Kinetics and Catalysis, Vol. 45, No. 5, 2004, pp. 679–683. From Kinetika i Kataliz, Vol. 45, No. 5, 2004, pp. 719–723.

Effect of Steam in CO_2 Reforming of CH_4 over a $Ni/CeO_2–ZrO_2–Al_2O_3$ Catalyst[1]

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Received July 10, 2003

Abstract—CO_2 reforming of CH_4 was carried out with and without steam over a $Ni/CeO_2–ZrO_2–Al_2O_3$ catalyst. The catalytic performance, amount of carbon deposit and the EXAFS of the Ni *K*-edge of samples were measured. The results show that when the catalyst is used for CO_2 reforming of CH_4 without the addition of steam, the catalyst gradually deactivates, however, addition of a small amount of steam to the feed gas can significantly inhibits the deactivation, which is due to the great suppression of coke formation on the catalyst during the reaction. The EXAFS result shows that, maybe due to the penetration of more carbon atoms into the Ni lattice, the coordination number of the nearest Ni–Ni of the sample after the reaction without steam reduces more than that of samples after the reaction with a small amount of steam in the feed gas.

INTRODUCTION

In recent years there has been a growing interest in CO_2 reforming of CH_4 to produce synthesized gas (I). Via this reaction, CH_4 and CO_2, both natural, abundant, and greenhouse gases, can be converted to a synthetic gas with a low H_2/CO ratio (~1.0). Although steam methane reforming (II) has been industrialized to produce synthetic gas with a high H_2/CO (≥3.0) [1], CO_2 reforming of CH_4 has considerable advantages because by steam reformation of methane only one kind of greenhouse gas, CH_4, can be converted, and the syngas produced by CO_2 reforming of CH_4, which shows a low H_2/CO ratio (~1), can be utilized as a preferable feed gas to produce liquid fuels by the Fisher–Tropsch reaction [2].

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2, \qquad \text{(I)}$$

$$CH_4 + H_2O \rightleftharpoons 3H_2 + CO. \qquad \text{(II)}$$

Several supported transition metal catalysts (Ni, Ru, Rh, Pd, etc.) have been used for the carbon dioxide reforming of methane. However, considering the cost and availability, nickel-based catalysts are the most probable for use in industry [3–7]. Currently the biggest problem that prevents the reaction from being industrialized is the deactivation of the catalysts during the reaction. Although some groups have observed the increase in metal particle size during reforming, the contribution of sintering to deactivation is seen as minimal. More researchers agree that coke formation is the primary reason for the catalyst deactivation [8–13]. To suppress the coke deposition, several approaches have been proposed. For example, an alkaline or an alkaline earth metal is added in the catalyst [7, 14], or the sites for coke deposition are passivated with sulfur [15, 16]. Utilization of excess CO_2 can also suppress coke deposition, but leads to a low yield of CO, and furthermore, the excess CO_2 can not be easily separated from the synthetic gas product.

In our previous research we reported that high activity and stability are obtained upon the proper addition of Al_2O_3 into $Ni/CeO_2–ZrO_2–Al_2O_3$, while excess Al_2O_3 causes the catalyst to be deactivated more easily for CO_2 reforming of CH_4 [17]. In the present study, one $Ni/CeO_2–ZrO_2–Al_2O_3$ catalyst is used for CO_2 reforming of CH_4, and the effect of adding a small amount of steam into the feed gas is investigated. It is found that adding a small amount of steam into the feed gas can significantly improve the catalytic stability by inhibiting coke formation during the reaction.

EXPERIMENTAL

Catalyst Preparation

The catalyst samples were prepared by the hydrothermal synthesis method, using $Ni(NO_3)_2 \cdot 6H_2O$, $ZrOCl_2 \cdot 8H_2O$, $Ce(NO_3)_2 \cdot 6H_2O$, and $Al(NO_3)_3 \cdot 9H_2O$. The pH value of an aqueous solution containing calculated amounts of the compounds mentioned above was adjusted by ammonia to about 2.5, then the solution was introduced into an 80 cm^3 Teflon-lined stainless-steel autoclave and treated in a constant temperature oven at 115°C for 24 h. Thereafter the suspension in the autoclave was evaporated at 60–70°C to remove the water and then air dried at 115°C for 12 h. The dried material was decomposed for 1 h at 350°C in air and then calcined in air at 800°C for 8 h. Thereafter, the

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[1] This article was submitted by the authors in English.

sample was pressed into disks at 300 kg cm^2, and crushed and sieved to granules with a 40–60 mesh. For the catalyst sample, the contents of NiO and Al_2O_3 are 7.0 and 10.0 wt %, respectively, and the weight ratio of CeO_2/ZrO_2 is 68/32.

Catalyst Testing

The catalytic performance was measured with a *U*-shaped quartz microreactor (d = 4 mm) in a CO_2/CH_4 flow (molar ratio = 1.0, 16 ml/min) under atmospheric pressure at 800°C. The catalyst was initially reduced in a H_2 flow at 800°C for 2 h; 0.2 g reduced catalyst was used. To investigate the effect on the catalyst of adding a small amount of steam to the feed gas, the gas was passed through water in an inner vessel at different temperatures before being introduced into the catalyst bed. The freshly reduced catalyst and that which was used in the feed gas without steam are denoted as Ni-r and Ni-no, respectively. The catalyst samples used in the feed gas with 1.2 vol % (10°C saturation steam) and 4.2 vol % steam (30°C saturation steam) are denoted as Ni-10 and Ni-30, respectively. The effluent gas was analyzed by a gas chromatogram (GC) equipped with a 2 m TDX-01 column and a thermal conductivity detector (TCD) with argon as the carrier gas.

Carbon Deposition Evaluation

After the reaction was performed for a definite amount of time, the feed gas was shifted to argon flow at high temperatures, and the catalyst was cooled to room temperature. The amount of carbon deposited on the catalyst was measured by the increase in weight of the sample.

Catalyst Characterization

An X-ray powder diffraction (XRD) pattern of the reduced and the post-use samples was obtained using a D/MAX-γA diffractometer with CuK_α radiation with a wavelength of 0.15418 nm.

Extended X-ray absorption fine structure (EXAFS) measurements of the reduced sample and the post-use sample were performed on the 4WIB beam line (double crystal monochromator, Si (111); storage ring energy, 2.2 GeV; ring current, 50–90 mA; energy resolution, 3 eV) at the Beijing Synchrotron Radiation Facility (BSRF). The solid sample was ground to fine powder and held in an aluminum holder between two sheet polymer film windows. Ni *K*-edge spectra were recorded in the fluorescence mode.

The EXAFS data analysis used here involved a background subtraction by two polynomial functions, normalization by the jump height, μ(0) fitting by means of cubic spline functions and multiplication of the EXAFS in k space by a factor k^3. Fourier transform ranges for all samples were 15.0–120.0 nm^{-1}. The first Ni–Ni shell was fitted in k space with a theoretical function obtained with the FEFF8 using the structural parameters of Ni metal.

RESULTS AND DISCUSSION

Catalytic Properties Ni/CeO$_2$–ZrO$_2$–Al$_2$O$_3$

The catalytic properties for CO_2 reforming of CH_4 over the $Ni/CeO_2–ZrO_2–Al_2O_3$ catalyst were measured in a mixture of CH_4 and CO_2 (molar ratio 1.0) at 800°C. The feed gas passed through water in a vessel at various temperatures, so that the feed gas saturation contained steam at various temperatures. Figure 1 shows the changes of CH_4 and CO_2 conversions over time. It is seen that when the reaction is performed without steam in the feed gas (Ni-no), the initial CH_4 and CO_2 conversions are high but they decrease significantly with time; after 30 h the CH_4 conversion decreases to about 92% of its initial conversion. On the other hand, when the reaction is performed with 1.2 vol % steam in the feed gas, the initial CH_4 and CO_2 conversions are high and then slowly decrease with time; after 30 h the CH_4 conversion decreases to about 97% of its initial conversion. When the reaction is performed with 4.2 vol % steam in feed gas the CH_4 and CO_2 conversions do not show a significant decrease in the whole process of the 30 h reaction. These results indicate that the addition of a small amount of steam in the feed gas obviously improves the stability of the catalyst for CO_2 reforming of CH_4.

Carbon Deposition on the Samples

The amount of carbon deposited on samples after reaction for different times was measured and the results are showed in Fig. 2. It is calculated from the data of Fig. 2 that after the addition of 1.2 and 4.2 vol % steam in the feed gas, the carbon deposition rates lower to 2.5 and 5.9 times that of the reaction without the addition of steam, respectively. It indicates that the addition of steam in the feed gas can resist carbon deposition. The deposited carbon may be eliminated via the gasification reaction: $H_2O + C(s) \longrightarrow CO + H_2$ [8].

Catalyst Characterization

The XRD measurements of the reduced catalyst sample and the post-use samples in a feed gas with or without steam were carried out. The results indicate (in brief, the figures have been omitted) that for all of the samples used in a feed gas with or without steam, except for the expectable phase of CeO_2, ZrO_2 and metal Ni, several distinct new peaks appear (d = 0.3778, 0.2672, 0.2180 nm). They appear with no apparent difference and are attributed to the formation of the hexagonal $CeAlO_3$ phase, which should originate from the reaction between Ce_2O_3 and Al_2O_3. It seems that the $CeAlO_3$ formation should not be responsible for the catalyst deactivation. It is necessary to perform further

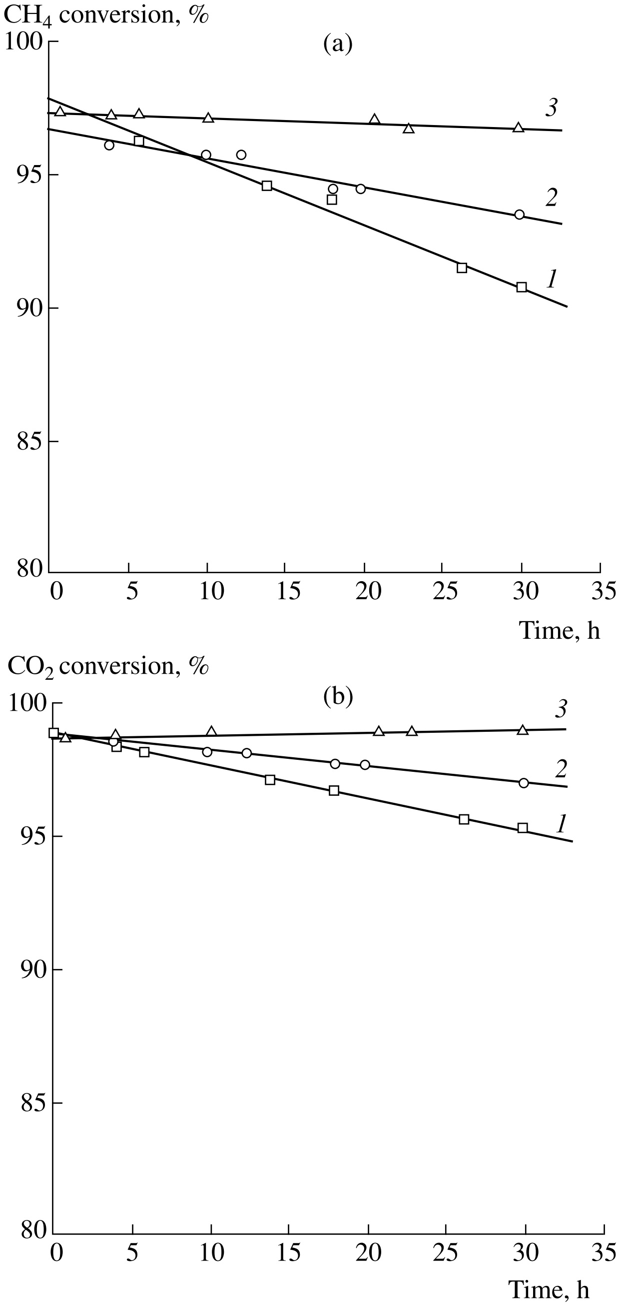

Fig. 1. Dependences of (a) CH_4 and (b) CO_2 conversion on time over reduced $Ni/CeO_2–ZrO_2–Al_2O_3$ catalyst. Reaction conditions: $P = 1$ atm, $T = 800°C$, $CH_4/CO_2 = 1.0$, $W/F = 1.2 \times 10^{-2}$ g s/ml: (*1*) Ni-no, (*2*) Ni-10, and (*3*) Ni-30.

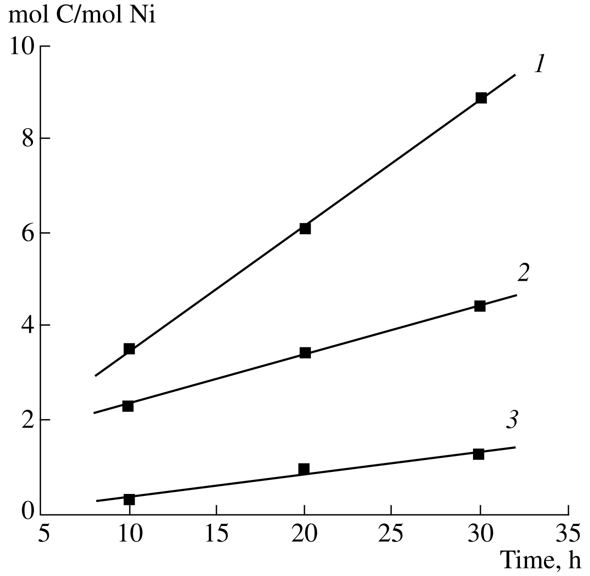

Fig. 2. Curves of carbon deposition over time on reduced $Ni/CeO_2–ZrO_2–Al_2O_3$ catalyst: (*1*) Ni-no, (*2*) Ni-10, and (*3*) Ni-30.

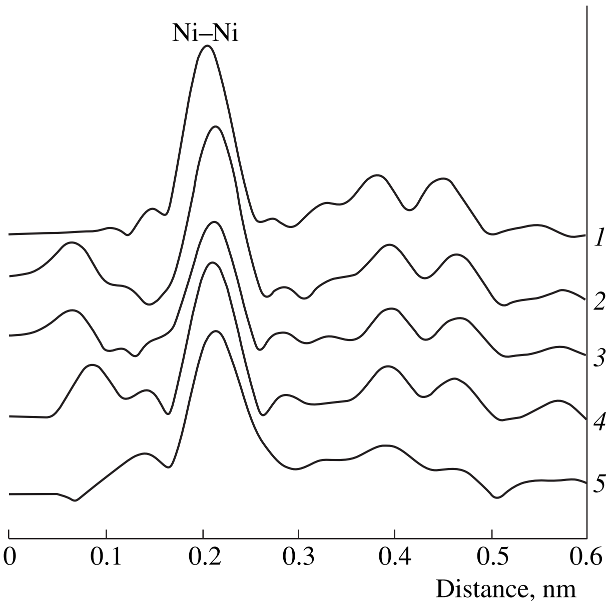

Fig. 3. RSFs of Ni *K*-edge of the reduced $Ni/CeO_2–ZrO_2–Al_2O_3$ catalyst before and after reaction for 30 h together with the reference sample of Ni foil: (*1*) Ni foil, (*2*) Ni-r, (*3*) Ni-no, (*4*) Ni-10, and (*5*) Ni-30.

research on the cause of deactivation and the influence on the stability by adding a small amount of steam into the feed gas.

In order to get more information about the catalyst deactivation, the EXAFS measurements of Ni *K*-edge were performed. The EXAFS analysis was performed for catalysts after use in the feed gas with or without the addition of steam, as well as for freshly reduced catalysts. The radial structure functions (RSF) of the Ni *K*-edge of the catalysts and the reference sample of Ni foil are displayed in Fig. 3. The peak situations of RSF for all catalysts are nearly the same as those of Ni foil. It indicates that the nickel was present mainly as Ni metal in all samples. The peak intensity of the first Ni–Ni shell of the sample obviously decreases after the reaction without steam. For the samples after reaction with

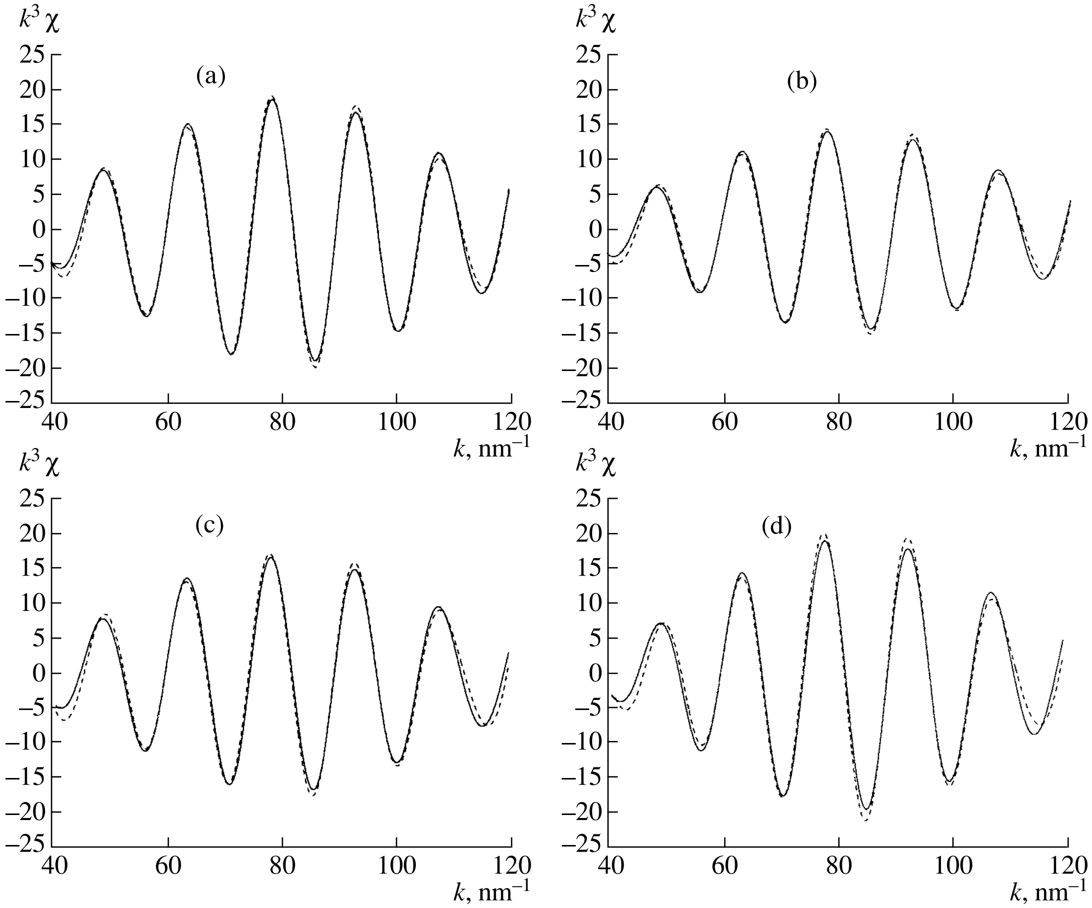

Fig. 4. k^3-weighted Fourier-filtered EXAFS functions of the Ni K-edge for reduced Ni/CeO_2–ZrO_2–Al_2O_3 catalyst before and after reaction for 30 h (R = 0.173–0.251 nm) fitted to the theoretical EXAFS function: (a) Ni-r, (b) Ni-no, (c) Ni-10, and (d) Ni-30.

steam in the feed gas, the peak intensity of the first Ni–Ni shell does not noticeably decrease.

The experimental EXAFS data fitted to the theoretical EXAFS equation with k^3 weighting in k space for the first Ni–Ni shell was performed. The results are displayed in Fig. 4 and the obtained structural parameters are listed in Table 1. The amount of carbon deposited after reaction for 30 h (from Fig. 2) is also listed in this table. Fig. 4 shows that fitting of experimental EXAFS data to the theoretical EXAFS function is successful. The coordination number of Ni–Ni decreases from 9.7 to 6.9 after the reaction without steam in the feed gas, whereas for the samples after reaction with steam in the feed gas they decrease to 8.8 and 9.0, respectively.

EXAFS fitting results and the amount of carbon deposition on samples after reaction for 30 h with or without steam as well as on the reduced sample

Sample	N	R/nm	$\Delta\sigma^2 \times 10^{-6}$, nm^2*	ΔE_0, eV**	C/Ni, mol ratio
Ni-r	9.7	0.2480	60.3	0.17	0
Ni-no	6.9	0.2476	57.5	–2.41	8.90
Ni-10	8.8	0.2478	63.6	–2.05	4.45
Ni-30	9.0	0.2495	55.0	–6.33	1.27

* Relative Debye-Waller factor.

** Correction of the inner potentials of the samples.

It has been reported that the adsorbed surface carbon atoms can migrate to the subsurface Ni layers and induce local reconstructing of the Ni surface [18], the carbon atoms may be permitted to penetrate more deeply into the Ni lattice [19], and may diffuse through the metal lattice [8, 20]. From the literature we can give a reasonable explanation for the decrease of coordination number of the first Ni–Ni shell in the samples used. The carbon atom originating from the CH_4 decomposition ($CH_4 \longrightarrow C + 2H_2$) and/or the CO disproportionation ($2CO \longrightarrow C + CO_2$) can penetrate into the Ni lattice during the reaction. The carbon atom may substitute for a Ni atom or hold the space of Ni atoms. It causes the coordination number to decrease and disturbs the coordination distance. While the results of fitting show that the coordination distance has no apparent shift, the difference is within the range of experiment error, so possibly the coordination distance change is too small to distinguish. The carbon atom is a light element; the EXAFS oscillation signal originating from carbon atom scattering to photoelectrons is weak. So we neglected the possible Ni–C coordination and the results fit very well. The appearance of a carbon atom around the Ni atom would cause a decrease in the nearest Ni atom numbers, therefore the coordination numbers of the first Ni–Ni shell would decrease. It can be deduced that the carbon atom number in the samples Ni-10 and Ni-30 is fewer than in sample Ni-no. This is confirmed by measurements of the amount of carbon deposition.

The metallic Ni is the activity center for CH_4 activation and decomposition [21–23]. The catalyst may be deactivated if excessive carbon atoms appear at the surface, or the bulk of the Ni particle and the Ni atom is wrapped by carbon atoms, as the catalytic performance test of the reaction without the addition of steam in the feed gas showed us. The results of carbon deposition measurement show that the addition of a small amount of steam can inhibit carbon formation, which is consistent with the EXAFS result. Because of the inhibition of carbon formation by steam, the stability of the catalyst is promoted. Therefore it is very beneficial to this reaction, which is limited by the catalyst deactivation due to the abundant carbon deposits.

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