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Characterization of Carbon Supported Nickel Catalysts by Chemical Methods

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A series of carbon supported nickel catalysts of various metal dispersion was characterized by temperature-programmed reduction and adsorption of hydrogen, carbon monoxide and oxygen. The examinations showed that some carbon species appear on nickel surface in the course of routine purging of the catalysts from hydrogen. The species weaken the adsorption of hydrogen but does not affect the adsorption of carbon monoxide. Dispersion of nickel determined from hydrogen, carbon monoxide and oxygen adsorption was the same, which indicates the usefulness of these adsorbates for characterizing of carbon supported nickel catalysts.

Key words: characterization, carbon, nickel catalysts, nickel dispersion

The interest in carbon supported metal catalysts is continuously growing due to several advantages offered by these materials. Carbon supports are inexpensive and inert and after activation they develop a high surface area desired for production of dispersed metal catalysts. However, in spite of the advantages, application of the catalysts is still limited and the main hindrance in their use is the difficulty in production of reproducible batch-to-batch catalyst, which arises from versatile chemistry of carbon support and natural contamination of commercial materials.

This paper is concern with the problem of characterization of carbon supported nickel catalysts. The following examinations were applied in this study: temperature-programmed hydrogenation of carbon appearing on supported nickel, temperature-programmed desorption of preadsorbed hydrogen, adsorption of carbon monoxide and oxygen. The results obtained demonstrate that all these adsorbates may be used to characterize nickel dispersion, provided experimental conditions of the measurements are correctly chosen.

EXPERIMENTAL

Apparatus. The examinations were carried out in a glass flow system [1] equipped with a gradientless microreactor [2]. A temperature controller maintained the reactor temperature within 1 K and provided linear temperature programming. Hydrogen, argon and helium were of 99.99% purity. Hydrogen was further purified by a palladium filter. Argon and helium were further purified by passing through a series of columns packed with Cu/SiO_2, silica gel and molecular sieve 5 A. The gas stream required was directed to measuring system by a four way valve and, before entering the reactor, it was additionally purified by passing through a MnO/SiO_2 column. In the case of the He stream that column was kept at 78 K, which reduced the concentration of impurities below 0.1 ppm. Composition of the gas stream leaving the reactor was monitored by a TCD cell and the results were collected with computer controlled system.

Materials. The catalysts were prepared by wet impregnation of thoroughly purified carbon support. The support was obtained from commercial active carbon, Norit RO 08, by heating at 2173 K in 0.004 bar He atmosphere [3]. After that treatment the support was free of sulphur and nitrogen compounds and the content of mineral impurities was lowered to small values: Ca – 0.15, Mg – 0.002 and Fe – 0.036 wt.%. The impregnation was performed with an aqueous solution of nickel nitrate and thereafter the material was dried in air at 363 K and stored. The obtained $(Ni/(NO_3)_2)/C$ precursor was used to prepare a series of Ni/C specimens of various nickel dispersion by applying various prereduction temperatures (Table 1).

Table 1. Pretreatment of Ni/C specimens.

Specimen	Temperature of prereduction K	Temperature of purging K
A	623	573
B	673	623
C	723	673
D	773	673

Measurement procedure. Typically 250 mg of the precursor was used for examination. The sample was *in situ* prereduced in a H_2 stream of 1 cm^3/s at linearly increasing temperature of 0.05 K/s from room to a selected temperature (see Table 1), whereupon the reduction was continued for 2 h. Then the examined sample was purged from hydrogen in a He stream (0.5 cm^3/s, 0.5 h, temperature indicated in Table 1), whereupon one of the following examinations were carried out:

1. Temperature-programmed hydrogenation of carbon (TPH-C_{ads}) was carried out in a H_2 stream of 0.5 cm^3/s at linearly increasing temperature of 0.35 K/s from 243 K to the temperature equal to the prereduction temperature (Table 1).
2. Temperature-programmed desorption of preadsorbed hydrogen (TPD-H_{ads}). The adsorption of hydrogen was performed at atmospheric pressure according to one of three procedures: a – at constant temperature of 273 K for 0.5 or 16 h (P-273 and P-273^{16}), b – at varied temperature, initially at 423 K for 0.1 h and subsequently at 273 K for 0.4 h (P-423), and c – at gradually decreasing temperature from 673 to 273 K, whereupon at 273 K for 0.4 h (P-673). After the adsorption, the reactor with the sample examined was flushed with a He stream (0.5 cm^3/s, 273 K, 0.1 h) to remove the weakly adsorbed hydrogen and the strongly adsorbed hydrogen was examined by TPD method. The examination was carried out in an Ar stream of 0.5 cm^3/s at linearly increasing temperature of 0.35 K/s from 243 K to the prereduction temperature (Table 1). Occasionally the examinations were completed by the measurement of the amount of CH_4 formed during H_2 preadsorption and/or by monitoring the CH_4 concentration in the course TPD-H_{ads} run.
3. Adsorption of carbon monoxide was carried out by pulse method, introducing every 180 s portions of 4.5 μmol of CO into a He stream (0.5 cm^3/s), flowing over the sample kept at 293 K.
4. Adsorption of oxygen was carried out by pulse method, introducing every 30 s portions of 1.5 μmol of O_2 into a He stream (0.5 cm^3/s) flowing over the sample kept at 273 K.

Supplementary examinations have evidenced that hydrogen, carbon monoxide and oxygen do not adsorb on the support used. Besides, it has been found that nickel carbonyl was not formed in the course of the CO adsorption, in accordance with an appropriate calculation [4].

RESULTS AND DISCUSSION

TPH-C_{ads} examinations. Figure 1 shows TPH-C_{ads} examinations of Ni/C specimens. The dashed lines, A–D, concern the samples pretreated in the standard way, *i.e.* reduced and subsequently purged from hydrogen, and the solid line, D_{ref}, concerns the sample reduced but non-purged from hydrogen. The spectra obtained for the samples pretreated in the standard way consist of a broad profile in the range 273–473 K followed by a slope over 473 K. The profile, very likely composed of two overlapped peaks, is attributed to hydrogenation of carbon dispersed atomically on the nickel surface [5].

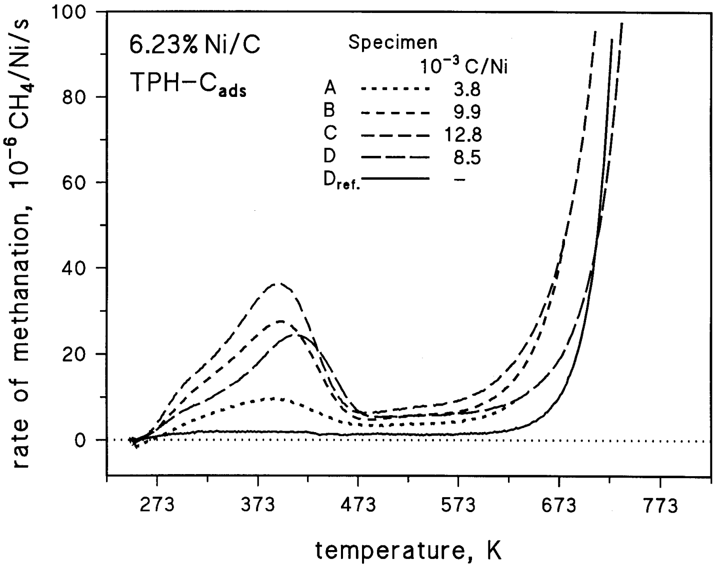

Figure 1. TPH-C$_{ads}$ spectra of Ni/C specimens.

The integration of the profiles in Figure 1 gives the amount of atomic carbon present on nickel surface after the standard, 0.5 h, purging in a He stream (Table 1). These values, expressed in mol of carbon per mol of nickel, are inserted in Figure 1. Complementary tests showed that after 16 h of purging the amount of surface carbon was two times larger for specimen A (purged at 573 K) and remains the same for specimens C and D (purged at 673 K). These results indicate that the amount of surface carbon attains a saturation value after 0.5 h of purging at 673 K. It is interesting that the amount of surface carbon is proportional to nickel dispersion (see data in Table 2), which implies that atomic carbon occurs mainly on nickel surfaces.

Detailed analysis of the spectra in Figure 1 suggests that the slope over 473 K comprises a broad peak at about 623 K. It is supposed that the peak is connected with condensed carbon species, which appear on nickel surface in consequence of cooling of the sample, prior to TPH-C$_{ads}$ test [6,7].

The above TPH-C$_{ads}$ examinations demonstrates that in the course of routine purging of Ni/C catalysts the surface of nickel is freed from adsorbed hydrogen, however, and at the same time it is contaminated with carbon species originated from the support. Naturally, there arises the questions on the effect of surface carbon on adsorption of hydrogen, carbon monoxide and oxygen, the adsorbates generally used for characterisation of nickel dispersion.

The effect of carbon on H_2 adsorption on nickel. The spectra in Figure 1 indicate that carbon, present on the nickel surface, may undergo hydrogenation during H_2 adsorption. Complementary examinations showed that during P-273 adsorption only about one forth of the initial volume of carbon was hydrogenated to methane, which indicates that the subsequent TPD-H_{ads} test was carried out for a carbon covered nickel. At the same time, similar examinations showed that during P-273^{16}, P-423 and P-673 adsorption the surface carbon was entirely converted to methane, which indicates that subsequent TPD-H_{ads} tests were carried out for the carbon free nickel surface.

Figure 2 presents TPD-H_{ads} spectra obtained after various preadsorption procedures. The examinations show that carbon present on the nickel surface (after P-273 adsorption) weakens the strength of hydrogen adsorption and diminishes the adsorption of hydrogen (expressed in mol of H_2 per mol of Ni). In the case of all the examinations for carbon free nickel surface (after P-273^{16}, P-423 and P-673 adsorption) the uptake of hydrogen is identical, which is important when hydrogen is used to measure the dispersion of nickel.

Complementary examinations revealed that in the case of the carbon covered nickel (after P-273 adsorption) a considerable amount of methane was evolved during the TPDSH$_{ads}$ test (curve CH_4 in Fig. 2). Therefore, the total amount of hydrogen evolved in this test equals the sum of hydrogen liberated in the form H_2 and in the form of CH_4.

The effect of carbon on CO and O_2 adsorption on nickel. The estimation of the effect of carbon on adsorption properties of nickel is a complex task, as it is hardly possible to get Ni/C specimen free of both hydrogen and carbon species on the metal surface. Therefore, the adsorption of CO and O_2 on the carbon covered nickel (after the standard purging) was compared with the adsorption on the hydrogen covered

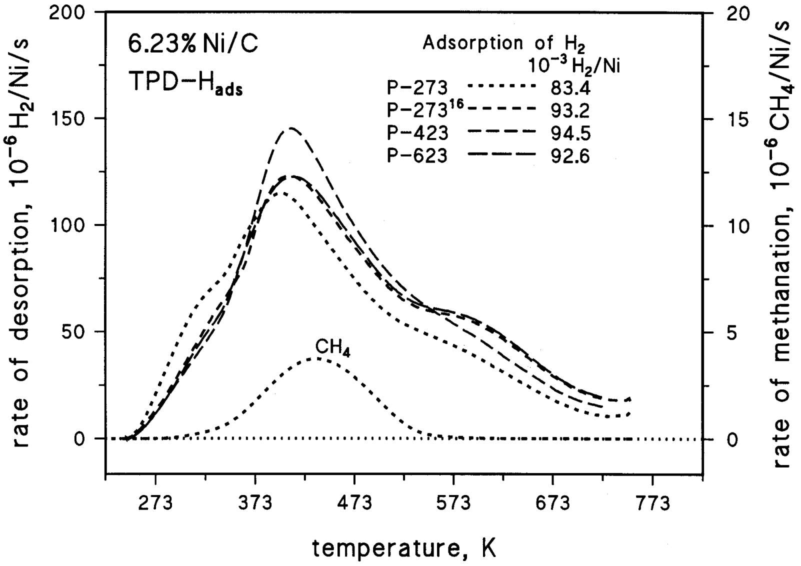

Figure 2. The effect of hydrogen preadsorption on TPD-H_{ads} spectra.

nickel (reduced and not purged from hydrogen). In the case of CO it was found that the uptake on carbon and hydrogen covered nickel was exactly the same, which indicates that neither carbon nor hydrogen retards the adsorption. Analogous examination for the O_2 adsorption on the carbon covered and hydrogen covered nickel failed: the uptake of O_2 on the hydrogen covered nickel was considerably lower than the uptake on carbon covered nickel. Taking into account the high reactivity of oxygen towards nickel, it is supposed that carbon does not affect the O_2 adsorption and that the effect of hydrogen is connected with the formation of a surface "nickel hydroxide" layer that blocks the adsorption.

The effect of nickel dispersion on H_2, CO and O_2 adsorption. Figure 3 shows TPD-H_2 profiles of Ni/C specimens of various dispersion of nickel, obtained in consequence of various prereduction temperatures (Table 1). Preadsorption of hydrogen was carried out according to P-423 procedure, so the spectra concern the nickel free of the carbon species on metal surface. The examinations indicate that the decrease of the nickel dispersion (Table 2) lowers the height of the signals but does not affect their shape and position. This suggests that adsorption of hydrogen on carbon supported nickel is independent of nickel dispersion, which is important for characterization of the catalysts.

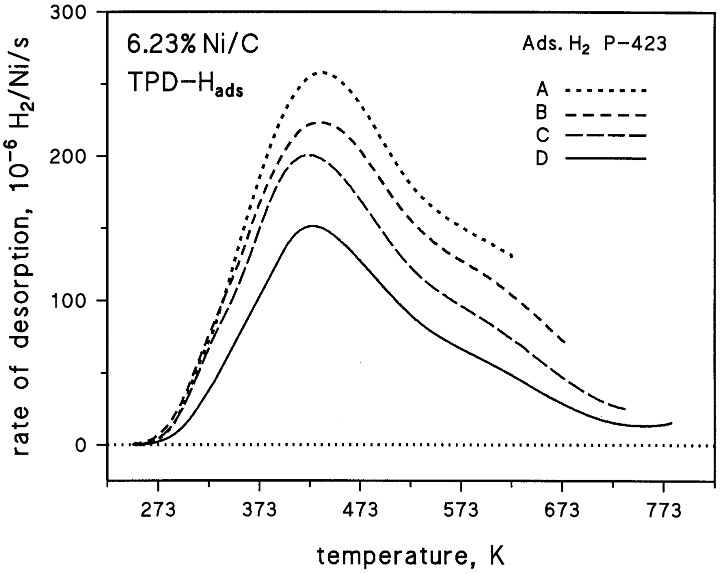

Figure 3. The effect of nickel dispersion on TPD-H_{ads} spectra.

Table 2. Dispersion of Ni/C specimens.

Specimen	TPD of H_2	Ads. of CO	Ads. of O_2
A	0.365	0.623	0.470
B	0.335	0.509	0.438
C	0.279	0.375	0.342
D	0.189	0.227	0.205

The TPD spectra in Figure 3 were used to determine the uptake of hydrogen. Taking into account that the measurements were terminated at various temperatures, the obtained values were recalculated to the final 773 K, assuming that the shape of the spectra is independent of the prereduction temperature. The uptake of hydrogen, carbon monoxide and oxygen were used to determine the dispersion of nickel (the fraction exposed), assuming the following stoichiometries of adsorption: $H/Ni_s = 1$, $CO/Ni_s = 0.5$ [9], and $O/Ni_s = 1.7$ [10]. The results obtained are summarized in Table 2. The comparison shows (i) a poor agreement of the results for specimens A and B, of high nickel dispersion and (ii) a good agreement of the results for specimen C and D, of low nickel dispersion. Analysis of the discrepancy for specimens A and B suggests that the values calculated from CO and O_2 adsorption are overestimated, due to multiple CO adsorption on corners and edges of small Ni crystallites [11,12] and overheating of small Ni crystallites in the course of the O_2 adsorption. Good agreement of nickel dispersion found for C and D specimens (Table 2) demonstrates that H_2, CO and O_2 adsorption may equally be used for the characterization of moderately dispersed carbon supported nickel catalysts. At the same time it is supposed that significant divergence in metal dispersion found often from each of these measurements is connected with impurities present in carbon supports.

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