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CO and CO_2 hydrogenation under mechanochemical treatment

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Abstract

The effect of mechanochemical treatment on the hydrogenation of CO and CO_2 was studied using a flow milling vial as a catalytic reactor. Traditional catalysts for the methane formation (Ni, Zr, Zr–Ni-containing samples, Zr hydride and Zr–Ni hydrides of various genesis), as well as inactive NiO and ZrO_2, were examined. The following features of the mechanically driven CO hydrogenation were observed: (i) Zr and Zr–Ni hydrides demonstrated the highest activity in the formation of CH_4; (ii) the hydrogen present in the reaction mixture suppressed the formation of CH_4; (iii) Ni was found to be ineffective in the formation of CH_4 but active in the reaction of CO disproportionation; (iv) on the oxide samples, a small amount of CH_4 was formed owing to the mechanical activation. Deep structural transformations of the metal and hydride samples under milling in the reaction mixture were found to be responsible for the changes in their catalytic activity. Only zirconium hydride exhibited catalytic activity for CO_2 hydrogenation. In this case, no phase transformation was observed.

Keywords: Mechanically induced hydrogenation; Carbon monoxide hydrogenation; Carbon dioxide hydrogenation; Zirconium hydride; Zirconium–nickel hydride; Zirconium–nickel alloy

1. Introduction

Mechanical treatment is commonly used as a method for synthesizing the precursors of the catalytically active materials and for preparing heterogeneous catalysts with special properties [1–5]. According to the recent reports, it is feasible to carry out the hydrogenation reactions under the high-energy impact milling utilizing a milling vial as a static catalytic reactor and bimetallic amorphous alloys and hydrides as catalysts [6–8]. The complex processes take place during the gas–solid interaction under the mechanical activation: the presence of gas components modifies the conditions of the solid-state reactions resulting in the formation of non-equilibrium systems including amorphous materials and alloys with a high concentration of low-coordination sites spurring the hydrogenation reactions [7–9].

We found that the CO hydrogenation to CH_4 catalyzed by Zr–Ni-H_X and ZrH_Y can be carried out under flow conditions at atmospheric pressure and 40°C, when a special flow milling vial is used as a flow catalytic reactor [9,10]. In the present study, we used the Ni- and Zr–Ni-containing materials of different genesis, as well as Ni and Zr, the traditional catalysts for the methane formation [11–13]. To separate the role of reactive milling, we examined NiO and ZrO_2 in CO hydrogenation. The hydride hydrogen is found to be particularly active in the hydrogenation processes [6,7,14,15]. Because of this, we compared the dynamics of CO and CO_2 hydrogenation in the presence and absence of H_2 in the gas phase. The

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structural studies were carried out on different stages of reaction using X-ray diffraction.

The phenomena taking place under the mechanochemical treatment are rather complicated because of interrelation between gas–solid and catalytic reactions. For this reason, the aim of this work is to demonstrate the peculiarities of the mechanochemical hydrogenation, as compared to the usual catalytic reaction without detailing the total mechanism.

2. Experimental

Some properties of the samples examined are summarized in Table 1.

All the experiments were carried out at atmospheric pressure using a reaction mixture containing CO or CO_2 and H_2 in the ratio of 1 : 1.5 with an overall flow rate of 10 ml min^{-1} at about 40°C. The experiments with the hydrides were carried out in the presence or absence of H_2 in the reaction mixture at the same overall flow rate. The flow mechanochemical reactor was described in detail previously [9,10]. The reactor input was attached to a setup for preparing gas mixtures; the reactor outlet was combined on-line with a gas chromatograph for analyzing the effluent gas. The flow rate of reaction mixture was measured before and after the reactor. To recover water vapor, an ice-cooled trap was included in the line after the reactor. The following experimental procedure was used: (i) the samples without any special treatment (1.8 g) were placed into the reactor; (ii) the system was flushed by He; (iii) He was replaced with a reaction mixture; (iv) when the reagent concentrations at both the input and outlet of the reactor were found to be equal, the milling was started. The duration of each run ranged from 15 to 120 min. To study the dynamics of the process, the reaction mixture was analyzed every 5–10 min. The milling and gradientless flow conditions were ascertained before the catalytic experiments. The average energy intensity of the reactor was 6.5 W g^{-1}.

The X-ray diffraction (XRD) patterns of the solids at different stages of the gas–solid interaction were obtained using a Dron-3 diffractometer with a $Cu(K_\alpha)$ anode.

The content of impurities in Zr and Ni samples was found to be less than 0.1 at%. The amorphous ZrNi alloy and ZrNi hydride were prepared in the mechanochemical reactor by the treatment in Ar or in Ar and H_2, respectively [10]. Crystalline hydrides were prepared by the method described in [16] and kindly given to us by Professor V.V. Lunin, the Lomonosov Moscow State University.

3. Results

3.1. Oxide samples

To estimate the effect of mechanical activation on the hydrogenation process, we examined the NiO and ZrO_2 samples which, according to the special catalytic experiments, were inert in the methane formation up to 200°C. Under the mechanical treatment in the CO/H_2 reaction mixture, CH_4 was produced on both oxides: after 10 min milling of NiO and after 5 min milling of ZrO_2. The rates of CH_4 formation, as well as conversions of CO, were very low during all the experiments. The maximum rates of 3.1×10^{-9} and 2.9×10^{-9} mol g^{-1} s^{-1} were found for NiO and ZrO_2, respectively. Remarkable broadening of the NiO and ZrO_2 peaks was observed in XRD patterns after the mechanochemical treatment.

3.2. Metal samples

The next series of experiments was carried out with the catalysts commonly used for the CH_4 formation: Ni, Zr, mixture of Zr and Ni, and α-ZrNi alloy (Table 1). The milling of Ni in a CO/H_2 mixture resulted in only CO_2 and nickel carbonyl formation. The broadening of the characteristic peaks of Ni in XRD pattern pointed to a highly dispersed and imperfect structure. Thus, under the mechanochemical conditions, the classical catalyst for the methane formation was found to be active only in the CO disproportionation due to adsorption of CO in a molecular form.

In the case of Zr, a small amount of CH_4 was observed from the beginning of the run. The rate of CH_4 formation varied slightly during the treatment, whereas the conversion of CO, as well as the rate of H_2 sorption, rapidly increased (Fig. 1). The XRD data indicate that some zirconium hydride was formed. A low content of a cubic phase with a lattice parameter of $a = 4.66$ Å was also detected. This phase, most likely,

Table 1

Phase compositions and specific surface areas of the samples utilized in the mechanochemical hydrogenation of carbon oxides

Initial sample	BET specific surface area, ($m^2\ g^{-1}$)	Conditions of mechanical treatment	Phase composition after treatment	BET specific surface area after treatment ($m^2\ g^{-1}$)
NiO	2	CO+H_2 (1 : 1.5), 30 min	Highly dispersed NiO	5.2
ZrO_2 monoclinic	10	CO+H_2 (1 : 1.5), 60 min	Highly dispersed ZrO_2	7.4
Ni	<0.1	CO+H_2 (1 : 1.5), 60 min	Highly dispersed Ni	—
Zr	<0.1	CO+H_2 (1 : 1.5), 50 min	ZrH_2 + cubic phase[a]	1.2
Zr+Ni (50 : 50 at%), mixture	<0.1	CO+H_2 (1 : 1.5), 45 min	α-ZrNi+Ni+ZrH_2	0.5
α-ZrNi (50 : 50 at%), prepared from Zr+Ni milling in Ar [10]	<0.1	CO+H_2 (1 : 1.5), 60 min	Ni+ZrH_2+cubic phase	10.5
α-$ZrNiH_X$ (X<2) amorphous, prepared from α-ZrNi by milling in H_2 [10]	2	CO+H_2 (1 : 1.5) or CO		1.3
		60 min	Ni+ZrH_2+ZrO_2, traces;	
		120 min	Ni+cubic phase+ZrO_2, traces	
$ZrNiH_{2.7}$ crystalline, prepared by method [16]	0.8	CO+H_2 (1 : 1.5) or CO		1.2
		60 min	$ZrNiH_{2.7\text{-}X}$ amorphous+ZrO_2, traces;	
		120 min	Ni+cubic phase+ZrO_2, traces	
$ZrH_{1.5}$ crystalline containing admixture of ZrO_2, prepared by method [16]	<0.1	CO+H_2 (1 : 1.5) or CO		3.1
		60 min	$ZrH_{1.5}$ amorphous+cubic phase+ZrO_2;	
		120 min	cubic phase+ZrO_2	

[a] Cubic phase with $a = 4.66$ Å; ZrO_XC_Y is the most probable.

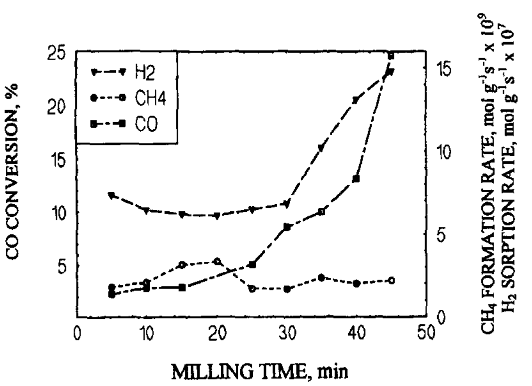

Fig. 1. Effect of mechanical treatment on interaction of CO/H_2 mixture with Zr; (∇) rate of H_2 sorption, (○) rate of CH_4 formation and (□) conversion of CO.

is ZrO_XC_Y. A similar structure was produced during the mechanochemical sorption of CO on Zr from the dissociation of CO molecules [17]. However, an unambiguous assignment demands additional tests carried out with other experimental techniques.

Thus, the competition between the formation of both CH_4 and the products of gas–solid interaction, zirconium hydride and zirconium oxycarbide, took place. Similar results were obtained for the Zr–Ni-containing samples, whose activities in the CH_4 formation, as well as in the sorption of CO (accumulation of carbon) and H_2, were about twofold lower than those for Zr. The reason seems to be the presence of the Ni phase in a $\alpha - \text{ZrNi} + \text{Ni} + \text{ZrH}_2$ multiphase system formed during the milling. All of the metal samples reacted with H_2 forming a hydride structure.

3.3. Hydride samples

We examined crystalline $ZrH_{1.5}$ and two kinds of Zr–Ni hydrides: amorphous α-$ZrNiH_X$ and crystalline $ZrNiH_{2.7}$. The kinetic curves for the CO conversion, CH_4 formation, and H_2 evolution are presented in Fig. 2A. On the Zr–Ni hydrides (Fig. 2A, a and b), the initial formation of CH_4 seems to be associated only with the milling action creating the low coordinate centers. Simultaneously, we observed sorption of CO and evolution of hydrogen from the sample. During the first 60 min, only 0.4–0.6% of the CO converted was transformed into CH_4, and the samples lost some 40% of its hydrogen. Nevertheless, according to XRD data, a highly dispersed ZrNi hydride structure was still retained. Further mechanical treatment led to a decrease and stabilization of the CO conversion contrary to the drastic increase in the rate of CH_4 formation. The structure of initial hydrides was degraded into a multiphase system consisting of Ni, cubic phase, and ZrO_2. Nearly 70% of the hydrogen dissolved evolved from the samples as H_2. It must be taken into account that no H_2 emission proceeded under treatment in vacuum. Amount of hydrogen evolved was found to be nearly equal to the amount of the CO converted. The highest activity in the CH_4 formation was observed for the crystalline $ZrH_{1.5}$ (Fig. 2A, c). Simultaneously with the sorption of CO, the rate of CH_4 formation rapidly increased during the first minutes of treatment. The sample lost about 29% of its hydrogen and transformed into a multiphase system containing highly dispersed $ZrH_{1.5}$ phase, traces of cubic phase ZrO_XC_Y, and $ZrO_2{\cdot}H_2O$ was also present in the products of reaction, which indicates particularly high activity of H_2.

3.4. Hydrogenation of CO by hydrogen dissolved in hydride samples

To test the reactivity of hydrogen dissolved in the hydride lattice, we studied the interaction of CO with hydride samples. The kinetic curves for the CO conversion, CH_4 formation, and H_2 evolution are shown in Fig. 2B. The most interesting was the fact that the rate of CH_4 formation increased in the absence of H_2 in the reaction mixture, whereas the conversion of CO decreased, as compared to that in the presence of H_2. The evolution of H_2 from the hydrides was also suppressed. In the presence of H_2, the major part of the hydrogen dissolved was emitted from the hydrides at the beginning of the run. In the absence of H_2 in the reaction mixture, the evolution of the major part of hydrogen proceeded in synchronism with the formation of CH_4 and took place after an induction period. Nevertheless, such a feature as the low rate of methane formation at the initial stage of treatment remained. The changes in the phase composition of solids induced by the gas–solid reactions were found to be similar to those observed in the presence of H_2 in the gas phase (Table 1). The reasons for reaction peaks during the runs are yet to be explained. Possibly, it may be caused by the significant increase in the specific surface area due to the carbon accumulation.

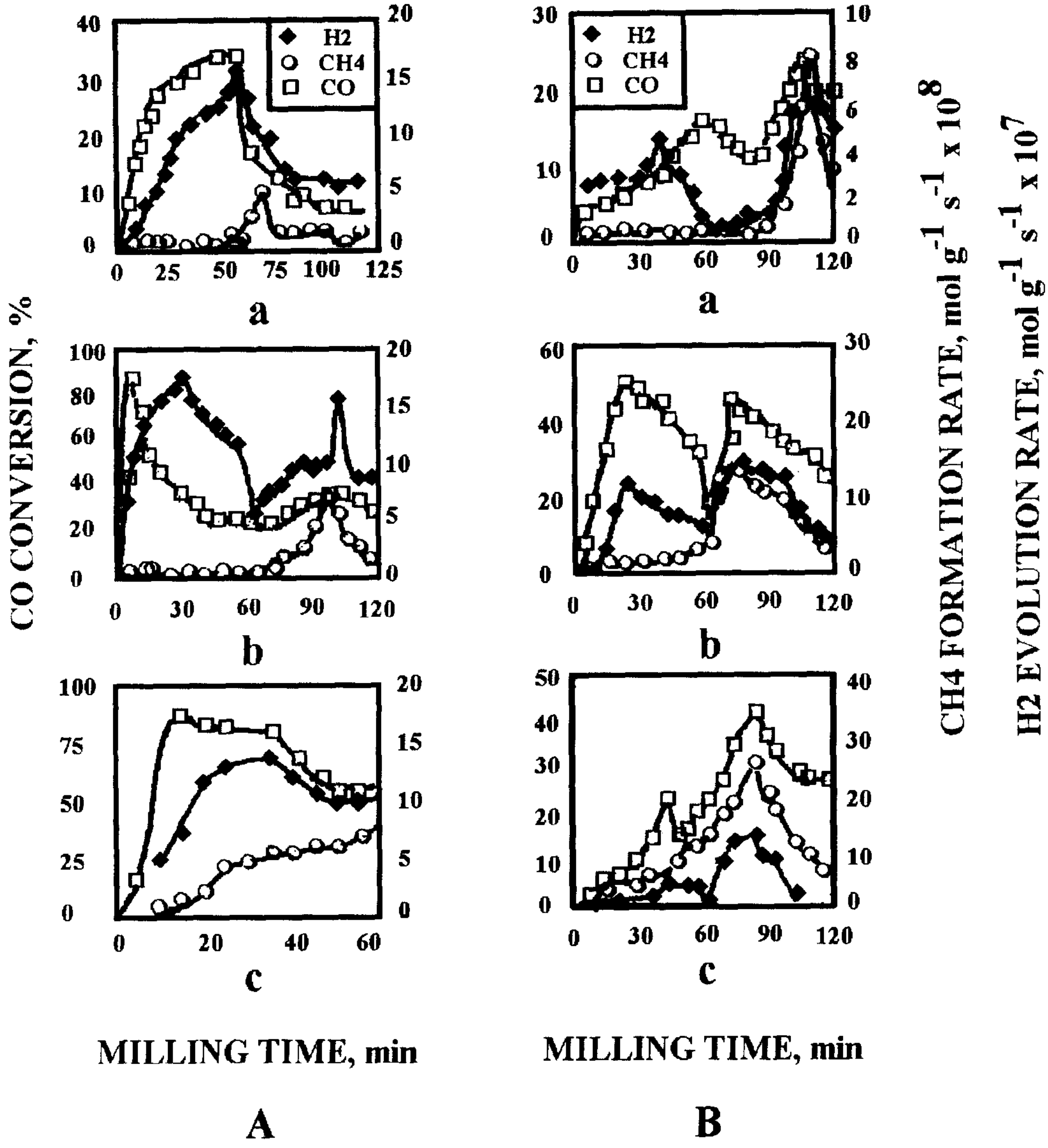

Fig. 2. Effect of mechanical treatment on interaction of (A) CO/H_2 mixture and (B) CO with (a) amorphous α-$ZrNiH_x$, (b) crystalline $ZrNiH_{2.7}$ and (c) crystalline $ZrH_{1.5}$; (◆) rate of H_2 evolution, (○) rate of CH_4 formation and (□) conversion of CO.

3.5. *Hydrogenation of CO_2*

Under mechanical treatment in a CO_2/H_2 reaction mixture, only $ZrH_{1.5}$ was shown to be a catalyst for the formation of CH_4 (Fig. 3). For this sample, the rates of CH_4 formation were found to be of the same order of magnitude for both carbon oxides (Fig. 2A, c and Fig. 3). However, in contrast to the CO hydrogenation, neither a remarkable sorption of CO_2 nor evolution of H_2 were observed. The CO_2 conversion ranged from 4 to 8%. About 90% of CO_2 converted was transformed into methane. No significant structural changes of the catalyst were detected.

The catalytic tests showed no measurable activity for the hydride samples in the absence of H_2 in a reaction mixture. In these experiments, we did not observe evolution of H_2, as well as sorption of CO_2 and the phase transformations of hydrides. The broad-

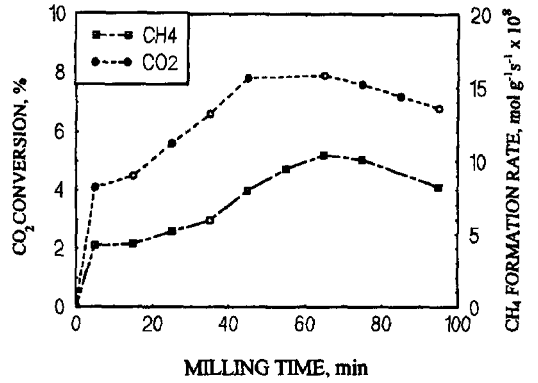

Fig. 3. Effect of mechanical treatment on the interaction of CO_2/H_2 mixture with $ZrH_{1.5}$; (□) rate of CH_4 formation and (○) conversion of CO_2.

ening of Zr- and ZrNi- peaks was observed in XRD patterns after the mechanochemical treatment.

4. Discussion

A careful examination of the experimental results led us to the following conclusions: (i) the mechanical treatment of solids creates low-coordinate centers for primary activation of the CO molecules then taking part in the gas–solid reactions and in CH_4 formation; (ii) the competition between these processes depends on their thermodynamic preference. Some of the data obtained are similar to those reported in [6–8,18]: the multiphase compositions formed during the gas–solid interaction differ from the initial solids in their mechanical properties, specific surface area, etc. As a result, the catalytic properties change too. However, in contrast to Ref. [8], we observed no improvement in the catalytic efficiency in the presence of Ni. The data obtained demonstrate the fundamental difference between catalytic and mechanically induced catalytic hydrogenation of CO. Contrary to the usual catalytic reaction, Ni was found to be ineffective in the CO hydrogenation to methane under mechanical treatment because of the formation of nickel carbonyl.

From additional experiments, we found out that mechanochemical hydrogenation of CO follows the carbidic mechanism [10,19], as was supposed in Ref. [6]. The thermodynamic preference of the zirconium oxides and carbide formation lead to the dissociative adsorption of carbon monoxide, as follows:

$$ZrH_2 + CO \rightarrow 1/2ZrO_2 + 1/2ZrC + 1/2C + H_2 \quad (-\Delta H = 367.5\,\mathrm{kJ/mol\,H_2}) \qquad (1)$$

$$2ZrH_2 + 2CO \rightarrow ZrO_2 + ZrC + CH_4 \quad (-\Delta H = 810.6\,\mathrm{kJ/mol\,CH_4}) \qquad (2)$$

Both active carbon and oxygen atoms introduced into the bulk structure produce an intermediate cubic structure of ZrO_XC_Y [17] or are accumulated inside the bulk. The carbon reacts with hydrogen to give CH_4. In the case of hydrides, the most reactive is the hydrogen dissolved in the lattice. The insertion of carbon and oxygen into the bulk is accompanied by the destruction of hydrides. As a result, the evolution of hydrogen takes place. The hydrogen evolved has the following reaction pathways: recombination into an H_2 molecule or interaction with active carbon. It was shown for the catalytic hydrogenation [14] that hydrides act as a membrane, which activates the hydrogen that passes through it from the gas phase.

The most interesting feature of this study is the suppression of CH_4 formation on hydrides in the presence of H_2 in the gas phase. It seems to be associated with two factors: (i) hydrogen from the gas phase reduces the fresh surface created under milling that contributes to the dissociative adsorption of CO and promotes the H_2 emission from hydride; (ii) the presence of H_2 in the gas phase promotes the recombination of H atoms emitted from the hydrides. Both processes can be responsible for the suppression of CH_4 formation. These phenomena are currently under investigation.

In contrast to the CO hydrogenation, we found no reports describing the mechanically driven hydrogenation of carbon dioxide. Fundamentally different features were found for this process, as compared to those for the mechanically activated hydrogenation of CO. Only one sample, $ZrH_{1.5}$, demonstrated activity for the hydrogenation of carbon dioxide. In this case, the presence of H_2 in a reaction mixture was a necessary condition for the CH_4 formation. We observed no remarkable competition between the catalytic and gas–solid reactions: about 90% of CO_2 converted was transformed into CH_4. It seems that total dissociation of the carbon dioxide molecule does not occur [20]. The hydrogen dissolved in the hydride lattice virtually took no part in the CH_4 formation.

Because of this, no measurable change in the phase composition of $ZrH_{1.5}$ was found after the mechanochemical treatment. Only one common feature was observed for the hydrogenation of both carbon oxides: Ni introduced into the catalyst suppressed its catalytic activity. On the basis of the data obtained, we have good reasons to suggest different mechanisms for the mechanically induced methanation of CO and CO_2.

5. Conclusions

This study demonstrates a fundamental distinction between the traditional catalytic and the mechanically induced hydrogenation of CO to methane. Of particular interest are the formation of CH_4 on NiO and ZrO_2, which are usually inactive in this reaction, and the suppression of CH_4 formation in the presence of metallic Ni in solids or in the presence of H_2 in the reaction mixture, when Zr–Ni and Zr hydrides are used. We suggest that the low-coordinate centers created under the mechanical treatment of solids play the major role in primary activation of CO. Only the active carbon accumulated on the surface or in the bulk of solids is found to be active in the CH_4 formation from CO. Hydrides seem to be reservoirs of hydrogen for the CO hydrogenation to methane. The peculiarities of the mechanically induced hydrogenation of CO_2 to methane are currently under investigation.

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