

Chemistry

A STUDY ON METHANATION OF CARBON MONOXIDE OVER CATALYSTS NiO/TiO₂ AND NiO/ γ -Al₂O₃

Luu Cam Loc, Nguyen Manh Huan, Nguyen Kim Dung,
Nguyen Huu Huy Phuc, and Ho Si Thoang

*Institute of Chemical Technology,
Vietnamese Academy of Science and Technology,
1, Mac Dinh Chi Str., Ho Chi Minh City, Vietnam*

Abstract. The catalyst 7.5% NiO/TiO₂ and seven samples of NiO/ γ -Al₂O₃ with NiO content from 7.5% to 60% have been obtained and studied. Physico-chemical characteristics of the catalysts were determined by methods of Adsorption (BET), X-ray Diffraction (XRD), Temperature-Programmed Reduction (TPR) and Hydrogen Pulse Titration. The catalytic properties of the obtained samples were investigated in the reaction of CO methanation at temperatures 180 – 220°C and mole ratios hydrogen/carbon monoxide 25-100. It has been found that the optimal regime for catalyst treatment is calcination at 600°C and reduction at 400°C. The catalyst 7.5% NiO/TiO₂ expressed very high activity but in case of NiO/Al₂O₃ for having high activity it was necessary to raise the content of NiO up to 37.7%. This catalyst has been indicated to be the most active in all the studied conditions. The determining factors for expressing high activity in the catalyst 7.5% NiO/TiO₂ are the presence of spinel NiTiO₃ and the optimal average size of nickel assemblies but in the catalyst 37.7% NiO/Al₂O₃ – the optimal size of active centers, big values of specific surface area and content of NiO and the high thermal stability.

1. INTRODUCTION

The reaction of methanation is used to remove CO from feeding gases in many industrial processes, such as coal gasification, ammonia synthesis and hydrogen production. According to authors [1-4], the activities of metals in this reaction could be placed as follows: Ru>Fe>Ni>Co>Rh>Pd>Pt> Ir. Ruthenium expresses the highest activity, selectivity and stability in the reaction, but it is also an expensive metal. Iron, although has high activity in the conversion of CO, but loses it quickly and the selectivity in methanation is poor. Platinum, palladium and rhodium have sufficiently high activity but low selectivity in the CO methanation. Besides they are expensive metals. Thus practically all the noble metals are not used as catalysts for the given reaction. Nickel occupies only an intermediary position in the given above row of activity order, but it is a cheap metal and its catalytic properties are relatively good. The advantage of nickel-based catalysts is included in their high selectivity, but nickel is also easily reacted with CO to form such compounds as carbonyl Ni(CO)₄, carbide Ni₃C, free carbon [5, 6]. However, this problem could be easily settled by selecting appropriate temperature and feed composition of the reaction. That is why nickel catalysts now are widely used in industrial processes of methanation. As indicated in [4, 7-10], they are supported contacts with such carriers as TiO₂, Al₂O₃, SiO₂. Research results by authors [7] showed that the best carrier is

TiO₂, therefore many studies in activity determination, kinetics and mechanism of the reaction have been carried out on the catalyst system NiO/TiO₂. However, in industrial applications the carrier aluminum oxide has been indicated to be more appropriate than titanium oxide. In this work we tried to study a series of NiO/ γ -Al₂O₃ with various percentages of nickel oxide for looking for some catalyst samples, which not only have high activity but answer the requirements of practical application into the methanation of carbon monoxide.

2. EXPERIMENTAL

2.1. Catalyst Preparation

The catalyst samples NiO/Al₂O₃ (except for the sample, prepared by co-precipitation and will be mentioned below) were prepared by the method of wet impregnation of Al(OH)₃ in Bayerite form with the solution of Ni(NO₃)₂.6H₂O. Before impregnation the carrier was washed by hot water and dried 6 hours at 80°C. The content of NiO in catalysts varied from 7.5% to 60%. All the obtained catalysts after impregnation were dried at 60°C, 100°C and 130°C, at each temperature 2 hours, and calcined 4 hours at 600°C. After that the products were granulated, ground and sieved to select the fraction of 0.32 – 0.64 mm. For comparison we have prepared also a sample with the carrier TiO₂ as described in [7]. This catalyst, as indicated below, was calcined at 400°C and 600°C before experiments. The composition of all the obtained catalysts is presented in Table 1.

Table 1. *Composition of the studied catalysts*

Catalysts	Carrier	NiO content, wt.%	Composition of Catalysts
7,5Ni/Ti	TiO ₂ Anatase	7,5	7,5%NiO/TiO ₂
7,5Ni/A	γ -Al ₂ O ₃	7,5	7,5%NiO/ γ -Al ₂ O ₃
13,7Ni/A	γ -Al ₂ O ₃	13,7	13,7% NiO/ γ -Al ₂ O ₃
20Ni/A	γ -Al ₂ O ₃	20	20% NiO/ γ -Al ₂ O ₃
37,7Ni/A	γ -Al ₂ O ₃	37,7	37,7% NiO/ γ -Al ₂ O ₃
37,7Ni/A*	γ -Al ₂ O ₃	37,7	37,7% NiO/ γ -Al ₂ O ₃ *
45Ni/A	γ -Al ₂ O ₃	45	45% NiO/ γ -Al ₂ O ₃
60Ni/A	γ -Al ₂ O ₃	60	60% NiO/ γ -Al ₂ O ₃

*) *This catalyst was obtained by a slow co-precipitation process (24 hours) from a solution (with a minimum amount of water) of the mixture of nickel and aluminum nitrates.*

2.2. Catalyst Characterization

The determination of specific surface area and pore volume of the catalysts and the experiments for pulse titration (by hydrogen) and temperature-programmed reduction (TPR) were carried out on the apparatus CHEMBET 3000; The X-ray Diffraction (XRD) study was carried out on the X-ray Diffractometer XD-5A (firm Shimadzu). Before measuring procedure the sample was treated 2 h. at 150-300°C in a nitrogen flow as described in [11].

The catalytic activity of catalysts was determined in a microflow reactor at temperatures 180°C, 200°C and 220°C; the flow volume velocity of feeds was 18 l/h, the mole ratio H₂/CO varied from 25 to 100 and the weight of catalyst was 0.1 or 1 g. The reaction products were analyzed on the Gas Chromatograph Agilent Technologies 6890 Plus. For analysis of carbon monoxide the capillary column HP-PLOT Molecular Sieve 5A and the Thermal Conductivity Detector were used and for analysis of methane the column HP-1 and the Flame Ionization Detector were used. In both the cases the size of column was 30 m of length, 0.12 μ m of inner diameter and 0.32 mm of outer diameter.

3. RESULTS AND DISCUSSIONS

3.1. Physico-Chemical Characteristics of Catalysts

The results on surface area and average size of pore radius of the carriers and studied catalysts are presented in Table 2. From the data of Table 2 it follows that specific surface area of TiO₂ is 4.5 time less than that of γ -Al₂O₃ but their pore sizes are differed from each other not considerably.

The supported sample 7.5Ni/Ti has a specific surface area slightly higher than that of the carrier TiO₂ but in case of alumina and alumina-supported catalysts the picture is reverse, i.e. the supported samples NiO/ γ -Al₂O₃ have lower values of specific surface area than the carrier and the more the content of nickel oxide the lower the surface area of the catalysts. Methods of preparation do not influence significantly the values of catalyst specific surface area. The reason of surface decrease is probably included in blocking the carrier surface by crystallized NiO, which is characterized by a lower surface area than that of alumina. The values of average pore diameter vary not very significantly, only from 23 to 31Å.

Table 2. Specific surface area (S_{BET}) and average pore diameter (r_p) values of the carriers and supported catalysts.

Samples	S_{BET} , m ² /g	r_p , Å ^o
TiO ₂	47	28
γ -Al ₂ O ₃	215	24
7,5Ni/Ti	52	-
7,5Ni/A	191	26
13,7Ni/A	135	31
20Ni/A	141	23
37,7Ni/A	125	31
37,7Ni/A*	129	-
45Ni/A	82	28
60Ni/A	55	-

The results of phase state characterization by XRD are given in Figure 1. From Fig. 1 it follows that in the sample NiO/TiO₂ are present crystals of anatase, rutile (small

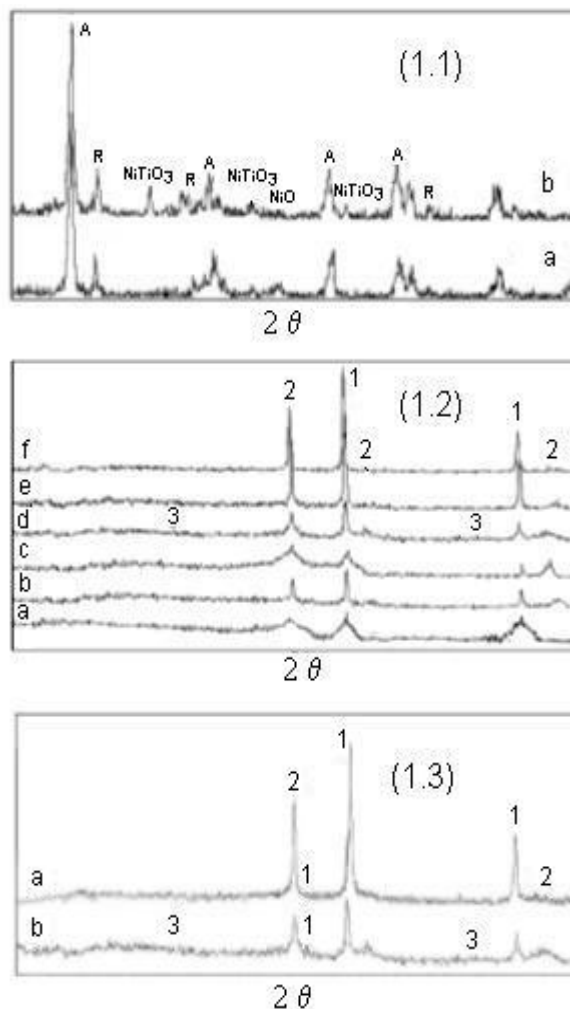


Fig. 1. XRD spectra of catalysts 1.1- Catalyst NiO/TiO₂, calcined at different temperatures: a) 400°C, b) 600°C 1.2- Catalyst NiO/Al₂O₃ with different contents of Nickel oxide, obtained by impregnation method, and calcined at 600°C, 7.5 Ni/A ; b) 13.7 Ni/A; 20 Ni/A; d) 37.7 Ni/A; e) 45 Ni/A; f) 60 Ni/A. 1.3- Catalyst 37.7%NiO/Al₂O₃, obtained by impregnation method (a) and slow co-precipitation method (b); A: Anatase, R: Rutile, 1: NiO, 2: NiAl₂O₄, 3: Ni₃Al.

quantity), NiO and spinel NiTiO₃. The last one was formed probably by the strong interaction between NiO and TiO₂ and evidently increased with temperature of calcination. In the spectra of catalysts NiO/Al₂O₃ there are only the peaks, characteristic of NiO and NiAl₂O₄ phases. The intensity of these peaks increased with the content of nickel oxide. For the sample 37.7Ni/A, obtained by impregnation method, characteristic peaks of NiO and NiAl₂O₃ are less intensive than those for the sample with the same composition but obtained by co-precipitation. Also the XRD spectrum of the sample, obtained by impregnation, indicates that in this sample there is some amount of Ni₃Al. In the spectra of

NiO/TiO₂ the characteristic peaks of NiTiO₃ are more intensive than those of NiO, but in the spectra of NiO/Al₂O₃, on the contrary, the intensities of characteristic peaks of spinel NiAl₂O₄ are less intensive.

The results of hydrogen pulse titration are given in Table 3. Before experiments the samples were reduced 2 hours at 450°C.

Table 3. Surface characteristics of the studied catalysts: values of specific surface area of catalysts (S_{BET}), surface area of Ni on 1 g of catalyst (S_1), surface area of 1 g of Ni (S_2); size of Ni assemblies (d_{Ni}) and dispersity of Ni on the surface (γ_{Ni}).

Catalyst	S_{BET} , m ² /g	S_1 , m ² /g	S_2 , m ² /g	d_{Ni} , nm	γ_{Ni} , %
7,5Ni/Ti	52	4	68	15	10
7,5Ni/A	191	9	157	6	24
13,7Ni/A	135	21	153	7	23
20Ni/A	141	20	104	9,7	16
37,7Ni/A	125	20	54	19	8
37,7Ni/A*	129	21	56	18	8
45Ni/A	82	15	34	30	5
60Ni/A	55	13	22	47	3

It follows from the data of Table 3 that with the same quantity of NiO (7.5%) in case of TiO₂ the surface of nickel per 1 g of carrier and the dispersity of nickel are less, but the size of nickel assemblies is bigger, than in case of Al₂O₃. This fact could be explained by less specific surface area of TiO₂, compared with Al₂O₃.

On the samples of NiO/Al₂O₃ we can see that when the content of NiO is rising its dispersity decreases and the average size of its assemblies increases. The reason of this phenomenon is probably included in strengthening of the interaction between nickel particles, leading to their sintering. The data of Table 3 indicate that it is possible to regulate the average size of nickel assemblies by varying the content of supported NiO. The sample 7.5Ni/Ti and samples NiO/Al₂O₃ with 20% and 37.7% of NiO were indicated to have optimal size of assemblies (10-20 nm) [7] for the reaction of CO methanation. Below 20% and over 37.7% of nickel oxide the assemblies of nickel on the catalysts NiO/Al₂O₃ have average size smaller or bigger than optimal one.

The surface characteristics of two samples with 37.7% of NiO on Al₂O₃ but obtained by different ways are very identical. It seems that their catalytic properties should be similar.

The results of TPR experiments are presented in Figure 2. The data on this figure show that in case of the sample 7.5Ni/Ti, calcined at 400°C, there is only one peak with T_{max} at about 524°C. This is probably the characteristic peak of NiO, interacted with carrier, because free NiO is reduced normally at 285-305°C. In the TPR diagram of the same sample but preliminary calcined at 600°C we can see the appearance of another peak with T_{max} at 550°C, characteristic of the spinel NiTiO₃ reduction [7]. It follows from this consideration that if the temperature for NiO/TiO₂ reduction lower 500°C we could not

reach the complete reduction of nickel ion. Indeed after a preliminary reduction 8 hours at 250°C the area of reduction peak of the 7.5Ni/Ti sample decreased not considerably, but a similar treatment at 400°C (Fig. 2.2) led to decreasing about 40%, compared with the area of reduction peak in the TPR diagram. If a preliminary reduction during 1 hour was carried out at 500°C in TPR diagram of the sample no reduction peak appeared more. It is interesting to note that the preliminary treatments mentioned above led to different values of the activation energy in reduction processes followed afterwards; i.e. the value of the activation energy for the reduction process E_{red} , proceeded immediately after calcination, was found to be 15 kJ/mol, after a preliminary reduction 8 hours at 250°C – 23 kJ/mol and after a preliminary reduction 8 hours at 400°C – 37 kJ/mol. It is clearly that since free NiO was reduced in the preliminary reductions, the part of nickel ion, remained after those processes, must be existed in interacted with carrier forms and more stable towards the reduction process. The higher the temperature of preliminary reduction the more the amount of this stable nickel ion. Indeed, it has been found that the content of free NiO, remained after the preliminary reduction at 250°C, was significantly more than that, remained after the preliminary reduction at 400°C.

The TPR diagram of the sample 7.5Ni/A has only one peak at $T_{max} = 438^\circ\text{C}$ (Fig.2.3), but in the TPR diagrams of other samples with more contents of NiO there are two peaks; the first peak is located at temperatures 461 – 517°C and the second one is located at 550- 560°C. From this result, as well as from the data of XRD studies, it is possible to conclude that the first peak characterizes the reduction process of NiO, interacted with aluminum oxide, but the second one is characteristic of the spinel NiAl_2O_4 reduction. It can be seen that the content of nickel aluminate in all the samples is less than that of nickel oxide but increased relatively faster with rising of NiO content. The small peak at $T_{max} = 250^\circ\text{C}$, observed on samples 13.7Ni/A and 37.7Ni/A, should be assigned to the reduction process of Ni_3Al . This form probably existed in a very dispersed state. The tendency of moving of the first peak towards higher temperatures can be explained by growing the NiO assemblies, making the reduction process to be more difficult. This interpretation corresponds with the results of pulse titration (d_{Ni}), presented in Table 3. From the other side, in the same conditions (after calcination at 600°C, followed by a reduction process 8 hours at 400°C), the TPR profiles of all the samples NiO/ Al_2O_3 have T_{max} values lower than those of the sample 7.5% NiO/ TiO_2 . This fact allows us to say that on the surface of $\gamma\text{-Al}_2\text{O}_3$ the reduction process of nickel oxide proceeds easier than on the surface of TiO_2 .

The TPR profile of the sample 37.7Ni/A, obtained by co-precipitation method is differed from that of the sample, obtained by impregnation method; in the first case T_{max} of both the characteristic peaks of nickel oxide and nickel aluminate are moved towards higher temperatures (Fig. 3.3). Also while the TPR profile of the sample, obtained by impregnation, contains the characteristic peak of Ni_3Al reduction with $T_{max} = 250^\circ\text{C}$, on surface of the sample, obtained by co-precipitation, this peak is likely absent. This conclusion is supported by the data of XRD studies, given in Fig. 1. The fact that the reduction of both the forms of nickel ion NiO and NiAl_2O_4 in the sample, obtained

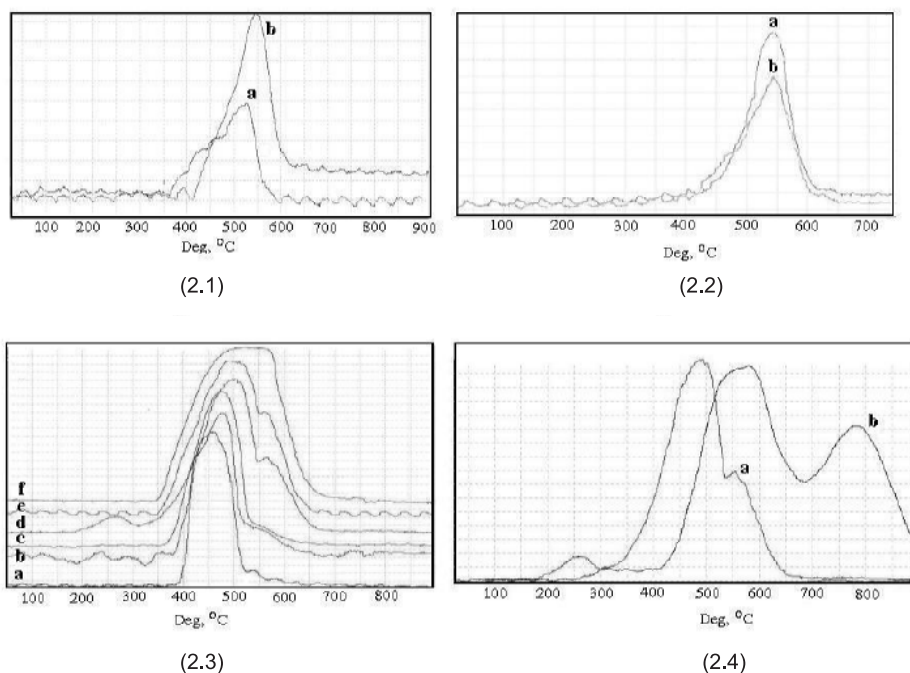


Fig. 2. TPR diagram of the studied samples: 2.1- Catalyst NiO/TiO₂ , calcined at 400°C(a) and 600°C(b); 2.2- Catalyst 7.5% NiO/TiO₂ after reduction 8 hours at 250°C(a) and 400°C(b); 2.3- Catalyst NiO/Al₂O₃ with different contents of Nickel oxide: a) 7.5 Ni/A, b) 13.7 Ni/A, c) 20 Ni/A, d) 37.7Ni/A, e) 45Ni/A, f) 60 Ni/A); 2.4- Catalysts 37.7%NiO/Al₂O₃, obtained by impregnation (a) and co-precipitation (b).

by co-precipitation, proceeds at higher temperatures than in the sample, obtained by impregnation, allows us to predict the higher catalytic activity of the second one.

3.2. Activity of Catalysts

At 250°C and mole ratio H₂/CO > 100 conversion of CO on all the studied catalysts reached 100%. From the other side, at 180°C and ratio H₂/CO = 25 some catalysts did not express any activity. Thus we had to choice the temperature range 180 – 220°C and the interval of H₂/CO ratio 25 – 100.

3.2.1. Conversion of CO on the Catalyst 7.5% NiO/TiO₂

The catalytic activity of the sample 7.5Ni/Ti after calcination 16 hours at 400°C are given in Table 4.

It follows from the data of Table 4 that the conversion extent of CO depends not only on the temperature and ratio H₂/CO, but on the regime of catalyst treatment (temperature of reduction). It is evidenced also that the conversion of CO increases with temperature and ratio H₂/CO. On the sample, reduced at 400°C, 100% conversion has been reached at 220°C and the hydrogen/carbon monoxide ratio 100. In practice this condition is usually accessible because the reaction proceeds in an excess of hydrogen.

Table 4. Conversion of CO (%) at different temperatures and mole ratios H_2/CO on the catalyst 7.5%NiO/TiO₂, calcined 16 hours at 400°C.

Ratio H ₂ /CO	After reduction 8 h at 250°C			After reduction 8 h at 400°C		
	180°C	200°C	220°C	180°C	200°C	220°C
25	3	8	18	25	34	55
33	18	21	23	30	45	67
50	37	51	62	50	84	99
100	71	87	90	89	99	100
Ratio H ₂ /CO	After reduction 1 h at 500°C			After reduction 1 h at 600°C		
	180°C	200°C	220°C	180°C	200°C	220°C
25	28	36	58	11	12	39
33	34	45	60	9	19	42
50	32	45	62	13	34	49
100	97	98	99	81	86	89

The influence of reduction regime:

Reduced at 250°C the catalyst expresses low activity. According to TPR data at this temperature the amount of reduced nickel oxide is still very low (see Fig. 2). This means that before reduction NiO possesses already some activity although not very high. Reductions of the catalyst at 400°C and 500°C led to the appearance of high activity. These results are coincided with the given above TPR data, indicating that at these temperatures the reduction process of the sample 7.5Ni/Ti proceeds intensively. Nevertheless, if the calculated from TPR profile data indicate that at 400°C only about 50% of nickel ion has been reduced while the complete reduction reached 100% at 500°C, the order of catalytic activities, measured after reduction at these temperatures, is in reverse one. This anomalous result can be explained as follows. In principle, after reduction at 500°C the number of active centers (metallic nickel assemblies) must be higher and, as consequence, catalytic activity should be higher, but at this temperature the sintering process of metallic nickel on catalyst surface takes place considerably and depresses its activity. A similar conclusion about sintering of nickel assemblies and increase of their average size has been done by authors [7]. The increase of reduction temperature to 600°C led to a further depressing of catalytic activity of the sample. Explanation of this phenomenon could be included in the structural changes of the catalyst. According to authors [12], at high temperatures a partial reduction of TiO₂ takes place to form TiO_x (with $x < 2$), which covers the surface and inhibits the process of adsorption of hydrogen, necessary for the reaction. Also it is interesting to note that on the sample, reduced at 500°C, in the reaction products there is a small amount of methanol (about 6%). This fact supports the idea about sintering of nickel to form big assemblies, which favor the process of associative adsorption of CO, necessary for the methanol formation.

The influence of calcination temperature:

The influence of calcination temperature on the activity of catalyst 7.5% NiO/TiO₂ is presented in Table 5.

As discussed above, for this catalyst the calcination at 600°C gave higher activity than the calcination at 400°C. Nevertheless, the calcination of a sample at 600°C, followed by the reduction at 250°C, led to its higher catalytic activity than in case of the another sample, reduced at 400°C but preliminary calcined at 400°C. Thus, the calcination temperature plays a very important role in catalytic activity of the studied catalyst. Indeed the calcination temperature 600°C and reduction temperature 400°C gave approximately complete conversion of CO (94 – 99%) in all the given conditions. These treatment conditions could be considered as optimal for having a highly active catalyst on basis of the sample 7.5% NiO/TiO₂.

Table 5. Conversion of CO (%) at different temperatures and mole ratios H₂/CO on the catalyst 7.5% NiO/TiO₂, calcined at 400°C and 600°C.

Ratio H ₂ /CO	Calcination at 400°C			Calcination at 600°C		
	Reduction 8 h. at 250°C			Reduction 8 h. at 250°C		
	180°C	200°C	220°C	180°C	200°C	220°C
25	3	8	18	6	69	90
33	18	21	23	9	85	90
50	37	51	62	82	89	90
100	71	87	90	85	91	90
Ratio H ₂ /CO	Reduction 8 h. at 400°C			Reduction 8 h. at 400°C		
	180°C	200°C	220°C	180°C	200°C	220°C
	25	25	34	55	94	98
33	30	45	67	95	98	99
50	50	84	99	95	98	99
100	89	99	100	98	98	99

Visually, the samples, calcined at 400°C and 600°C are different; after the calcination at 400°C the color of the calcined sample became grey-slightly yellow, but after the calcination at 600°C the color became bright yellow. As followed from XRD data, the main difference between samples, calcined at 400°C and 600°C, is the appearance of spinel NiTiO₃ in the sample after a calcination at 600°C. In both the samples the peaks, characteristic of NiO, have similar intensities. It is undoubtedly that the spinel form NiTiO₃ plays an important role in improving activity of the catalyst. Besides, according to the areas of reduction peaks, the total number of reduced nickel ions on the sample, calcined at 600°C, is about 10 times higher than that on the sample, calcined at 400°C. The strong effect of NiTiO₃ can be seen from a comparison of CO conversion at 200°C and ratio H₂/CO = 25 when conversion extents are far from 100%. The compared figures are 8% for the sample, calcined at 400°C, reduced at 250°C and 69% for the sample, calcined at 600°C, reduced at 250°C. In these conditions only a small part of nickel ions in both the forms NiO and NiTiO₃ were reduced, but the difference in catalytic activity is clearly very big.

In all the given above experiments, except for the sample, reduced at 500°C, the selectivity was about 99%; on the mentioned sample the analysis gave about 6% of methanol. The reason of this phenomenon, as discussed above, is included in probable existence of

big assemblies of metallic nickel, leading to associative adsorption of CO – a favorable form for the conversion of CO to methanol.

3.3. Activity of the system NiO/Al₂O₃ with different contents of NiO

As indicated above, the calcination temperature 600°C can be considered as optimal for the formation of highly active catalysts, so in this series we studied only the samples, calcined at 600°C. The results of such studies are given in Table 6.

Table 6. Conversion of CO (%) at different temperatures and mole ratios H₂/CO on NiO/Al₂O₃ samples reduced 8 h. at 250° C (catalyst weight 1 g).

Catalyst	Reaction temperature, °C	Ratio H ₂ /CO			
		25	33	50	100
7,5Ni/A	180	0-5%			
	200				
	220				
13,7Ni/A	180	-	-	1	4
	200	-	-	4	10
	220	2	8	16.2	18
20Ni/A	180	27	28	27	27
	200	47	50	51	58
	220	84	87	94	98
37,7Ni/A	180	37	41	44	59
	200	56	67	74.4	86
	220	87	94	96	96
45Ni/A	180	37	42	45	59
	200	58	67	76	86
	220	93	95	97	99
60Ni/A	180	44	44	51	59
	200	67	68	87	90
	220	97	98	99	99

Differing from the catalyst 7.5Ni/Ti, the sample 7.5Ni/A expressed very low activity in all the given conditions. The further increase of NiO content from 7.5% to 37.7% led to a significant growth of activity, but after this point the activity increased only slightly with NiO content. It is interesting to note that this character in changes of catalytic activity is certainly related to the surface characteristics of the catalysts. Indeed, as followed from Table 3, the samples with 7.5% and 13.7% NiO have high dispersity but the average size of nickel assemblies is still lower than “optimal size” [4]. When the content of NiO on the catalysts reached 20% and 37.7% the dispersity decreased slightly but the specific surface area of nickel per one gram of catalyst are still high and, especially, the average size of nickel assemblies are appropriate for the studied reaction. It is easily to understand that the size of nickel assemblies must play the determining role in forwarding the reaction to that or another direction. When the content of NiO exceeded 37.7% the values of specific surface area as well as dispersity of nickel fell but the average size of nickel assemblies increased and exceeded the “optimal” quantity. Certainly this circumstance has lead to

a decrease of catalytic activity. Thus, based on their catalytic and surface properties the studied catalysts could be divided into 3 groups as follows:

Group of the samples (7.5Ni/A and 13.7Ni/A) with low content of NiO, characterized by low values of specific surface area and average size of nickel assemblies. In this group also there is not any appearance of spinels NiAl₂O₄ and Ni₃Al, which probably should have some contribution to catalytic properties of the samples. This group has very low catalytic activity in the reaction of CO methanation.

Group of the samples (20Ni/A and 37.7Ni/A) with appropriate contents of NiO, characterized by “optimal” values of the average size, specific surface area and dispersity of nickel assemblies. On the surface of these catalysts there are various forms of nickel ions, i.e. NiO, NiAl₂O₄ and Ni₃Al. This group expresses very high catalytic activity in the studied reaction.

Group of the samples (45Ni/A and 60Ni/A) with very high contents of NiO but low values of specific surface area and dispersity of the nickel assemblies. The average size of nickel on these samples exceeded “optimal” quantity and the characteristic peaks of mentioned above spinels in XRD spectra (Fig. 1) practically disappeared. The catalytic activity of this group is lower than that of the second group.

In Table 7 are presented the results on dependence of catalytic activity of the studied NiO/Al₂O₃ samples upon various parameters of the reaction. As indicated by TPR data, on the NiO/Al₂O₃ samples the reduction process took place mainly in the temperature interval of 350 – 550°C. Therefore it is understandable that the reduction temperatures 400°C and 500°C led to the formation of catalysts with higher activity, compared with the catalysts, reduced at 250°C. This remark is valid for all the samples, especially for the samples with NiO contents from 7.5% up to 37.7%. At higher contents of NiO the effect of reduction temperature is not clear, for some cases the effect is even negative, especially for case when the sample was reduced at 500°C. It is clearly that at this temperature the sintering process of nickel assemblies must proceed intensively, leading to the decrease of dispersity and specific surface area of nickel although its concentration on the surface of catalysts remained still high. Thus, we can conclude that the optimal content of NiO in the NiO/Al₂O₃ catalysts in the reaction of CO methanation must be around 37.7% and the reduction process of catalysts has been carried out at 400°C.

The influence of reduction regime for catalysts, supported on Al₂O₃ is similar to that for the NiO/TiO₂ catalyst. The reduction regime at 500°C made these catalysts to express lower activity than the reduction at 400°C. This fact, as mentioned above, can be explained that at 500°C the sintering process of metallic nickel on catalyst surface takes place considerably and depresses its activity. As followed from the data of Table 8, the size of Ni assemblies (d_{Ni}) of the samples after reduction at 500°C is higher than that after reduction 8 hours at 400°C and exceeds the optimal value; the dispersity of nickel, on the contrary, is lower.

Also it is interesting to note that while the specific surface area of all the catalysts with low contents of NiO decreased about 20- 30 % after reaction proceeding the surface of the catalysts, containing 37.7% NiO and higher, remained unchanged after that (Table

Table 7. Conversion of CO on the catalysts NiO/Al₂O₃, reduced at 400°C and 500°C, in dependence on reaction temperature and mole ratio H₂/CO.

Catalyst	Reaction temperature, °C	Reduction 8 h. at 400°C				Reduction 1 h. at 500°C			
		H ₂ /CO ratio				H ₂ /CO ratio			
		25	33	50	100	25	33	50	100
7,5Ni/A	180	-	-	-	4	-	-	-	12
	200	-	-	-	8	-	-	-	78
	220	-	3	9	14	-	2.6	9	12
13,7Ni/A	180	28	23	26	28	17	15	22	31
	200	34	36	43	48	21	20	26.9	37
	220	60	66	73	76	27	23	43	53
20Ni/A	180	32	32	39	42	32	28	41	30
	200	52	53	67	69	61	54	71.4	69
	220	84	86	96	91	93	85	95	87
37,7Ni/A	180	80	92	99	99	98	98	99	100
	200	98	100	100	100	98	98	99	100
	220	100	100	100	100	99	99	100	100
45Ni/A	180	29	32	31	40	44	55	56	59
	200	51	56	55	65	85	91	91	89
	220	92	94	95	96	96	95	98	99
60Ni/A	180	28	31	32	30	25	31	33	37
	200	39	47	48	59	31	40	41	39
	220	62	80	87	90	52	77	77	78

Table 8. Surface area of Ni on 1 g of catalyst (S_1), surface area of 1 g of Ni (S_2); size of Ni assemblies (d_{Ni}) and dispersity of Ni on the surface (γ_{Ni}) of different catalysts after reduction at different temperatures (8 hours and 400 °C (I), 1 hour and 500 °C (II))

Catalyst	S_1 , m ² /g		S_2 , m ² /g		d_{Ni} , nm		γ_{Ni} , %	
	I	II	I	II	I	II	I	II
20Ni/A	10.4	6.6	52.0	33.2	19.4	30.4	7.8	5
37.7Ni/A	19.1	9.0	50.4	24.0	20	42	7.6	3.6
45Ni/A	17.1	7.2	37.8	16.0	26.8	63.1	5.7	2.4

9). The reason of this phenomenon is possibly included in higher ability to be sintered of small nickel assemblies, compared with that of the bigger ones.

3.4. Activity of the catalysts 37.7% NiO/Al₂O₃, obtained by different ways.

Table 10 shows the comparative results in the conversion of CO on two 37.7%NiO/ γ -Al₂O₃ samples, obtained by different ways: impregnation (A) and co-precipitation (B).

As followed from XRD and TPR data, between both the catalysts A and B there are very identical surface characteristics (see Table 3), although some difference in their

Table 9. Comparison of the specific surface area of catalysts NiO/Al₂O₃ before (S_{BET}) and after (S^*_{BET}) the reaction

Catalysts	S_{BET} , m ² /g	S^*_{BET} , m ² /g
7,5Ni/A	190	148
13,7Ni/A	135	93
20Ni/A	141	90
37,7Ni/A	125	126
45Ni/A	82	68
60Ni/A	55	54

structural states can be noted. It has been seen in Fig.1.3 that the intensities of characteristic peaks of NiO and NiAl₂O₄ in the catalyst B were higher than that in the catalyst A, nevertheless only in the catalyst A we could observe the characteristic peak of Ni₃Al phase. Probably this circumstance causes some difference in their catalytic properties.

Table 10. Conversion of CO (%) at different temperatures and mole ratios H₂/CO on the catalysts 37,7Ni/A, obtained by different ways: impregnation (A) and co-precipitation (B) and reduced 8 h. at 250° C and 400° C.

H ₂ /CO ratio	Reduction at 250°C					
	Catalyst A			Catalyst B		
	180 ^o C	200 ^o C	220 ^o C	180 ^o C	200 ^o C	220 ^o C
25	37	56	87	62	77	88
33	41	67	94	74	84	87
50	44	74	97	81	88	89
100	59	86	96	86	88	90
	Reduction at 400°C					
	Catalyst A			Catalyst B		
	180 ^o C	200 ^o C	220 ^o C	180 ^o C	200 ^o C	220 ^o C
25	81	98	99	71	83	90
33	92	99	100	80	86	91
50	99	99	100	85	91	93
100	99	100	100	90	92	95

Table 10 shows that the reduced at 250°C catalyst B expressed higher activity at 180°C and 200°C but slightly lower activity at 220°C, compared with the catalyst A. This fact can be explained by higher amount of metallic nickel, formed by a partial reduction from the more abundant NiO and NiAl₂O₄ surface of catalyst B. The reason of lower activity at 220°C of the catalyst B is still not clear but it is not excluded that this temperature is too high for the reaction on the catalyst, obtained by method of co-precipitation. This remark could be applicable to the sample with the same composition but reduced at 400°C. In this case the catalyst B expressed lower activity than the catalyst A in all the reaction conditions. As said earlier, the catalyst B is characterized by higher contents of NiO and NiAl₂O₄ than the catalyst A but main reduction peaks on this catalyst are located at higher temperatures (Fig. 2.4). This means that in general the process of

reduction in this catalyst proceeds more difficult. Maybe this is the reason of lower activity of the catalyst B in the given conditions of reaction.

4. CONCLUSION

- (1) At temperatures 180°C – 220°C the catalyst 7.5% NiO/TiO₂, calcined at 600°C and reduced at 400°C, expressed very high activity in the reaction of CO methanation in mixtures, rich by hydrogen. It can be proposed that this high activity of the catalyst is related to the presence of spinel NiTiO₃ and the optimal average size of nickel assemblies as active centers.
- (2) The activity of catalysts NiO/ γ -Al₂O₃ in CO conversion depends on the NiO content and the sample with 37.7% NiO has been found to be the most active for the reaction. In this series of catalysts it has been shown that active centers Ni⁰ assemblies are formed from starting phases NiO and NiAl₂O₄. It can be seen that at 220°C the catalyst 7.5% NiO/TiO₂ expressed the same activity as the catalyst 37.7% NiO/Al₂O₃ did, but at lower temperatures the second contact has been shown to be more active. This advantage can be assigned to the better surface characteristics and higher thermal stability of the considered catalyst.
- (3) The catalysts, expressing high activity at low temperature (180°C), could be taken for further investigations to look for appropriate industrial catalysts, used in CO methanation.

REFERENCES

1. R. Karaselçuk, A. Inci. Isli, A. E. Aksoylu, CO hydrogenation over bimetallic nickel-vanadium catalysts, *Applied Catalysis A: General*, **192**, (2000) 263.
2. S. Takenaka, T. Shimizu, K. Otsuka, Complete removal of carbon monoxide in hydrogen-rich gas stream through methanation over supported metal catalysts, *Intern. Journal of Hydrogen Energy*, **29** (2004) 1065.
3. H. H. Hwu, B. Fruhberger, and J. G. Chen, Different modification effects of carbidic and graphitic carbon on Ni surface, *J. Catal.*, **221** (2004) 170.
4. J. I. Villacampa, C. Ryo, E. Romeo, J. A. Montoya, P. D. Angel, A. Monzóna, Catalytic decomposition of methane over Ni-Al₂O₃ co-precipitated catalysts - Reaction and regeneration studies, *Applied Catalysis A: General*, **252** (2003) 363.
5. E. E. Peterson, A. T. Bell, In book "Catalyst Deactivation", Marcel Dekker, Inc., 1985.
6. C. H. Bartholomew, Mechanisms of catalyst deactivation, *Applied Catalysis A: General*, **212** (2001) 17.
7. Sui-Wen Ho, Chih-Yang Chu, and Shih-Guan Chen, Effect of thermal treatment on the nickel state and CO hydrogenation activity of titania-supported nickel catalysts, *J. Catal.*, **178** (1998) 34.
8. V. Stuchlý and K. Klušaček, Unsteady-state Carbon monoxide methanation on an Ni/SiO₂ catalyst, *J. Catal.*, **139** (1993) 62.
9. T. Terciolu, J.F. Akryurtlu, Carbon monoxide hydrogenation on supported manganese-ruthenium catalysts, *Applied Catalysis A: General*, **136** (1996) 105.

10. A. E. Aksoylu, A. Inci. Isli, Z. I. Onsan, Interaction between nickel and molybdenum in Ni-Mo/Al₂O₃ catalysts. III. Effect of impregnation strategy, *Applied Catalysis A: General*, **183** (1999) 357.
11. Luu Cam Loc, Nguyen Thao Trang, Nguyen Kim Dung, Ho Si Thoang, Nguyen Quoc Tuan, Deactivation of multi-oxides catalysts in complete oxidation of p-xylene, *Proc. Workshop of the National Program on Fundamental Sciences, Section Physical and Theoretical Chemistry*, Hanoi, April 2002, 35. (Vietnamese).
12. J. Escobar, J.-A. De Los Reyes, T. Viveros, Nickel on TiO₂-modified Al₂O₃ sol-gel oxides - Effect of synthesis parameters on the supported phase properties, *Applied Catalysis A: General*, **253** (2003) 151.

Received March 31, 2005.

