ISSN 0023-1584, Kinetics and Catalysis, 2011, Vol. 52, No. 5, pp. 749–755. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © Luu Cam Loc, Nguyen Manh Huan, N.A. Gaidai, Ho Si Thoang, N.V. Nekrasov, Yu.A. Agafonov, A.L. Lapidus, 2011, published in Kinetika i Kataliz, 2011, Vol. 52, No. 5, pp. 764–771.

Reaction Mechanism of CO Methanation on Nickel Catalysts, as Studied by Isotopic and Nonstationary Methods

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Received September 21, 2010

Abstract—Kinetic isotope effects were measured upon the replacement of hydrogen by deuterium in the reaction of carbon monoxide methanation on nickel catalysts supported on TiO_2 and γ-Al_2O_3. Data on the mechanism of the process were obtained with the use of a nonstationary method. A step–scheme was proposed, in which the interaction of oxygen-containing compounds with hydrogen is a slow step of the process.

DOI: 10.1134/S0023158411050107

INTRODUCTION

The methanation of carbon monoxide on nickel catalysts is used for its removal from waste gases in many industrial processes, such as coal gasification, ammonia synthesis, and hydrogen generation. Although there are many publications dedicated to methanation, there is no unanimous opinion about the kinetics and mechanism of this reaction on the nickel catalysts. Basic differences concern the nature of intermediate compounds, which participate in the slow step of the process. Such intermediate compounds can be various oxygen derivatives of CO [1–4] or carbide particles, which are formed upon the dissociation of CO [5–12] or a complex of CO with hydrogen [13–17]. With the use of different isotopes, it was found [8, 9] that inactive surface carbon, which does not participate in the reaction, is formed in addition to active carbon, which participates in the formation of methane, in the course of the methanation reaction on Ni/kieselguhr and Ni/SiO_2 catalysts. Based on data obtained by a response method [18], it was hypothesized that this carbon is also formed on Ni/SiO_2 under nonstationary conditions. Nonstationary methods were used for studying the mechanism of CO methanation on Ni/α-Al_2O_3 and Ni/SiO_2 [12, 13, 17]. According to Mori et al. [17], the rates of formation of methane and water coincide; however, according to Underwood and Bennett [12], water is formed at a lower rate than methane. The same rates of formation of the reaction products—methane and water—suggest that a sufficient amount of carbon–oxygen-containing intermediate compounds occurs on the catalyst surface. Mori et al. [17] also measured the kinetic isotope effect (KIE), which appears during the replacement of hydrogen by deuterium. The occurrence of this KIE suggests the participation of hydrogen in the slow step of the process. According to available published data, in the majority of cases, the values of KIE in heterogeneous catalysis are greater than unity; that is, the rate of the process decreases upon the replacement of a light isotope by a heavy one (for example, protium by deuterium or tritium) [19, 20]. A positive isotope effect was found in the reaction of CO methanation [21, 22]. On ruthenium catalysts, the value of the isotope effect was 2.2 [21], whereas it was 1.86 on polycrystalline nickel foil [22]. Dalla Betta and Shelef [23] did not detect a change in the rate of CO methanation on Ni/ZrO_2, Ru/Al_2O_3, and Pt/Al_2O_3 catalysts upon the replacement of hydrogen by deuterium. The isotope effect in the reaction of CO hydrogenation was also not observed on Rh/Al_2O_3 [24], but the reaction rate increased after the replacement of hydrogen by deuterium; that is, an inverse isotope effect was observed. An inverse isotope effect was also found in the hydrogenation of CO on Rh/ZrO_2 and Ru/SiO_2 [25, 26]. The inverse effect on Ru/Al_2O_3 was greater than that on Ru/Al_2O_3 [26]. An inverse isotope effect was also observed in the reaction of CO hydrogenation on palladium [27] and nickel [17, 28–31] catalysts.

As can be seen, available data on the kinetic isotopic effects and reaction schemes of CO methanation are contradictory. The aim of this work was to study the mechanism of CO methanation on different nickel catalysts with the application of isotopic and nonstationary methods. The joint use of these methods, in our opinion, will help one to shed light to the reasons for the appearance of particular KIEs and to reveal the special features of the mechanism of the process.

Table 1. Isotope effects in the reaction of CO methanation on nickel catalysts

Catalyst	Reaction	*T*, °C	Conversion	Reaction rate, μmol g^{-1} h^{-1}	β
NiAl	$CO + 3H_2 = CH_4 + H_2O$	230	0.40	28.5	0.62
	$CO + 3D_2 = CD_4 + D_2O$		0.40	46.0	
NiCeAl	$CO + 3H_2 = CH_4 + H_2O$	210	0.41	28.4	0.86
	$CO + 3D_2 = CD_4 + D_2O$		0.41	32.9	
NiCaAl	$CO + 3H_2 = CH_4 + H_2O$	230	0.35	6.60	1.1
	$CO + 3D_2 = CD_4 + D_2O$		0.35	6.0	
NiTi	$CO + 3H_2 = CH_4 + H_2O$	240	0.23	5.56	1.4
	$CO + 3D_2 = CD_4 + D_2O$		0.23	3.97	

EXPERIMENTAL

The following nickel catalysts, whose optimum compositions and other characteristics were published elsewhere [32–35], were used in the experiments: 7.5 wt % NiO/TiO_2 (**NiTi**), 37.5% $NiO/\gamma\text{-}Al_2O_3$ (**NiAl**), (37.5% NiO + 10.2% CaO)/$\gamma\text{-}Al_2O_3$ (**NiCaAl**), and (37.5% NiO + 0.1% Ce_2O_3)/$\gamma\text{-}Al_2O_3$ (**NiCeAl**). The catalysts were prepared by the impregnation of supports with the aqueous solutions of the following componounds: $Ni(NO_3)_2 \cdot 6H_2O$, $Ce(OH)_4 \cdot 6H_2O$, and $Ca(HCOO)_2 \cdot 2H_2O$. The obtained catalysts were dried at temperatures of 60, 100, and 130°C for 2 h at each temperature and then calcined at 600°C for 4 h.

The values of KIE were calculated as the ratio of the rates of formation of methane and deuteromethane in the reactions of CO hydrogenation with hydrogen and deuterium, respectively, at the same temperature and the same reaction mixture composition. This value can be different from the constant ratio k_H/k_D if rate equations are not exponential.

Kinetic isotope effects were measured in a gradient-free flow-circulation sealed glass system in the temperature range of 210–320°C at atmospheric pressure. Initial mixtures contained 2.5 vol % CO. The H_2/CO and D_2/CO ratios were 30. The conversion of CO varied from 0.23 to 0.52. The gas-chromatographic analysis of reaction mixtures was carried out on the column packed with molecular sieves 5 Å. The weight of the catalyst sample loaded into the reactor was 1 g. Before the experiences, the catalysts were reduced in a flow of H_2 (space velocity, 3000 h^{-1}; temperature, 450°C) for 8 h.

Experiments under nonstationary conditions were performed by a response method in a small-volume system at atmospheric pressure and a flow rate of 3 l/h. The composition of a gas mixture after a jump change in the concentration of one or both reaction components was analyzed on a GC/MS 6890 N/MSD 5973 chromatograph with a mass-selective detector (Agilent Technologies). The residence time of a gas mixture (i.e., the ratio of the reactor volume to the flow rate of the supplied mixture) did not exceed 0.35 s, which was considered in the construction of relaxation curves. In all of the experiments, the relaxation time was shorter than the reaction turnover time; that is, a basic requirement was fulfilled, which allowed us to consider the observed relaxation as intrinsic [36, 37], caused by the reaction mechanism, not by side processes (the relaxation time is the time during which the concentration of a reaction product changes by a factor of *e* with respect to its concentration in a stationary state, and the turnover time is the reciprocal of the stationary reaction rate, expressed in s^{-1}). For monotonic relaxation curves, the turnover time was 1.05 s, and the relaxation time was 0.60 s. The experiments were carried out at the initial carbon monoxide concentrations of 0.5 and 1.0 mol %, hydrogen contents of 50 and 99 mol %, and a temperature of 220°C. A 0.1-g catalyst sample was loaded in the reactor. The catalysts were reduced before the experiment.

RESULTS AND DISCUSSION

Table 1 summarizes the KIE values (β in the reaction of CO methanation. Both inverse ($\beta < 1$) and normal positive ($\beta > 1$) KIEs were observed. As noted above, the occurrence of a KIA suggests the participation of hydrogen in the slow step of the formation of methane. Obviously, the appearance of inverse KIEs is caused by the specific character of the mechanism of a process with the participation of molecular hydrogen and by the properties of an activated complex. Isotope effects can be calculated with the aid of the theory of absolute reaction rates [20, 38, 39] on the main condition that they relate to elementary steps. KIE appears as a result of changes in the zero point energy of molecules. In this case, the replacement by a heavier isotope decreases the reaction rate because the zero point energy of heavier molecules is lower than that in the same molecules containing lighter isotopes. In multistep processes, overall isotope effects can be observed; that is, they can include the effects that appear at both steps and preceding rapid steps. In this case, the appearance of inverse effects can be a consequence of the stepwise nature of the process, when a decrease in the rate at a

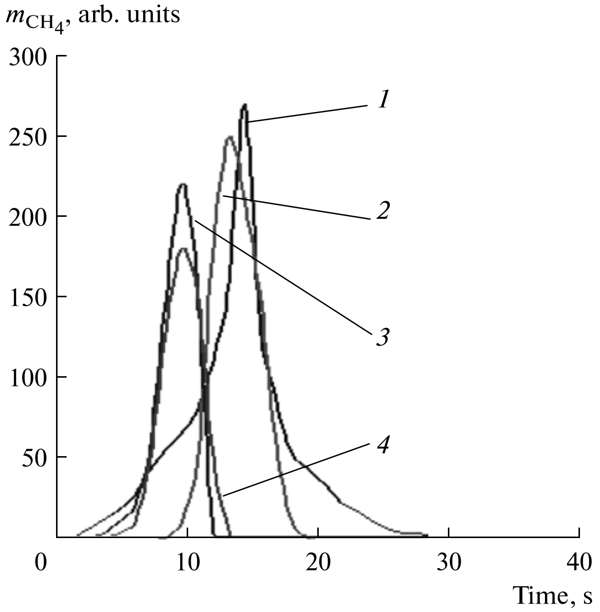

Fig. 1. Changes in the concentration of CH_4 in the response of H_2/He/[CO (1%) + He (99%)] on NiAl depending on the duration (s) of intermediate helium blowing: (*1*) 0, (*2*) 5, (*3*) 10, and (*4*) 20.

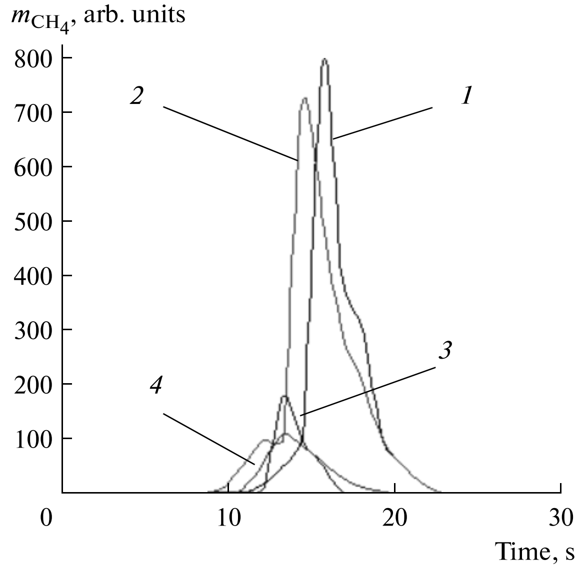

Fig. 2. Changes in the concentration of CH_4 in the response of [CO (1%) + He (99%)]/He/H_2 on NiAl depending on the duration (s) of intermediate helium blowing: (*1*) 0, (*2*) 5, (*3*) 10, and (*4*) 20.

slow step is overlapped because of a shift of the equilibrium at rapid steps. In the general form, the kinetic isotope effect is the product of KIE at the slow step (β_s) and the thermodynamic isotope effect at the rapid steps (α) [38]:

$$\beta = \beta_s\alpha^n,$$

where n is the exponent (its values lie within the range of $0 \le n \le 1$). When $\alpha < 1$ (although $\beta_s > 1$), the values of $\beta < 1$ are possible; that is, inverse isotope effects can occur.

For explaining the reasons for the appearance of various KIEs and obtaining data on the reaction mechanism, we studied the nonstationary processes of achieving a stationary state under varied conditions on nickel catalysts.

Figures 1 and 2 show changes in the amount of methane in the responses of H_2/He/[CO(1%) + He (99%)] and [CO (1%) + He(99%)]/He/H_2, that is, upon the replacement of a flow of hydrogen (or CO) by helium and then s mixture of CO (1%) + He (or H_2). A slash corresponds to a sharp change in the process conditions; the given relaxation curves relate to the last change of conditions. Table 2 summarizes the following values: the delay time of the appearance of methane in a gas phase (t_0), the time of reaching a stationary state (t), the maximum concentration of products (t_{max}), and the amount of formed products per gram of a sample (m) at various durations of intermediate blowing with helium.

In all of the responses, methane appeared in the gas phase with a specific delay, which is caused by the consumption of time for the displacement of H_2 (in the first response) and CO (in the second response) and the subsequent adsorption of CO or H_2. The appearance of CH_4 in both of the responses indicates that both CO and H_2 participate in the reaction in adsorbed forms. In this case, the adsorption of reactive CO and H_2 species is not very strong because the helium blowing of a catalyst for a comparatively short time is sufficient for their desorption. Intermediate helium blowing for 5–20 s before the supply of CO (in the first response) and hydrogen (in the second response) led to a decrease in the amounts of the resulting products. The amount of methane formed on NiTi decreased especially strongly, where methane was not detected in the response of H_2/He/[CO(1%) + He (99%)] even after helium blowing for 10 s (Table 2). The amount of formed methane in this response decreased most slowly on NiAl (by a factor of 1.44). This means that hydrogen is most strongly bound to NiAl and most weakly to NiTi. On NiCeAl and NiCaAl, the amount of formed methane decreased with the time of blowing by a factor of about 8; that is, the strength of the adsorption of hydrogen decreases in the order

$$\text{NiAl} > \text{NiCeAl} \approx \text{NiCaAl} > \text{NiTi}.$$

On all of the catalysts, except for NiAl, the amounts of CH_4 and H_2O in the response of [CO (1%) + He (99%)]/He/H_2 changed more slowly with increasing time of helium blowing than that in the response of H_2/He/[CO (1%) + He (99%)]. This means that CO was adsorbed more strongly than hydrogen. The smallest and greatest changes in the amounts of formed methane in the response of [CO (1%) + He(99%)]/He/H_2 were on NiCaAl and NiAl (by fac-

Table 2. Characteristics of the responses of H_2/He/[CO (1%) + He (99%] and [CO (1%) + He (99%]/He/H_2 on nickel catalysts

Catalyst	Characteristic	Helium blowing time, s							
		0		5		10		20	
		CH_4	H_2O	CH_4	H_2O	CH_4	H_2O	CH_4	H_2O
H_2/He/[CO(1%) + He(99%)]									
NiAl	t_0, s	0.6	0.6	3.6	3.3	3.4	3.6	4.8	5.1
	t, s	28.2	31	18	18.3	11.6	11.6	13.2	13
	t_{max}, s	15	18	13.2	15.2	10.2	9.6	9.6	9.1
	m, μmol/g	0.0213	0.016	0.0204	0.0125	0.0181	0.0114	0.0148	0.0092
NiCeAl	t_0, s	19.2	20.4	27.6	26.1	28.8	29.3	42.6	45.2
	t, s	75	76.6	69	66.1	69	68.3	66.6	68.2
	t_{max}, s	60	65	61.8	63	60	57	57	54.2
	m, μmol/g	0.892	0.274	0.5045	0.2365	0.3041	0.1956	0.112	0.1059
NiCaAl	t_0, s	0.6	0.6	11.4	10.6	12	11.3	13.2	12.7
	t, s	44.4	56.2	41.4	28	48	48.5	76.2	60.7
	t_{max}, s	34.8	42.3	35.4	33.2	36	35.6	49.3	46
	m, μmol/g	2.139	0.018	2.0627	0.0153	1.4488	0.0095	0.2633	0.0076
NiTi	t_0, s	9	9	10.8	9.3				
	t, s	123.6	134.3	110.4	104.5				
	t_{max}, s	56.4	62.3	61.2	57.2				
	m, μmol/g	3.911	0.029	2.7797	0.023	0	0	0	0
[CO(1%) + He(99%)]/He/H_2									
NiAl	t_0, s	12.6	11.6	9	8.6	9.6	9.1	10.2	9.5
	t, s	21	23	20.4	18.6	15.6	15.1	18.6	16.7
	t_{max}, s	15.6	14	15.4	13	13.6	12	13.2	12.4
	m, μmol/g	0.065	0.060	0.059	0.046	0.014	0.009	0.009	0.004
NiCeAl	t_0, s	2.4	2	1.2	1	1.2	0	0.6	0
	t, s	7	6	9.6	8	6.6	5	9	8
	t_{max}, s	4.2	3.6	4.2	3.2	4.8	3.5	3	2.6
	m, μmol/g	0.016	0.010	0.009	0.007	0.008	0.005	0.006	0.003
NiCaAl	t_0, s	4.8	6.2	8.4	7.9	9	8.2	5.4	5.2
	t, s	13.2	16.5	12	10.9	12	11.4	8.4	8.2
	t_{max}, s	11.4	13	11.2	9.2	9.6	9.5	7.8	7.5
	m, μmol/g	0.019	0.015	0.016	0.009	0.013	0.007	0.010	0.003
NiTi	t_0, s	3.6	4.2	3	2.6	1.2	1.5	1.8	2
	t, s	6.6	8.2	5.4	4.1	3.6	3.8	3.6	3.9
	t_{max}, s	4.8	5.7	4.2	3.8	2.4	2.1	2.4	2.6
	m, μmol/g	0.012	0.010	0.010	0.007	0.008	0.005	0.004	0.003

Note: t_0 is the delay time of the appearance of methane in a gas phase; t is the time taken to reach a stationary state; t_{max} is the time taken to reach a maximum product concentration; and m is the amount of the formed product per gram of catalyst.

tors of 1.9 and 7.2, respectively); on NiCeAl and NiTi, the changes were approximately identical (by factors of 2.7 and 3.0, respectively). It is likely that CO was most weakly adsorbed on NiCeAl because, in the response of H_2/He/[CO (1%) + He (99%)], the greatest delay of the appearance of methane in the gas phase was observed, as compared with other nickel catalysts. Thus, the strength of CO adsorption decreases in the following order:

$$\text{NiCaAl} > \text{NiTi} > \text{NiAl} > \text{NiCeAl}.$$

Figures 3 and 4 show the relaxation curves of water formation in the responses of H_2/He/[CO (1%) + He (99%)] and [CO (1%) + He (99%)]/He/H_2 on NiAl. Comparing them with analogous responses, in which the formation of methane was detected, we can say that CH_4 and H_2O simultaneously appear in the gas phase. The same agreement was also observed on other nickel catalysts. This fact suggests that intermediate oxygen-containing compounds occur on the surface of nickel catalysts, and these compounds participate in the slow steps of the process. In the presence of an excess of hydrogen, undissociated CO molecules were detected on the surface of a nickel catalyst [12]; the interaction of these molecules with adsorbed hydrogen leads to the formation of reaction products. It is likely that, under these conditions, the dissociative adsorption of CO followed by the hydrogenation of C_{ads} does almost not occur.

The relaxation curves given in Figs. 5 and 6 were obtained upon supplying a reaction mixture to NiAl and NiCaAl catalysts pretreated with helium, hydrogen, or CO. The shape of the relaxation curves on NiCeAl, which are not shown here, is the same as on NiAl, whereas the shape of the relaxation curves on NiTi is the same as on NiCaAl. In all of the experiments performed after the pretreatment of a catalyst with helium or hydrogen, the relaxation curves were characterized by a monotonic increase in the amount of methane up to a stationary concentration. A stationary state was reached more rapidly after treatment with hydrogen because, in this case, no time is required for the adsorption H_2. The rapidity of reaching a stationary state in the responses of H_2/[CO (0.5%) + H_2 (50%) + He (49.5%)] also depends on how rapidly CO displaces adsorbed hydrogen.

The catalysts can be subdivided into two groups according to the nature of relaxation curves in the responses of [CO (1%) + He (99%)]/[CO (0.5%) + H_2 (50%) + He (49.5%)]. On catalysts from the first group (NiTi and NiCaAl), a monotonic increase in the amount of formed methane in the responses of He/[CO + H_2 + He] and H_2/[CO + H_2 + He] was observed. This can be explained by the fact that hydrogen is adsorbed on the above catalysts much more weakly than CO; therefore, a time is required for the displacement of CO by hydrogen when the surface is occupied by CO. On the catalysts of the second group (NiAl and NiCeAl), the relaxation curves of methane formation in the responses of [CO (1%) + He (99%)]/[CO (0.5%) + H_2 (50%) + He (49.5%)] are characterized by the presence of maximum (Fig. 5), and this maximum appeared on NiCeAl earlier than on NiAl. This means that CO is adsorbed more weakly on the above catalysts than on the catalysts of the first group. Consequently, hydrogen, which is strongly adsorbed on them, can easily displace CO from the surface, and this displacement occurs sufficiently rapidly, leading to the appearance of a maximum at opti-

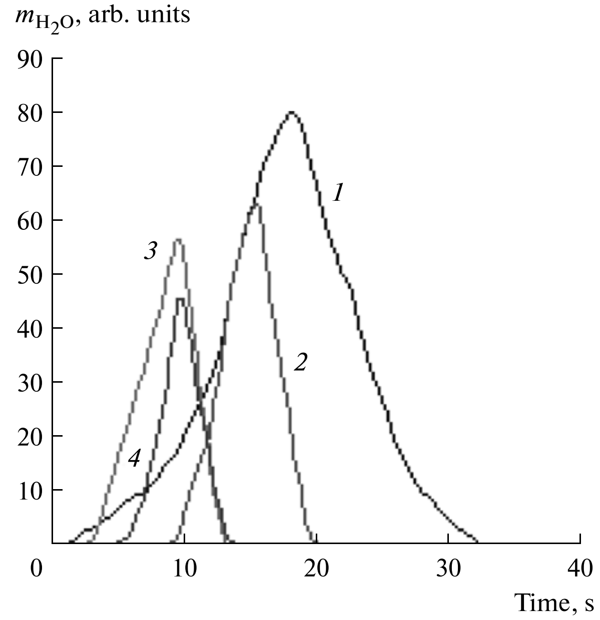

Fig. 3. Changes in the concentration of H_2O in the response of H_2/He/[CO (1%) + He (99%)] on NiAl depending on the duration (s) of intermediate helium blowing: (*1*) 0, (*2*) 5, (*3*) 10, and (*4*) 20.

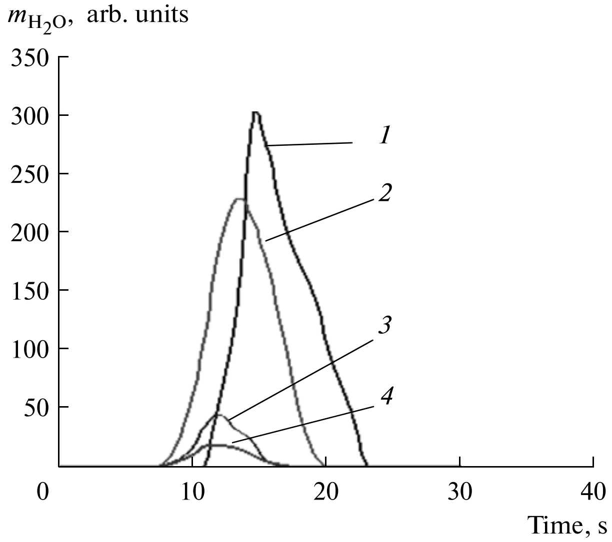

Fig. 4. Changes in the concentration of H_2O in the response of [CO (1%) + He (99%)]/He/H_2 on NiAl depending on the duration (s) of intermediate helium blowing: (*1*) 0, (*2*) 5, (*3*) 10, and (*4*) 20.

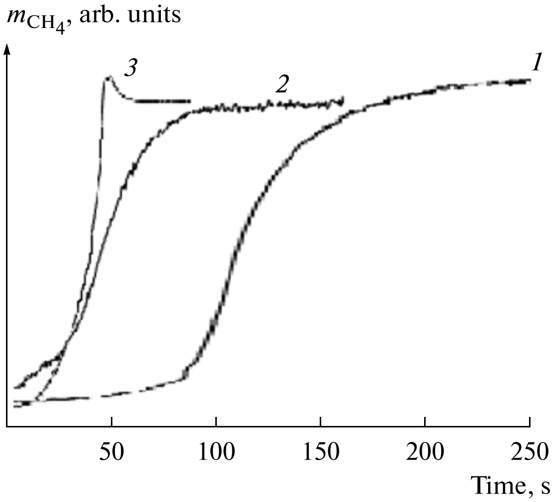

Fig. 5. Changes in the concentration of CH_4 in responses on Ni: (*1*) He//[H_2 (50%) + CO (0.5%) + He (49.5%)], (*2*) H_2/[H_2 (50%) + CO (0.5%) + He (49.5%)], and (*3*) [CO (1%) + He (99%)]/[H_2 (50%) + CO (0.5%) + He (49.5%)].

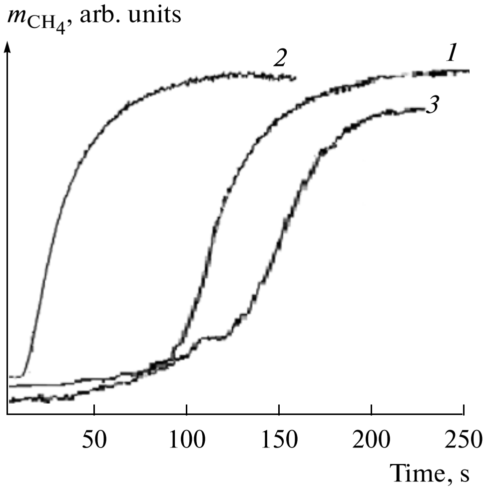

Fig. 6. Changes in the concentration of CH_4 in responses on NiCaAl: (*1*) He//[H_2 (50%) + CO (0.5%) + He (49.5%)], (*2*) H_2/[H_2 (50%) + CO (0.5%) + He (49.5%)], and (*3*) [CO (1%) + He (99%)]/[H_2 (50%) + CO (0.5%) + He (49.5%)].

mum surface concentrations of the reaction components. Subsequently, the amount of formed methane decreases to a stationary value.

Table 3 summarizes the delay times of the yield of methane and the establishment of a stationary state in the responses of H_2/[CO + H_2 + He], He/[CO + H_2 + He], and [CO + He]/[CO + H_2 + He]. As can be seen, the values of *t* in the responses of H_2/[CO + H_2 + He] on nickel catalysts differed not as strongly as in the responses of [CO + He]/[CO + H_2 + He] and He/[CO + H_2 + He]. This is due to the fact that CO was more strongly adsorbed on all of the catalysts than hydrogen, and the strength of CO binding to different catalysts differed more strongly in comparison with H_2. The time of the establishment of a stationary state in the response of [CO + He]/[CO + H_2 + He] increases in the order

$$\text{NiCeAl} < \text{NiAl} \ll \text{NiTi} \ll \text{NiCaAl},$$

which corresponds to the order of the strength of CO adsorption on the nickel catalysts. In this case, the following two groups of the catalysts can be distinguished: NiCeAl, NiAl and NiTi, NiCaAl. The relatively strong adsorption of CO and weak adsorption of H_2 were observed on the catalysts of the second group (NiTi and NiCaAl). On the contrary, the relatively strong adsorption of H_2 and weak adsorption of CO occurred on NiCeAl and NiAl. A combination of these factors leads to the fact that an inverse isotope effect was observed on the catalysts of the first group (Table 1); that is, $\beta < 1$. The KIE on NiTi and NiCaAl was positive ($\beta > 1$). Thus, different ability of catalysts to adsorb CO and H_2 (or deuterium) can substantially influence the value of KIE.

Based on the experimental data, we can propose the following reaction scheme for the methanation of CO on nickel catalysts:

1. $H_2 + Z = 2HZ$,
2. $CO + Z = COZ$,
3. $COZ + HZ = COHZ + Z$,
4. $COHZ + HZ = HCOHZ + Z$,
5. $HCOHZ + Z = CHZ + OHZ$,
6. $CHZ + HZ = CH_2Z + Z$,
7. $CH_2Z + HZ = CH_3Z + Z$,
8. $CH_3Z + HZ = CH_4 + 2Z$,
9. $OHZ + HZ = H_2O + 2Z$

Table 3. Delay time of the appearance of methane and the time taken to reach a stationary state in the responses of He/[CO (0.5%) + H_2 (50%) + He (49.5%)], H_2/[CO (0.5%) + H_2 (50%) + He (49.5%)], and [CO (1%) + He (99%)]/[CO (0.5%) + H_2 (50%) + He (49.5%)] on nickel catalysts

Response	Catalyst							
	NiAl		NiCeAl		NiCaAl		NiTi	
	t_0, s	*t*, s	t_0, s	*t*, s	t_0, s	*t*, s	t_0, s	*t*, s
He/[CO + H_2 + He]	6	266	12	125	15	265	5	152
H_2/[CO + H_2 + He]	1	96	20	112	1	111	8	149
[CO + He]/[CO + H_2 + He]	10	68	5	23	5	255	5	158

(here, Z is an active surface site).

The results of experiments performed under nonstationary conditions show that oxygen-containing carbon compounds (COZ, HCOZ, or HCOHZ) should be formed at a slow step. These are steps 3–5. However, the occurrence of a KIE makes it possible to immediately exclude step 5 from them, in which hydrogen does not participate. The slow step can be finally selected after studying the kinetics of the reaction in question. Detailed kinetic data will be reported elsewhere.

Thus, the joint use of isotopic and nonstationary methods made it possible to explain the reason for the appearance of particular observed kinetic isotope effects, to relate them to different strengths of CO and H_2 adsorption on the nickel catalysts, and to propose a step–scheme for the methanation of CO.

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research and the Vietnamese Academy of Science and Technology (grant no. 09-03-90301 Viet_a).

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