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Water–gas shift reaction over nickel hydroxides

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Charcoal-supported nickel hydroxides were investigated in the water–gas shift reaction and found to exhibit high catalytic activity. Nickel hydroxide structures of the type α*-$Ni(OH)_2 \cdot xH_2O$ are supposed to be the most probable bearers of the catalytic activity. A redox $Ni^{2+} \rightleftharpoons Ni^{3+}$ transition is accomplished in these catalysts.

Keywords: water–gas shift; nickel hydroxide; reaction mechanism; heterogeneous catalyst

1. Introduction

The water–gas shift reaction (WGSR) is one of the classical industrial catalytic reactions [1] for which at present both the oldest high-temperature iron–chromium catalyst and the low-temperature copper catalyst are used [2]. Sulfided Co–Mo and Ni–Mo catalysts exhibit high activity in the presence of sulfur-containing compounds [2]. However, the number of elements that manifest high activity for this reaction is limited [3].

So far, highly active nickel-containing WGSR catalysts are not known to be used in industry [3]. It has been noted that the water–gas shift is one of the reactions that proceeds during the complex process of methane steam reforming over supported nickel in the high-temperature range (over 500°C) [4].

This study reports high catalytic activity of supported nickel hydroxides in the water–gas shift reaction. Based on a set of experimental studies, we propose a probable reaction mechanism.

2. Experimental

2.1. SAMPLE PREPARATION

A sample, denoted as NH/C, was prepared by using activated charcoal

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(CECA-ACLH, BET area = 750 $m^2 g^{-1}$, 0.25–0.50 mm particle size) according to the following procedure. A definite amount of charcoal was impregnated with aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$, p.a. grade, followed by drying at 130°C. An aqueous solution of 10 wt% potassium hydroxide was further added to the dried mass until the pH reached a stable value of 12. After aging for 60 min the slurry was filtered and washed until absence of NO_3^- ions and dried at 120°C. The dried sample contained 19.7 wt% NiO, the alkali content (as Na_2O) in the catalyst being less than 0.1 wt%. The catalytic activity of this sample was compared to that of an alkali-free industrial WGS copper–zinc–alumina catalyst (NSTK, Chimco Co, Vratza, Bulgaria) containing 23 wt% CuO.

2.2. CATALYTIC ACTIVITY

The catalytic activity was studied at atmospheric pressure in a gradientless flow circulating system, as part of a glass apparatus, under differential conditions. It was measured as the productivity in carbon monoxide conversion per gram of nickel in the catalyst (mol CO h^{-1} g_{Ni}^{-1}). The degree of conversion was determined by measuring the CO and CO_2 contents at the outlet of the infrared gas analyzer. The gas mixture contained 5.1 vol% CO in argon. The catalytic activity measurements were performed at H_2O partial pressure of 223 Torr (1 Torr = 133.3 Pa) and space velocity of 3000 h^{-1}. This study was conducted at conversions between 60 and 97.5%.

Each sample was heated to 150°C in argon flow, then the reaction mixture was admitted at the same temperature and finally conducted to the working temperature. In some cases the samples were pretreated in a different way which is mentioned in the text.

2.3. X-RAY DIFFRACTION

X-ray diffraction (XRD) measurements were carried out by means of a conventional Philips powder diffractometer using Cu K_α radiation selected by a secondary graphite monochromator. Fresh samples and used samples after 60 h of time on stream were examined.

2.4. X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

X-ray photoelectron spectra were recorded on an ESCALAB MK II instrument using an Al K_α excitation source. Corrections related to a charge on the samples were made with respect to the position of the C 1s peak at 284.6 eV. Both fresh and used samples after 60 h of operation under working conditions were studied.

3. Results and discussion

Fig. 1 shows the temperature dependence of the catalytic activity of NH/C in

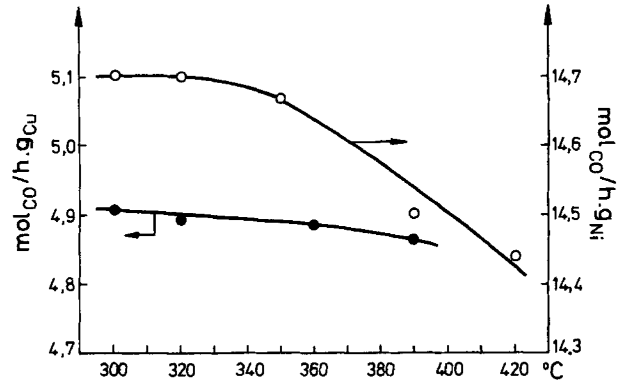


Fig. 1. Catalytic activity versus temperature: (○) NH/C sample, (●) industrial copper catalyst.

the water–gas shift reaction. Data on a conventional copper WGSR catalyst containing 20 wt% CuO are also presented. It is clearly seen that the NH/C sample exhibited higher catalytic activity (the decrease in activity on raising the temperature is due to thermodynamic reasons). Bearing in mind that the copper catalysts are among the most active WGSR systems used at present, we can conclude that the nickel catalyst studied demonstrates high activity for this reaction.

The catalytic activity of the investigated samples was substantially dependent on the pretreatment procedure. Fig. 2 shows the time dependence of the catalytic activity of NH/C samples treated under different conditions. It is seen that the sample with onset of operation at 300°C attained maximum activity in a very short per-

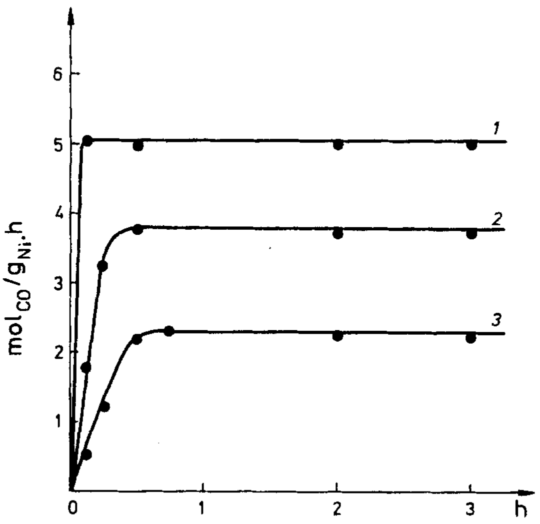


Fig. 2. Time dependence of productivity for NH/C samples subjected to different pretreatment: (1) conventional procedure; (2) argon–water vapour mixture (P_{H_2O} = 233.7 Torr, 300°C, 2 h; (3) argon (300°C, 2 h).

iod of time (fig. 2, curve 1). Preliminary treatment of the catalyst in argon at 300°C caused the sample to attain the steady state much more slowly, this state being described by lower catalytic activity than that with the conventional procedure (fig. 2, curve 3). An intermediate case of both the degree and time to attain the steady state activity could be accomplished by preliminary treatment at 300°C for 2 h in argon–water vapour mixture ($P_{H_2O} = 233.7$ Torr, fig. 2, curve 2). The dependencies observed can be explained by the hypothesis that different treatment modes lead to the formation of various amounts of active phase in the sample for WGSR.

Fig. 3 presents the dependence of the catalytic activity of the NH/C sample on water vapour partial pressure. Experimental results indicate a reaction order of 0.73 with respect to water. The majority of studies of iron [2,5] and copper [2,6,7] WGSR catalysts report reaction order in water between 0.5 and 0.7. The effect of the water vapour partial pressure on the catalytic activity can be associated with specific formation of an active surface on the investigated catalysts. Such an effect has been found with iron catalysts [8].

Information about the probable catalytically active phase could be obtained from X-ray diffraction. Table 1 shows principal XRD data on the NH/C catalyst. The main phase found in the fresh sample was nickel hydroxide, β-$Ni(OH)_2$, and a small amount of NiO. After operation of the sample under working conditions the NiO lines and two lines of the metallic nickel increased their intensity. Two lines, characteristic of α-$Ni(OH)_2$ and α*-$Ni(OH)_2$ structures, also appeared. The former species exhibits imperfect crystalline organization. Its "turbostratic" structure consists of randomly oriented slabs separated by intercalated water. Both structures are less stable and less stoichiometric than the β-$Ni(OH)_2$ one [12].

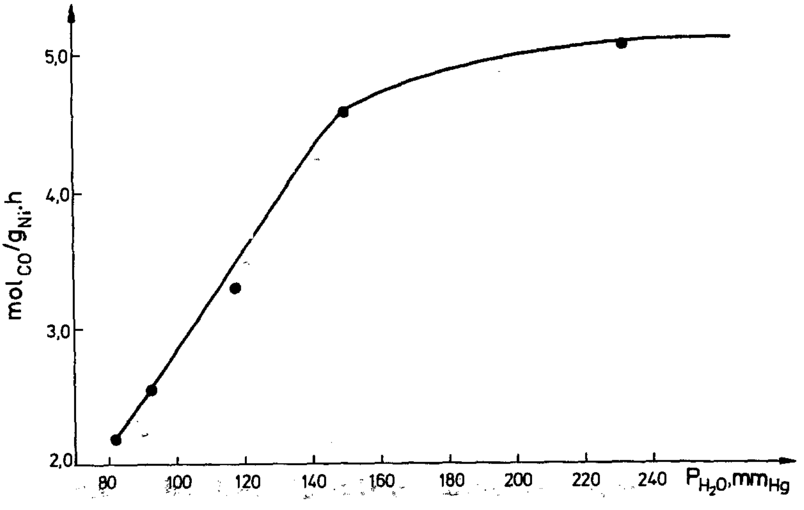


Fig. 3. Dependence of the productivity of NH/C at 300°C on water vapour partial pressure.

Table 1
X-ray diffraction data

Fresh sample		Used sample	
identified phase	d (nm)	identified phase	d (nm)
β-$Ni(OH)_2$ [9]	0.269	NiO	0.242
	0.234		0.2089
	0.156		0.148
	0.148	Ni	0.204
NiO [11]	0.2088	β-$Ni(OH)_2$	0.149
		α^*-$Ni(OH)_2$ [11]	0.149
			0.422

β-$Ni(OH)_2$ can be visualized as a layered structure, each layer having a hexagonal planar arrangement of Ni(II) ions with octahedral coordination of oxygen.

The catalyst performance under reduced water vapour partial pressure gave rise to a certain increase in the amount of metallic nickel. It should be noted, however, that the nickel oxide phase predominated even at very low partial pressures applied, the nickel hydroxide (NH) phases being present in detectable quantities.

The most likely phase that takes part in the catalytic WGS process seems to be an appropriate form of NH. No metallic nickel active in WGSR was registered in the temperature range investigated. Besides, the sample did not manifest any methanation activity, specific for metallic nickel, under the conditions applied and within the accuracy of the analytical method. The presence of a large amount of water vapour in the reaction mixture should cause hydroxylation of the nickel oxide surface and oxidation of the metal surface. The oxidation and hydroxylation of the metal surface was verified by results from XPS which, in contrast with XRD, is a surface sensitive method.

Data on the probable active hydroxide phase and its relation to the reaction mechanism were obtained by means of XPS measurements. Fig. 4 shows O 1s spectra of the NH/C sample after treatment under working conditions. Using computer simulation, the experimental curve could be fitted as a sum of three basic states of oxygen. We propose the following interpretation of the separate components. The peak at 530.0 eV corresponds to oxygen in nickel oxide [13,14]. Hydroxyl oxygen in $Ni(OH)_2$ is related to the peak at 531.7 eV [13,15]. The peak at 533.6 eV can be interpreted as originating from oxygen in nickel hydroxide gel which contains both Ni(II) and Ni(III) [16]. Such a type of nickel hydroxide gel has been observed at the positive electrodes of nickel alkaline storage batteries [16]. Evaluation of the peak areas gives the following arbitrary ratio: $S_{NiO} : S_{Ni(OH)} : S_{NiOOH} = 0.20 : 0.68 : 0.12$. Absorptions typical of NiO (530.0 eV) and $Ni(OH)_2$ (531.8 eV), observed with the fresh sample, demonstrated a $S_{NiO} : S_{Ni(OH)} = 0.20 : 0.80$ ratio.

The following conclusions can be drawn after completing this investigation.

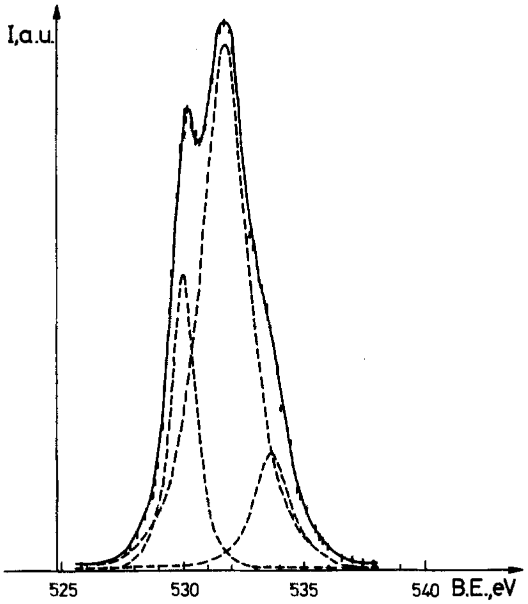


Fig. 4. O 1s X-ray photoelectron spectra of the NH/C sample after operation under working conditions.

The X-ray diffraction and X-ray photoelectron studies give reliable evidence to think that NH structures participate as an active component in the WGS process. Nickel hydroxides occur yet in the fresh sample. Due to the influence of the reaction medium, a specific working composition of the catalyst is formed. An active nickel hydroxide phase is also formed in the nickel oxide (calcined samples) through hydroxylation by water vapour in the reaction mixture. In this case its amount is considerably small.

The XPS study suggests that the active NH phase contains NiOOH-like structures which are bearers of the observed Ni(III).

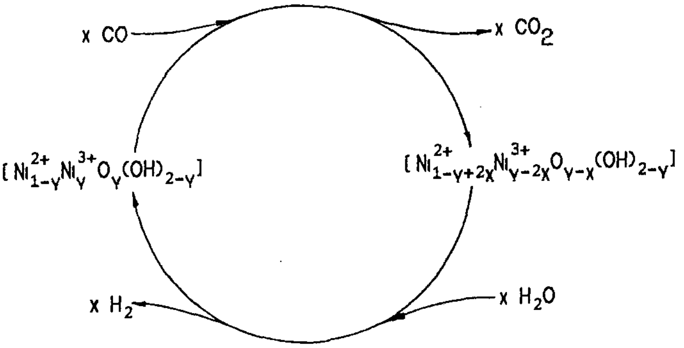
We think that the most probable NH phase which takes part in the catalytic act is of the type α^*-Ni(OH)$_2\cdot x$H$_2$O [11]. This highly defective material differs from the thermodynamically stable hydroxide species by the presence of a layer of water molecules in the van der Waals gap and by the hydroxide layer stacking [11]. This species is formed under the influence of the reaction medium by modification of the primary NH phase or a NH phase formed on hydroxylation of nickel oxide.

The participation of NH phases in the redox WGS reaction can be associated with the occurrence of a reversible redox transfer between the active species in nickel batteries (Ni(II)$\rightleftharpoons$Ni(III)) [12]. There exists sufficient body of evidence [17] for electro-chemical α-Ni(OH)$_2 \rightleftarrows \gamma$-NiOOH transitions [12]. According to some modern concepts [12,18], particular attention should be given to the possibility to proceed a topotactical solid state process in the nickel hydroxide without phase transition:

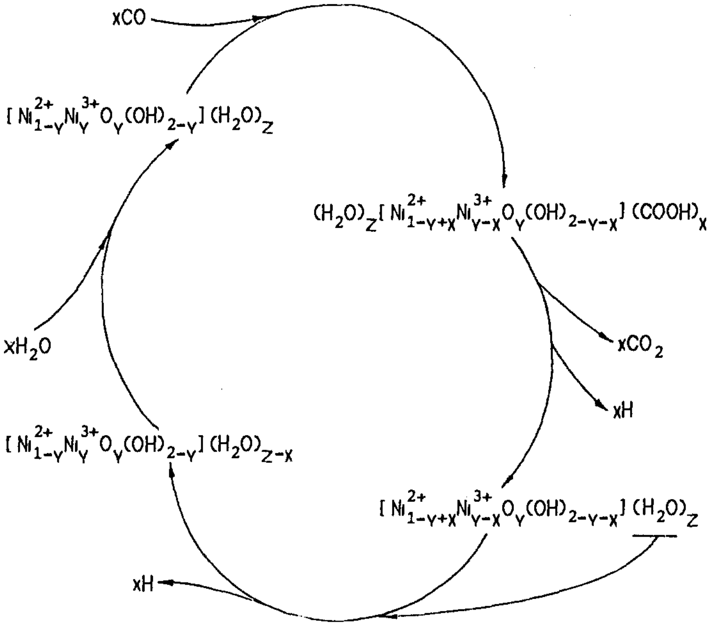
$$Ni(OH)_2 + xOH^- \rightleftharpoons NiO_2H_{2-x} + xe^- + xH_2O\,. \tag{1}$$

Based on the above mentioned and on current concepts of the water–gas shift reaction mechanism [3], we propose a probable mechanism of the process (scheme 1) which involves a redox mechanism including the participation of lattice oxygen and a Ni(II)$\rightleftharpoons$Ni(III) transition.

However, it is very likely that the WGS reaction proceeds over the nickel hydroxide via an associative mechanism [3] shown in scheme 2. The associative mechanism considers the formation of an intermediate surface formate (carbonate or bicarbonate is also possible) and the occurrence of the redox Ni(II)$\rightleftharpoons$Ni(III) transi-



Scheme 1.



Scheme 2.

tion. Formation of the intermediate species facilitates the catalytic process. In this case an energetic compensation between the oxidation step and the reduction step is possible which results in lowering of the activation energy.

Both schemes presented clarify the crucial role of water activation in the reaction mechanism. The α^*-$Ni(OH)_2 \cdot xH_2O$ species, already mentioned as probable active component of the catalyst, is able to intercalate in the interlayer space of water molecules. Recently, it has been shown that water molecule intercalation in the catalyst lattice considerably facilitates its heterolytic decomposition and, therefore, its participation in the intermediate steps of the catalytic reaction [18]. A promoting effect of alkali (K^+) additives to the nickel hydroxide system, observed in this laboratory [19], supports this speculation.

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