Microwave-activated carbon dioxide reforming of propane over Ni/TiO$_2$ catalysts

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The use of microwave activation in Ni/TiO$_2$-catalyzed carbon dioxide reforming of propane increases the catalytic activity and significantly reduces the coke formation in comparison with conventional thermal heating. During microwave activated reaction, C$_2$—C$_3$ olefins were formed, apart from CO and H$_2$, and the selectivity to olefins reached 6%. It was suggested that exposure to microwave radiation may induce local high-temperature heating of catalytically active phases and catalyst sites, which is not inherent in conventional heating. According to X-ray absorption spectroscopy (XAS = XANES + EXAFS), unlike conventional thermal heating in a hydrogen flow, on exposure to microwave radiation, the Ni^{2+} cations are partly reduced to Ni^0.
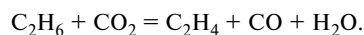
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Carbon dioxide reforming of methane can be promising for industrial production of hydrogen, synthesis gas with a specified H$_2$/CO ratio in the "gas-to liquid" (GTL) processes, and for greenhouse gas disposal.[1] Carbon dioxide reforming of light C$_1$—C$_3$ paraffins to syngas is an endothermic catalytic transformation of hydrocarbons. As an example, consider the reforming of methane:

$$CH_4 + CO_2 = 2\,CO + 2\,H_2 \quad (\Delta H_{298K} = 247\ \text{kJ mol}^{-1}).$$
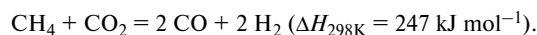
For this reaction to proceed to a high conversion, a temperature above 700 °C and a catalyst such as Co/SiO$_2$, Co/MgO, or Co/CaO are required.[2] Some authors used the Ni—Me$_x$O$_y$/γ-Al$_2$O$_3$ compositions as catalysts.[3] The redox properties of the surface were controlled by modifying Ni/γ-Al$_2$O$_3$ by weakly basic oxides with a moderate redox potential (Me$_x$O$_y$ = CeO$_2$, La$_2$O$_3$, *etc.*). The addition of CeO$_2$ to the Ni/γ-Al$_2$O$_3$ catalyst decreases the contribution of the water shift reaction, which hence increases the process selectivity to CO. Furthermore, surface modification with oxides increases the rate of interaction of carbon fragments with reactive oxygen species on the surface and with the oxide lattice oxygen; this suppresses the carbon deposition on the catalyst surface.

Previously, carbon dioxide reforming of ethane in the presence of nanostructured cesium oxide has been described.[4] In this case, carbon monoxide formation is accompanied by the parallel oxidative dehydrogenation of ethane to give ethylene:

$$C_2H_6 + CO_2 = C_2H_4 + CO + H_2O.$$

The carbon dioxide reforming of propane is also a promising process. The catalysts tested for reforming of propane include Mo—Ni/Al$_2$O$_3$[5] and chromium oxide-[6] and gallium oxide-based[7] systems. The catalytic reduction of carbon dioxide accompanied by oxidative dehydrogenation of propane over Cr$_2$O$_3$, ZnO, or Ga$_2$O$_3$ catalyst is described by the following equation:

$$CO_2 + C_3H_8 = CO + C_3H_6 + H_2O.$$

It was found that this reaction proceeds without formation of side gaseous products such as methane or ethane only in the presence of gallium oxide.[7]

An important problem of carbon dioxide reforming is coke formation. Fast catalyst deactivation induced by coking necessitates the search for new bimetallic catalysts. It was shown[8] that addition of minor amounts of molybdenum considerably increases the stability of Ni/Al$_2$O$_3$ catalysts. For successful synthesis of efficient catalysts, it is important to obtain highly dispersed metals (Ni, Cr) with active surface, which would be stable in high-temperature processes and as inert to coking as possible. Also, the efficiency of reforming increases in the presence of carbon dioxide as a result of partial hydrogen release from the process and decrease in the coking intensity.[9]

Our previous studies[10] demonstrated that the use of microwave energy *in situ* for reactions with noble metal-based catalysts can increase their catalytic activity 3—5-fold and decrease the temperature of the onset of dehydrogenation of polycyclic hydrocarbons, for example, tercyclohexane dehydrogenation, by 100—200 °C.[11] The key

advantage of microwave energy transfer over thermal heating is that the energy is supplied through radiation rather than through heat transfer. This enables fast energy penetration into the bulk of materials (catalysts) that absorb the microwave radiation. A previous study[12] defined a number of supports and catalysts that are able to absorb microwave radiation to be heated to high temperatures needed for carbon dioxide conversion of propane. These materials include metals (Pt, Ni) supported on carbon, metal (Ta, W) carbides, and titanium oxide.

The purpose of this study was to compare the carbon dioxide reforming of propane carried out with thermal and microwave heating of the Ni/TiO$_2$ catalyst. The choice of the catalyst was due to the fact that nickel is traditionally used in the carbon dioxide reforming reactions of lower C_1—C_3 paraffins, while the TiO$_2$ support can absorb the microwave energy, being thus heated to high temperatures.

Experimental

Preparation of the catalysts. TiO$_2$ powder (P-25, Degussa, phase composition: anatase (75%) and rutile (25%), specific surface area 50 m^2 g^{-1}) served as a support. The nickel precursor was deposited on the support surface and then reduced to Ni^0. For this purpose, an excess of the initial solution containing 0.37 mol L^{-1} of nickel nitrate and 3.3 mol L^{-1} of urea was added in portions to the support. The volume of the solution was taken in such a way that the final catalyst contained 5 wt.% Ni. The initial solution was acidified to pH 3.4 with dilute HNO$_3$ in order to avoid Ni^{2+} adsorption on the support during preparation of the suspension. The suspension thus formed was stirred for 6 h at 96 °C. Thermal hydrolysis of urea resulted in precipitation of the poorly soluble highly dispersed nickel precursor. Thermogravimetric data for the precipitate obtained by similar heating of the initial solution without the support suggests that the precursor is nickel hydroxy carbonate (Ni$_2$(OH)$_2$CO$_3$). The suspension was cooled down and filtered. The precipitate was washed many times with cold water with decantation, stirred for 1 h in hot water, separated on a filter, and additionally washed on the filter with cold water. Then the resulting Ni(5%)/TiO$_2$ catalyst sample was dried for 12 h at 110 °C .

Commercial catalysts, NiO(6—10%)/Al$_2$O$_3$ (GIAP-8), and Cr$_2$O$_3$(5—8%)/Al$_2$O$_3$ (GIAP-14) manufactured by Maxam-Chirchiq (Uzbekistan) were used as references.

Catalytic activity measurements. The catalyst (1 g) was charged into a flow type reactor, which was a quartz tube with an internal diameter of 7 mm. The catalyst reduction and carbon dioxide reforming of propane were carried out using microwave heating or conventional thermal heating. The reactor was placed into an electrically heated furnace or, when operating with the Ni(5%)/TiO$_2$ catalyst, into a Vigor domestic microwave oven. Then the catalyst was heated in a hydrogen flow (15 mL min^{-1}) to 310—350 °C and kept for 2 h. Then the H$_2$ flow was replaced by C$_3$H$_8$: CO$_2$ = 1 : 1 (mol.) fed at a space velocity of 4000 h^{-1} and the catalysts were heated to the reaction temperature.

The temperature was measured by thermocouple placed in the middle of the catalyst bed. In the case of microwave heating, the temperature was controlled by moving the reactor in the microwave oven chamber, which had an electric field gradient along the height. In the case of thermal heating, the temperature was specified by a Termodat 17 controller.

The amount of carbon deposits was determined by weighing the reactor before and after the experiment.

The gas at the reactor outlet was analyzed on a Crystallux chromatograph with a heat conductivity detector and two columns: 5 Å molecular sieves (2 m) for quantitative determination of H$_2$, CH$_4$, and CO and HayeSep-Q (3 m) for analysis of CO, CO$_2$, C$_2$H$_4$, C$_2$H$_6$, C$_3$H$_6$, and C$_3$H$_8$. For quantitative analysis of gases (vol.%), two loops of invariable volume were used. Figure 1 shows an example of chromatograms of reaction products containing all of these gases.

X-Ray absorption spectroscopy (XAS) of the Ni(5%)/TiO$_2$ catalyst. Nickel *K*-edge X-ray absorption spectra (8333 eV) were measured on a HASYLAB synchrotron (E4 station) (DESY, Hamburg) using a two-crystal Si(111) monochromator tuned to 70% of the maximum intensity (to eliminate the higher harmonics from the X-ray beam). The spectra were recorded in the transmission mode at liquid nitrogen temperature to reduce the Debye—Waller disorder factor. The samples were pressed into pellets 13 mm in diameter. For energy calibration, a nickel foil was placed between the second and third ionization chambers during recording the spectra. As standard nickel compounds, Ni foil, NiO, and Ni$_2$(OH)$_2$CO$_3$ were used; their spectra were recorded under similar conditions.

The data were processed using the VIPER program.[13] The amplitudes and scattering phases of the neighboring atoms were calculated by the *ab initio* FEFF8.10 program[14] for NiO and Ni foil. The experimental and theoretical spectra were compared in both the reciprocal (*k*, wavenumber) and real (*r*, coordinate) spaces. The shell radius (distance to the nearest atom), coordination number, Debye—Waller factor (σ^2), and the deviation between the calculated and experimental energetic absorption edge positions (ΔE) used as the fitting parameters to fit the theoretical spectra to the experimental data.

Three catalyst samples were studied: one dried at 110 °C, one reduced in an H$_2$ flow at 350 °C (conventional heating), and one reduced at 310 °C (microwave heating).
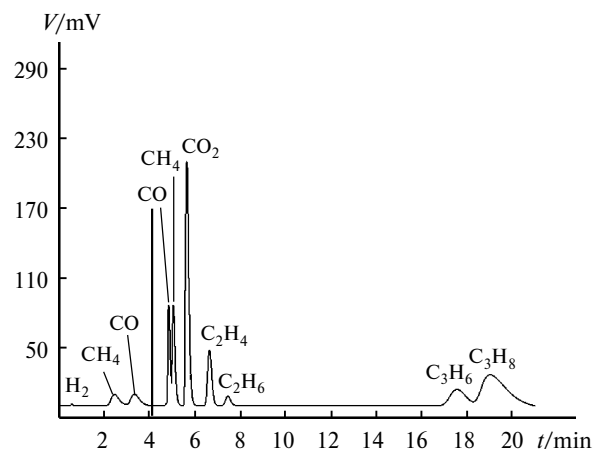
Fig. 1. Example of chromatograms of the products of propane reforming catalyzed by Ni(5%)/TiO$_2$ (0—4 min, analysis of 5 Å sieves; 4—21 min, analysis on a HayeSep-Q column).

Results and Discussion

The NiO/Al_2O_3 and Cr_2O_3/Al_2O_3 catalytic systems used in this study for comparison with the Ni(5%)/TiO_2 catalyst cannot be heated in a microwave field; therefore, they were tested only after thermal heating. Table 1 summarizes characteristics of the carbon dioxide reforming of propane for the test samples and experimental conditions.

It can be seen from Table 1 that in the presence of the thermally heated (700 °C) catalyst, C_2—C_3 olefins are formed only over the Cr_2O_3/Al_2O_3 sample, which is typical of aluminum chromium catalysts.[9] The reactions catalyzed by Ni/TiO_2 and Ni/Al_2O_3 give mainly syngas with the H_2 : CO > 2 ratio in the gas products, which is favorable for the subsequent use of this mixture in methanol synthesis. However, the reaction with nickel catalysts is accompanied by substantial coke deposition, which hampers the practical use of these catalysts.[15]

Unlike thermal heating, microwave activation of the Ni(5%)/TiO_2 catalyst results in small amounts of C_2—C_3 olefins in the reaction products. In the presence of microwave-activated Ni(5%)/TiO_2, the conversion of propane and CO_2 is considerably higher at the same temperature, while the carbon deposition on the catalyst decreases more than twofold. This finding suggests that microwave activation of the carbon dioxide reforming is a promising trend for development of novel heterogeneous catalysts.

A comparative study of the electronic state and local environment of nickel in the Ni(5%)/TiO_2 sample after conventional thermal heating and microwave activation was performed by X-ray absorption spectroscopy (XAS = XANES + EXAFS). Figure 2 shows the K XANES spectra of the Ni(5%)/TiO_2 catalyst and reference nickel compounds normalized to one Ni atom.

The spectrum of the initial dried sample (see Fig. 2) differs from the spectra of Ni foil and NiO and resembles
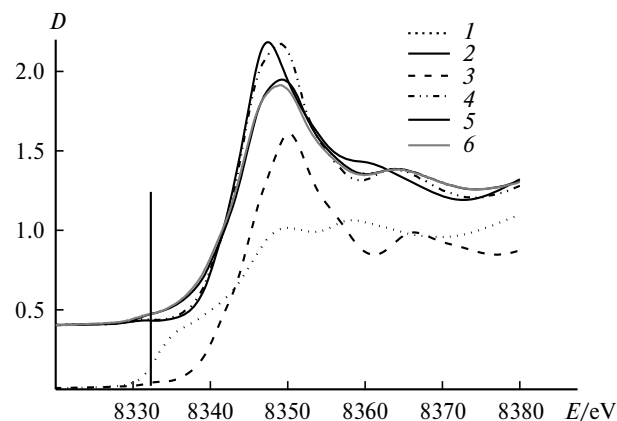
Fig. 2. Normalized XANES spectra of the nickel reference compounds (*1*, Ni foil; *2*, $Ni_2(OH_2)CO_3$; *3*, NiO) and Ni catalyst (5%)/TiO_2 (*4*, initial; *5*, after microwaving, 310 °C, H_2; *6*, after conventional thermal treatment, 350 °C, H_2).

the spectrum of $Ni_2(OH)_2CO_3$. Hence, the active sites in this sample exist as Ni^{2+} cations in the same coordination state as nickel ions in the presumed $Ni_2(OH)_2CO_3$ precursor. The reduction of the dried sample in an H_2 flow in a microwave field at 310 °C and conventional reduction in an H_2 flow at 350 °C result in decreasing intensity of the white line.

Figure 3 shows the Ni K EXAFS spectra (Fourier transform of the oscillating part of X-ray absorption spectra) for the Ni(5%)/TiO_2 catalyst and reference nickel compounds.

The EXAFS spectra of the initial dried Ni(5%)/TiO_2 catalyst differ from the spectra of Ni foil and NiO and resemble the spectrum of $Ni_2(OH)_2CO_3$. The spectrum of the catalyst pretreated in air at 110 °C exhibits two peaks at an uncorrected distance of ~1.5 and ~2.5 Å. The positions of these peaks correspond to the peaks in the spec-

Table 1. Characteristics of carbon dioxide conversion of propane at 650 °C (gas mixture space velocity 4000 h^{-1}, C_3H_8 : CO_2 = = 1 : 1, mol.)

Characteristics	Ni(5%)/TiO_2	Ni(5%)/TiO_2	NiO(6—10%)/Al_2O_3	Cr_2O_3(5—8%)/Al_2O_3
Type of heating	Microwave	Thermal	Thermal	Thermal
T/°C	650	650	650	700
Gas composition (vol.%), including:				
H_2	46.9	44.2	44.9	21.5
CO	34.0	18.7	22.4	20.0
CH_4	12.8	14.6	27.9	25.9
CO_2	0.8	12.2	4.8	13.2
C_2H_4	1.8	0.0	0.0	11.8
C_2H_6	1.8	0.0	0.0	1.2
C_3H_6	0.2	0.0	0.0	2.1
C_3H_8	1.7	10.3	0.0	4.3
Carbon deposits (%)/h	12.8	27.5	40.6	10.4
Conversion of C_3H_8 (%)	89.8	58.0	100.0	84.8
Conversion of CO_2 (%)	95.2	50.2	75.8	53.3

Table 2. EXAFS data for the Ni(5%)/TiO$_2$ catalyst and references

Sample	Pair	Distance/Å	C.N.	$\sigma^2 \cdot 10^3/\text{Å}^2$	ΔE/eV
Initial	Ni—O	2.056±0.009	4.8±0.4	5±1	2±1
	Ni—Ni	3.106±0.005	5.3±0.4	3±1	2±1
After treatment at 310 °C,					
H$_2$, microwave	Ni—O	2.073±0.005	4.2±0.2	7±1	2±1
	Ni—Ni	2.514±0.010	0.9±0.1	4±1	2±1
	Ni—Ni	3.089±0.006	6.8±0.5	12±1	2±1
at 350 °C, H$_2$	Ni—O	2.080±0.006	4.2±0.2	7±1	2±0.7
	Ni—Ni	3.075±0.008	8.5±0.8	10±1	2±1

trum of Ni$_2$(OH)$_2$CO$_3$ that belong to Ni—O and Ni—Ni atomic pairs. In the spectrum of the sample reduced at 310 °C in an H$_2$ flow in a microwave field, a new peak appears at ~2 Å, which coincides with the first peak in the spectrum of metallic Ni foil (Ni—Ni atomic pair). In the spectrum of the sample after conventional reduction at 350 °C in an H$_2$ flow, this peak is absent.

Table 2 presents the average coordination numbers and the real distances found in the calculation of the first and second spheres.

According to calculation, the coordination number of the Ni—O atomic pair is 4.8±0.4 in the initial (air-dried) sample and 4.2±0.2 for the samples treated in H$_2$ flow both in a microwave field at 310 °C and in the conventionally reduced sample at 350 °C. The real distance in this atomic pair (~2.06 Å) in the air-dried sample increases to 2.07 Å after its reduction in a microwave field and to 2.08 Å after conventional reduction at 350 °C. The real distance in the Ni—Ni atomic pair characteristic of a similar atomic pair in NiO is ~3.10 Å in the initial sample, ~3.09 Å in the sample reduced in the microwave field, and ~3.08 Å in the conventionally reduced sample. The calculated data for the Ni—O atomic pair in the catalyst proved to be close to the results obtained for the simulated

spectrum of the Ni$_2$(OH)$_2$CO$_3$ reference, whereas data for the Ni—Ni atomic pair similar to that observed in the spectrum of nickel oxide were intermediate between the data for the second coordination sphere for the two references (Ni$_2$(OH)$_2$CO$_3$ and NiO). The coordination number for this Ni—Ni atomic pair increased from 5.3±0.4 to 6.8±0.5 upon the reduction of dried sample in the microwave field and to 8.5±0.8 upon conventional reduction. The calculation showed also that after reduction of the catalyst sample in H$_2$ in the microwave field, a peak inherent in metallic nickel in Ni foil with a Ni—Ni distance of ~2.52 Å appears in its spectrum. The coordination number in this shell is close to 1.

Thus, microwave-activated carbon dioxide reforming of propane catalyzed by Ni(5%)/TiO$_2$ results in higher propane and CO$_2$ conversion and lower coking as compared with the thermally induced reaction and in appearance of C$_2$—C$_3$ olefins in the products. X-Ray absorption spectroscopy demonstrated that, unlike conventional thermal heating in a hydrogen flow, on exposure to microwave radiation, the Ni^{2+} cations are partly reduced to Ni^0. A change in the local environment of catalytically active sites affects the selectivity of carbon dioxide reforming of propane.

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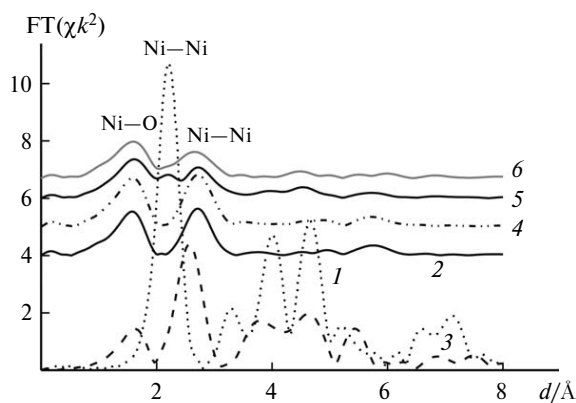
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