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Plasmochemical Preparation of $NiO–Al_2O_3$ Catalysts

I. Sh. Normatov, N. Shermatov, and U. Mirsaidov

Nikitin Institute of Chemistry, Academy of Sciences of Tajikistan, ul. Aini 299/2, Dushanbe, 734063 Tajikistan

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Abstract—$NiO–Al_2O_3$ catalysts were prepared by hydrogen bombardment of aluminum hydroxide impregnated with nickel chloride. After bombardment for 2 h, the material was found to contain nickel aluminum spinel with a heavily distorted structure.

INTRODUCTION

Stimulation of chemical reactions by physical means is widely used in the technology of inorganic materials and makes it possible to notably raise the reaction rate. Among the underlying mechanisms of the physicochemical processes involved is the generation of various structural defects [1, 2], which is of particular importance in catalysis and catalyst fabrication. For example, the presence of a distorted spinel phase in $Fe_2O_3–Al_2O_3$ materials enhances their catalytic activity for oxidation of ammonia [3].

The purpose of this work was to prepare $NiO–Al_2O_3$ catalysts by plasma synthesis.

EXPERIMENTAL

$Al(OH)_3$ supports were prepared as described in [4]. The specific surface area of the supports (130 m^2/g) was determined by oxygen adsorption measurements in vacuum, using an electronic balance with a sensitivity of 5×10^{-5} g.

After impregnation with a nickel chloride solution and drying, the support was transferred to the holder of an rf plasma reactor (Fig. 1).

Atomic hydrogen was generated by passing hydrogen gas through an rf discharge between two electrodes, one connected to the feeder of an LGD-12 rf generator (1.275 GHz), and the other grounded. The distance between the center of the discharge region and the support could be varied by moving the latter. In this way, we were able to vary the activation power. The support was bombarded with hydrogen atoms at L/d = 15 and 30.

The support temperature during bombardment was monitored by two Chromel–Alumel thermocouples.

RESULTS AND DISCUSSION

Figure 2a shows the x-ray pattern of the support impregnated with nickel chloride and then bombarded with hydrogen for 40 min at L/d = 30. The material was found to consist of boehmite and nickel oxide, as also evidenced by the IR spectrum, which showed absorptions at 420, 460, 560, and 1080 cm^{-1}, attributable to NiO and AlO(OH) (Fig. 3).

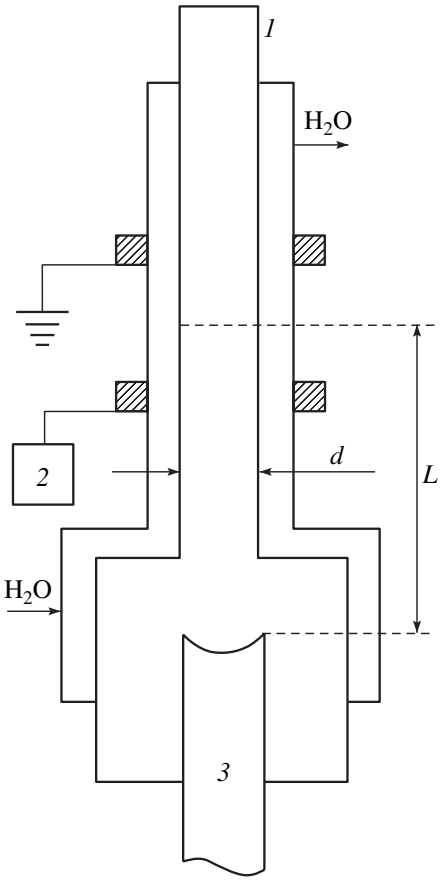

Fig. 1. Schematic of the experimental setup: (*1*) quartz reactor, (*2*) rf generator, (*3*) holder; L is the distance from the center of the discharge region to the support, and d is the reactor diameter.

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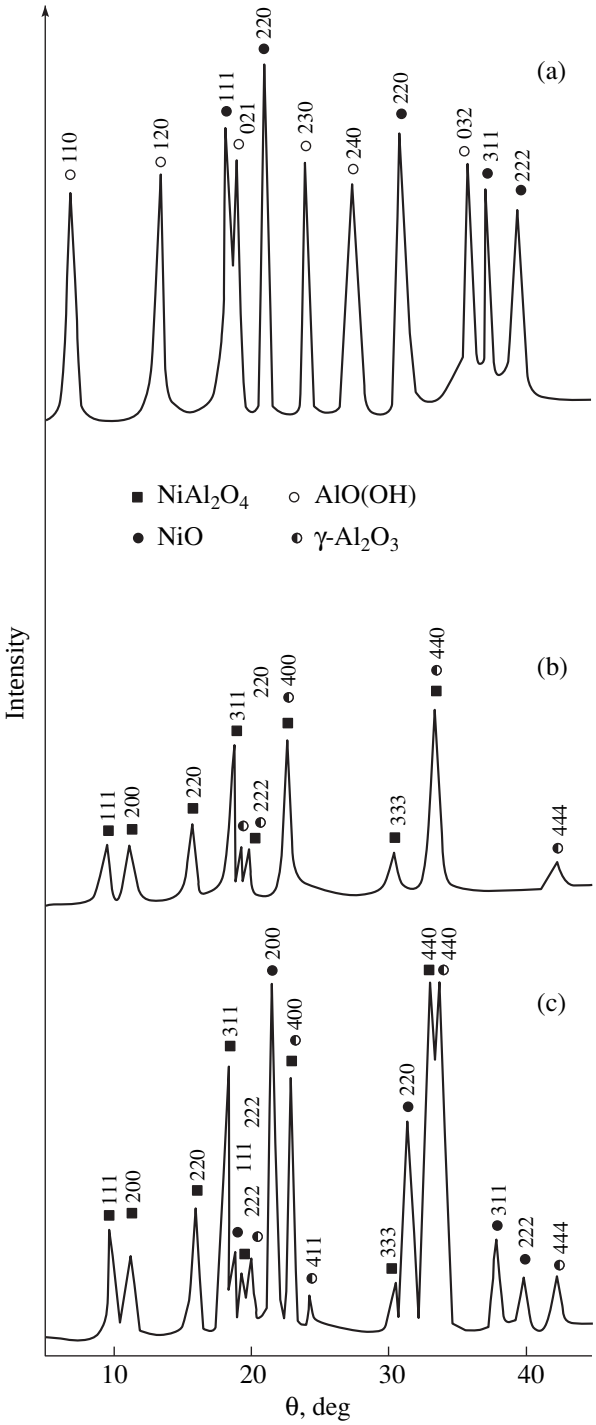

Fig. 2. X-ray pattern of the support impregnated with nickel chloride and then bombarded with hydrogen for (a) 40 min at L/d = 30, (b) 80 min at L/d = 15, and (c) 120 min at L/d = 15.

Therefore, the process can be described by the reaction scheme

$$Al(OH)_3 + NiCl_2 \xrightarrow{\sum_i H_i} AlO(OH) + NiO + 2HCl,$$

where $\sum H_i$ indicates the atomic hydrogen flow.

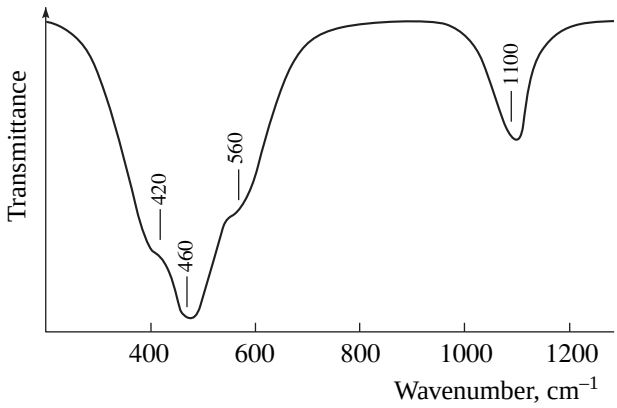

Fig. 3. IR absorption spectrum of the support impregnated with nickel chloride and then bombarded with hydrogen for 40 min.

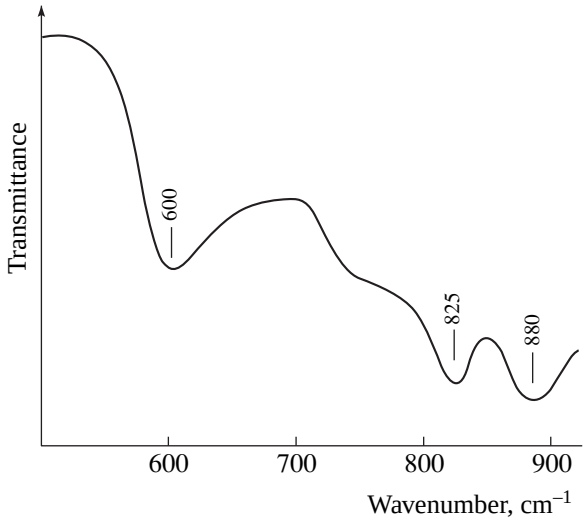

Fig. 4. IR absorption spectrum of the support impregnated with nickel chloride and then bombarded with hydrogen for 120 min.

Hydrogen bombardment leads to the dehydration of aluminum hydroxide and boehmite formation. Water absorption by nickel chloride, promoted by hydrogen bombardment, leads to the formation of nickel hydroxide. The thermal energy supplied by hydrogen activates water removal, leading to the formation of NiO.

The x-ray pattern shown in Fig. 2a contains reflections from orthorhombic boehmite with lattice parameters a = 4.41 ± 0.05 Å, b = 9.41 ± 0.05 Å, and c = 2.845 ± 0.05 Å.

After hydrogen bombardment at L/d = 15 (increased hydrogen flow and, accordingly, processing power), the material consisted of $NiAl_2O_4$ and γ-Al_2O_3 (Fig. 2b).

Clearly, the formation of γ-Al_2O_3 is the final stage of the process $Al(OH)_3 \longrightarrow AlO(OH) \longrightarrow Al_2O_3$. The spinel originates from the diffusion of Ni atoms to the distorted structure of boehmite.

The increased hydrogen flow leads to the reduction of nickel chloride. The energy supplied by bombardment enhances the mobility of nickel atoms. The diffusion of Ni and the transformation of boehmite into γ-Al_2O_3 culminate in the formation of a strongly distorted spinel phase with a = 7.88 Å.

Increasing the bombardment duration to 120 min increases the amounts of NiO, γ-Al_2O_3, and $NiAl_2O_4$ (Fig. 2c).

Figure 4 shows the IR absorption spectrum of the support impregnated with nickel chloride for 8 h and then bombarded with hydrogen for 120 min. The bands at 600 and 880 cm^{-1} are due to γ-Al_2O_3, and the band at 825 cm^{-1} is characteristic of AlO_4^- tetrahedra in the structure of nickel aluminum spinel.

CONCLUSION

Our IR absorption and x-ray diffraction data demonstrate that hydrogen bombardment of $NiCl_2 + Al(OH)_3$ mixtures leads to the formation of orthorhombic boehmite at an intermediate stage.

Increasing the hydrogen flow leads to rapid reduction of nickel chloride and Ni indiffusion into the distorted structure of boehmite. This process and the transformation of boehmite into γ-Al_2O_3 under bombardment culminate in the formation of a heavily distorted spinel phase.

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