (5.0 wt%Ni-2.7 wt%La₂O₃-0.50 wt%Ru-0.10 wt%Rh/ θ -Al₂O₃); (○) Cat.9 (5.0 wt%Ni-2.7 wt%La₂O₃-0.50 wt%Ru/ θ -Al₂O₃); (●) Cat.7 (5.0 wt%Ni-2.7 wt%La₂O₃/ θ -Al₂O₃); (□) Cat.5 (5.0 wt%Ni-0.20 wt%Ru/ θ -Al₂O₃); (■) Cat.1 (21.0 wt%Ni/ γ -Al₂O₃); (solid line) CO conversion; (dotted line) CO₂ conversion.

Table 2
Summary of TPR profiles for reference and prepared catalysts and features of preferential methanation on these catalysts

Catalyst		TPR profile		Preferential methanation of CO	
No.	Composition	Peak temperature (°C)	Feature (Fig. no.)	Temperature total CO conversion (°C) (Fig. no.)	Feature
1	21.0 wt%Ni/ γ -Al ₂ O ₃ (Commercial Cat.1)	478	High, satellite peak at 344 °C (Fig. 2)	488 (Fig. 7)	CO-CO ₂ co-methanation occurred
2	5.0 wt%Ni/ θ -Al ₂ O ₃ (commercial Cat.2)	499	Low and broad (Fig. 2)	500 (CO conv. 85%)	CO-CO ₂ co-methanation occurred
3	5.0 wt%Ni-2.7 wt%La ₂ O ₃ -0.20 wt%Ru/ θ -Al ₂ O ₃	299	Smooth monotonous (Figs. 3 and 5)		
4	5.0 wt%Ni-2.7 wt%La ₂ O ₃ -0.20 wt%Rh/ θ -Al ₂ O ₃	382	Monotonous but not uniform (Fig. 3)		
5	5.0 wt%Ni-0.20 wt%Ru/ θ -Al ₂ O ₃	477, 286	Two broad peaks (Fig. 4)	290 (Fig. 7)	Above 50% CO conv. CO ₂ conv. added
6	5.0 wt%Ni-0.20 wt%Rh/ θ -Al ₂ O ₃	477, 371, 274, 202	Considerably broad peaks consisted of four satellite ones (Fig. 4)		
7	5.0 wt%Ni-2.7 wt%La ₂ O ₃ / θ -Al ₂ O ₃	496	Smooth broad peaks (Fig. 4)	325 (Fig. 7)	Above 60% CO conv. CO ₂ conv. was added
8	5.0 wt%Ni-2.7 wt%La ₂ O ₃ -1.0 wt%Rh/ θ -Al ₂ O ₃	233, 147	Distinct two peaks (Fig. 5)		
9	5.0 wt%Ni-2.7 wt%La ₂ O ₃ -0.50 wt%Ru/ θ -Al ₂ O ₃	284	Smooth monotonous with very little satellite one at 147 °C (Fig. 5)	250 (Fig. 7)	
10	5.0 wt%Ni-2.7 wt%La ₂ O ₃ -0.20 wt%Ru-0.10 wt%Rh/ θ -Al ₂ O ₃	305, 192	Relatively broad (Fig. 6)	245 (Fig. 7)	
11	5.0 wt%Ni-2.7 wt%La ₂ O ₃ -0.50 wt%Ru-0.10 wt%Rh/ θ -Al ₂ O ₃	292	Smooth monotonous high peak (Fig. 6)	230 (Fig. 7)	
12	5.0 wt%Ni-2.7 wt%La ₂ O ₃ -1.0 wt%Ru-0.20 wt%Rh/ θ -Al ₂ O ₃	250, 142	Two irregular peak (Fig. 6)	275 (Fig. 7)	
13*	5.0 wt%Ni-2.7 wt%La ₂ O ₃ -0.50 wt%Ru/SiO ₂			250	First foundation [9]

* Reference catalyst presented in [4,9]. Cat.9 has the same composition, but absolute loading of each component on Cat.9 is twice of the reference catalyst 13 due to the difference of the specific gravity of support.

supported 5.0 wt%Ni-2.7 wt%La₂O₃-0.50 wt%Ru catalyst (Cat.9), and the four-component supported 5.0 wt%Ni-2.7 wt%La₂O₃-0.50 wt%Ru-0.10 wt%Rh catalyst (Cat.11).

Comparison made from Fig. 7 is as follows: The commercial Ni catalyst (Cat.1) showed a low methanation activity and complete conversion of CO was attained at around 488 °C but CO₂ methanation occurred simultaneously above 50% CO conversion. The reaction temperature range well corresponds to the TPR profile. Another commercial catalyst (Cat.2) tested in TPR showed similar behaviors. The two-component Ni-La₂O₃ catalyst (Cat.7) showed a considerable high conversion compared with the commercial catalyst and complete conversion of CO attained at 325 °C. This enhancement is attributed to increased dispersion of Ni by La₂O₃ [4,8]. But the other two-component catalyst Ni-Ru (Cat.5) showed even better result compared to Ni-La₂O₃. Complete conversion of CO occurred at 290 °C. The reason for enhanced activity is attributed to the hydrogen spillover effect of Ru. Preferential methanation of CO was observed in both cases until its total conversion.

It can be seen that for the three- and the four-component catalysts; (Cat.9) and (Cat.11), total conversion of CO occurred at very low temperatures, 250 and 230 °C, respectively. The 250 °C in the catalyst (Cat.9) coincides with that in the same catalyst composition [4], although in this case the absolute loading amount of each component was about half due to the light specific gravity of SiO₂ support than Al₂O₃ support.

In coexistence of CO and CO₂, the methanation of CO occurred preferentially on every catalyst except the commercial catalyst. For all of the multi-component catalysts the methanation of CO₂ proceeded after CO was almost completely consumed. These indicate that the strong adsorption strength of CO onto the multi-component catalysts during the reaction is far stronger than that of CO₂ and then the adsorbed CO inhibits the CO₂ adsorption and methanation. The lowest temperature for total conversion of CO was seen at 230 °C on four-component catalyst (Cat.11).

Then, three kinds of combination in Ru-Rh loading concentrations; 0.20 wt%Ru-0.10 wt%Rh (Cat.10), 0.50 wt%

Ru-0.10 wt%Rh (Cat.11), and 1.0 wt%Ru-0.20 wt%Rh (Cat.12), were adopted while fixing the part of 5.0 wt%Ni-2.7 wt%La₂O₃. Comparison of catalytic performance is made in Table 2. Those comparisons in TPR had been made above in Fig. 5. Well corresponding to Fig. 5 the highest active catalyst was confirmed in the case of the combination of 0.50 wt%Ru-0.10 wt%Rh (i.e, Cat.11). The numerical comparison on the conversion of CO for each catalyst is summarized in Table 2.

4. Conclusions

Since the performance of commercial methanation catalyst is almost invalid for the preferential methanation of CO due to its low activity, the novel catalyst was developed in this study based on the known high active methanation catalyst. The Rh-modified with 0.10 wt% onto the highly active known three-component catalyst, 5.0 wt%Ni-2.7 wt%La₂O₃-0.50 wt%Ru, exhibited the highest activity. Preferential CO methanation with complete CO conversion was achieved on this catalyst at 230 °C. This temperature is 20 °C lower than that on the three-component catalyst. Above these temperatures, CO₂ methanation successfully progressed. These Ni-based composite catalysts have a potential to complete elimination of CO from the H₂- and CO₂- rich mixed gas. Good co-relationship between TPR profiles in both peak shape and peak temperature and methanation activities was recognized.

Acknowledgements

The authors wish to acknowledge the support of Research Institute of King Fahd University of Petroleum and Minerals for this work. Thanks are also due to Mr. U.B. Majeed and K. Alam for their support in some of the experiments.

References

- [1] F. Joensen, J.R. Rostrup-Nielsen, *J Power Sources* 105 (2002) 195.
- [2] D.L. Trimm, *Appl. Catal. A Gen.* 296 (2005) 1.
- [3] T.V. Herwijnen, H.V. Doesburg, W.A. Du Jong, *J. Catal.* 28 (1973) 391.
- [4] T. Inui, M. Funabiki, Y. Takegami, *Ind. Eng. Chem., Prod. Res. Dev.* 19 (1980) 385.
- [5] T. Inui, *Stud. Surf. Sci. Catal.* 77 (1993) 17.
- [6] M.M. Hossain, M.A. Al-Saleh, M.A. Shalabi, T. Kimura, T. Inui, *Appl. Catal. A Gen.* 278 (2004) 65.
- [7] M.A. Al-Saleh, M.M. Hossain, M.A. Shalabi, T. Kimura, T. Inui, *Appl. Catal. A Gen.* 253 (2003) 453.
- [8] T. Inui, T. Miyake, Y. Takegami, *J. Jpn. Petrol. Inst.* 25 (4) (1982) 242.
- [9] T. Inui, M. Funabiki, M. Suehiro, T. Sezume, *J. Chem. Soc., Faraday Trans. I* 75 (1979) 787.
- [10] T. Inui, M. Suehiro, Y. Saita, T. Miyake, Y. Takegami, *Appl. Catal.* 2 (1982) 389.
- [11] S. Ahmed, S.A. Ali, K. Alam, S.H. Hamid, *Arab. J. Sci. Eng.* 24 (1999) 71.
- [12] O. Gorek, P. Pfeifer, K. Schubert, *Catal. Today* 110 (2005) 132.
- [13] A.E. Aksoylu, Z.I. Onsen, *Appl. Catal. A Gen* 164 (1997) 1.
- [14] K.O. Xavier, R. Sreekala, K.K.A. Rashid, K.K.M. Yusuff, B. Sen, *Catal. Today* 49 (1999) 17.
- [15] S.H. Fujita, N. Takezawa, *Chem. Eng. J.* 68 (1997) 63.
- [16] H. Over, M. Muhler, *Progr. Surf. Sci.* 72 (2003) 3.