Reducibility of silica supported nickel oxide

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The reduction of nickel/silica catalysts was studied in parallel by temperature programmed reduction (TPR) and X-ray diffraction (XRD) methods. The calcined materials contain nickel in the form of nickel oxide and nickel hydrosilicates and a part of the oxide particles is covered with the hydrosilicate species. This oxide is reduced in the same way as unsupported nickel oxide in the absence of water, and in a similar way to nickel hydrosilicates in the presence of water.

Keywords: nickel/silica catalysts; TPR studies; in situ XRD measurements

1. Introduction

Nickel/silica catalysts are widely applied in industry, and numerous studies have been devoted to the last stage of their formation, i.e. the reduction of NiO/SiO_2 precursors to Ni/SiO_2 catalysts [1–18]. These examinations have shown that the precursors are more difficult to reduce than NiO powder, and that the variation depends on the method used for their preparation. This effect has been explained for NiO/SiO_2 materials prepared by adsorption and by coprecipitation methods. XRD, EXAFS and XPS examinations revealed that nickel appears in these specimens in the form of nickel silicates [7,11,13,18]. This finding is consistent with TPR tests which show the presence of difficult to reduce nickel species, resembling nickel silicates [7,13,17]. In contrast to those materials, inconsistent results have been obtained for NiO/SiO_2 materials prepared by an impregnation method. For these specimens, XRD and EXAFS examinations have recorded merely a NiO compound [6,14], whereas TPR tests show the presence of two forms of NiO species: reduction in a similar way to unsupported NiO, and reduction in a similar way to nickel silicates [9,14]. The difficulty in reducing nickel oxide was attributed either to slow nucleation of a metal phase for small NiO crystallites [1–4] or to the presence of silica species in/on the crystallites [13,14]. Despite considerable efforts, the effect of silica on the reduction is not conclusively explained, and this communication presents further studies on this problem. The examinations were carried out for NiO/SiO$_2$ materials prepared by adsorption, coprecipitation, and impregnation methods. The reduction was realized at a linear temperature rise, and the progress of the reaction was followed in parallel by (i) measuring H$_2$ consumption and (ii) XRD examinations.

2. Experimental

2.1. APPARATUS

The examinations were carried out in a glass flow system [19] combined either with a quartz gradientless microreactor [20] or a metal X-ray camera-chemical reactor [21]. The microreactor was used to perform thorough TPR examinations. A temperature controller maintained the reactor temperature to within 1°C over the range −200–800°C and provided linear temperature programming. Consumption of hydrogen from a $H_2 + Ar$ mixture flowing through the reactor was measured by means of a TCD cell. The camera-reactor made it possible to reduce a sample in the same way as in the TPR test, and to carry out XRD examinations. The measurements were performed with a Rigaku-Denki diffractometer using Ni-filtered Cu Kα radiation.

2.2. MATERIALS

The examinations were carried out for various nickel/silica materials, distinguished by preparation method and nickel loading. This communication presents the main results obtained for three specimens:

A: 2% Ni/SiO$_2$, obtained by the adsorption method [12,22,23]. The adsorption was performed at room temperature, using silica from Merck (grain size 0.06–0.2 mm, surface area 360 m^2/g) and an ammoniacal solution of nickel nitrate at pH 9.8. After 24 h of adsorption the material was washed, dried, and calcined in air (400°C, 2 h).

B: 25% Ni/SiO$_2$, EURO-Ni, obtained by the coprecipitation method [15–18]. The material was received in a dried form, and the calcination was performed under the same conditions as for the specimen A.

C: 4% Ni/SiO$_2$, obtained by wet impregnation of silica from Merck with aqueous solution of Ni(NO$_3$)$_2$. After drying, the material was calcined in the same way as for specimen A.

The specimens which were investigated are characterized in table 1.

2.3. MEASUREMENT PROCEDURE

The measurements were carried out for calcined specimens, denoted as A, B, C, and additionally for reoxidized specimens, denoted as A′, B′, C′. The latter were

Table 1
Characterization of examined specimens [a]

Specimen	Calcined at 400°C	Reduced at 500°C			Reoxidized at 400°C	
	$D(XRD_{NiO})$ (nm)	α	$D(S_{Ni})$ (nm)	$D(XRD_{Ni})$ (nm)	$D(S_{NiO})$ (nm)	$D(XRD_{NiO})$ (nm)
A 2%Ni/SiO_2	–	0.54	2.2	–	2.5	–
B 25%Ni/SiO_2	–	0.97	3.6	2.7	4.1	3.3
C 4%Ni/SiO_2	13.4	~ 1.00	6.0	11.4	6.9	9.9

[a] α: degree of reduction; $D(S_{Ni})$, $D(S_{NiO})$: size of particles, calculated from O_2 uptake; $D(XRD_{Ni})$, $D(XRD_{NiO})$: size of crystallites, calculated from XRD measurement.

obtained as a result of reoxidation of prereduced samples. The prereduction was performed in a H_2 stream (80 cm^3/min) at a linearly increasing temperature (8.3°C/min) from 20 to 500°C, whereupon the reduction was continued for 1 h more. Afterwards, the sample was flushed with a He stream (40 cm^3/min, 400°C, 0.5 h) and reoxidized by introducing 39 mm^3 O_2 pulses into the He stream (40 cm^3/min) flowing over the sample. The oxidation was performed in two stages, at 0 and at 400°C. The uptake of oxygen at 0°C was used to estimate the amount of surface nickel, assuming that O/Ni_s ratio attained 1.7 [24,25], and the summed uptake at 0 and at 400°C was used to evaluate the total amount of nickel, assuming that NiO is formed [26]. These findings were used to calculate the mean size of Ni particles, $D(S_{Ni})$, assuming that nickel forms spherical particles, the whole surface of the particles is accessible to oxygen adsorption, and the number of nickel atoms per square metre of nickel is equal to 1.55×10^{19} [27]. The size of NiO particles in reoxidized specimens, $D(S_{NiO})$, was calculated from $D(S_{Ni})$, assuming a simple transformation of Ni particles into NiO particles.

Before the TPR test, the NiO/SiO_2 sample (250 mg of A, 25 mg of B, and 100 mg of C) was predried in a He stream (40 cm^3/min, 400°C, 0.25 h). The reduction was performed in a 80% H_2 + Ar stream (40 cm^3/min) at a linearly increasing temperature (8.3°C/min) from 20 to 800°C. The stream leaving the reactor was dried in a −78°C trap, and the change of H_2 concentration in the mixture was measured by means of the TCD cell. After the TPR test, the sample was not used for further examination.

The effect of water on the reduction of NiO/SiO_2 was examined by comparing the results of the following TPR runs:

– standard experiment in which H_2O concentration over the sample was not affected by an external action, TPR^{0} test,

– at decreased H_2O concentration, TPR^{-w} test,

– at increased H_2O concentration, TPR^{+w} test.

The decrease of H_2O concentration in the TPR^{-w} test was attained by using a sample premixed with a 2 g portion of alumina powder predried in situ at 600°C [28]. During the test, the alumina sorbed the water produced and thereby minimized the H_2O concentration in the gas phase. On the other hand, the increase of H_2O concentration in the TPR^{+w} test was accomplished by saturation of the $H_2 + Ar$ stream with water at 0°C.

The TPR^{o} and TPR^{-w} tests were complemented by analogous runs in which the examined sample was reduced in a H_2 stream (40 cm^3/min), and the H_2O concentration in the stream leaving the reactor was measured. The results of these runs are included in the presentation of TPR^{o} and TPR^{-w} spectra, drawing them with a solid line or a dashed line at minimal and significant H_2O concentrations, respectively.

Before XRD measurement, the examined sample was pre-dried in situ in helium and reduced in hydrogen at a linear temperature increase, just as in the TPR^{o} test. After the treatment, the sample temperature was lowered to 200°C (to 150°C for C′), and the XRD spectrum was recorded. This procedure made possible the examination of both calcined/reoxidized and reduced samples, as well as examination in the course of the reduction. The spectra recorded for reduced and for reoxidized samples were used to evaluate the mean size of Ni and of NiO crystallites, $D(XRD_{Ni})$ and $D(XRD_{NiO})$, respectively. The calculations were performed using Scherrer's equation, taking the half-width of the reflections corrected for instrumental broadening.

3. Results and discussion

The data inserted in table 1 form a general impression of the reducibility and the dispersion of nickel in the examined specimens. The reduction becomes easier, and at the same time the dispersion becomes lower in the order: A, B, C. For specimen A, the measurement of adsorption of oxygen indicates extremely high dispersion of nickel, and the recorded XRD spectra were insufficient for quantitative interpretation. The dispersion is also high in specimen B, and the determined size of Ni and NiO particles/crystallites agrees with the reported values [6,18]. Similarly as in the previous reports [6,9,14], the dispersion is low in specimen C, which had been prepared by the impregnation method, and the significant divergence in the size found from oxygen adsorption and from XRD measurements may suggest a bimodal distribution of the crystallites.

It is known that H_2 and H_2O concentrations in the gas phase influence the reduction of Ni/SiO_2 materials [17]. As regards this work, in the course of the TPR tests the H_2 concentration was within 77–80 vol% range, and this change could not affect the recorded spectra, whereas the H_2O concentration varied within the range of 0–3 vol%, and this change could strongly affect the spectra. For individual TPR runs this concentration was as follows:

– TPR^{o}: at low temperature the examined sample adsorbs the produced water which minimizes the H_2O concentration in the gas phase and thereby favours the reduction, and at high temperature the sample releases previously adsorbed water which increases the H_2O concentration and thereby retards the reduction. In consequence, in these runs the H_2O concentration changes from a minimal value to 3 vol%.

– TPR^{-w}: H_2O concentration changes in the same way as in the TPR^{0} test, however, the concentration is minimized up to a higher temperature.

– TPR^{+w}: H_2O concentration changes within the range of 0.6–3 vol%.

In general the TPR tests reported in the literature are realized under conditions in which the concentration of water over the examined sample develops in the course of the test without any external action. Thus, the literature examinations in principle correspond to TPR^{0} examinations of this work. However, the reported spectra may differ from the TPR^{0} spectra in this work due to (i) differences in preparation and pretreatment of the examined sample, and (ii) differences in the experimental conditions of the measurements such as the weight of the examined sample and the flow rate of the reducing gas, the concentration of hydrogen in the gas, and the shape of the reactor system which affects conditions for heat and mass transfer.

Figs. 1A, 1B and 1C show TPR examinations of specimens A, B, C, respectively. The spectra obtained for specimen A show a broad profile in the 300–800°C range. The TPR^{-w} profile (not shown in this figure) was similar to the TPR^{0} profile, and the TPR^{+w} profile is slightly shifted towards higher temperature. Taking into account previous studies [7,13,14], these tests suggest that various nickel silicates exist permanently in specimen A.

The specimen B is easier to reduce than the specimen A, very likely because of the presence of nickel oxide like species (see below) and higher concentration of nickel silicate species. The reduction of specimen B is strongly affected by water vapour: the TPR^{-w} spectrum exhibits a peak at ~ 320°C, followed by a tail at higher temperature whereas the TPR^{+w} spectrum shows a profile in the 350–700°C range. Similarly, as was demonstrated for NiO/Al_2O_3 materials [28], these results indicate that a fraction of the nickel oxide species existing in this specimen undergoes reduction in a similar way to unsupported nickel oxide in the absence of water, and in a similar way to nickel silicates in the presence of water. It is symptomatic that the reduction rate begins to decrease just when water appears in the gas phase (see fig. 1B) which suggests that a still larger fraction of nickel species could be reduced at low temperature if the removal of water was more effective.

The TPR^{0} spectrum obtained for specimen C resembles the reported spectra for similar materials [9,14]. It exhibits two peaks of hydrogen consumption, at ~ 290°C and at ~ 380°C, suggesting the presence of two forms of NiO species. The TPR^{+w} spectrum is similar, but it is shifted to higher temperature by ~ 70°C. In contrast to these spectra, the TPR^{-w} spectrum exhibits a single peak at ~ 250°C, much the same as that for NiO powder [19], which indicates that the whole of nickel oxide appears in a form similar to NiO powder. Thus, this result shows that water is a factor which conditions the appearance of an easy or a difficult to reduce form of nickel oxide.

Water radically affects the reduction of reoxidized specimens (figs. 1A′, 1B′

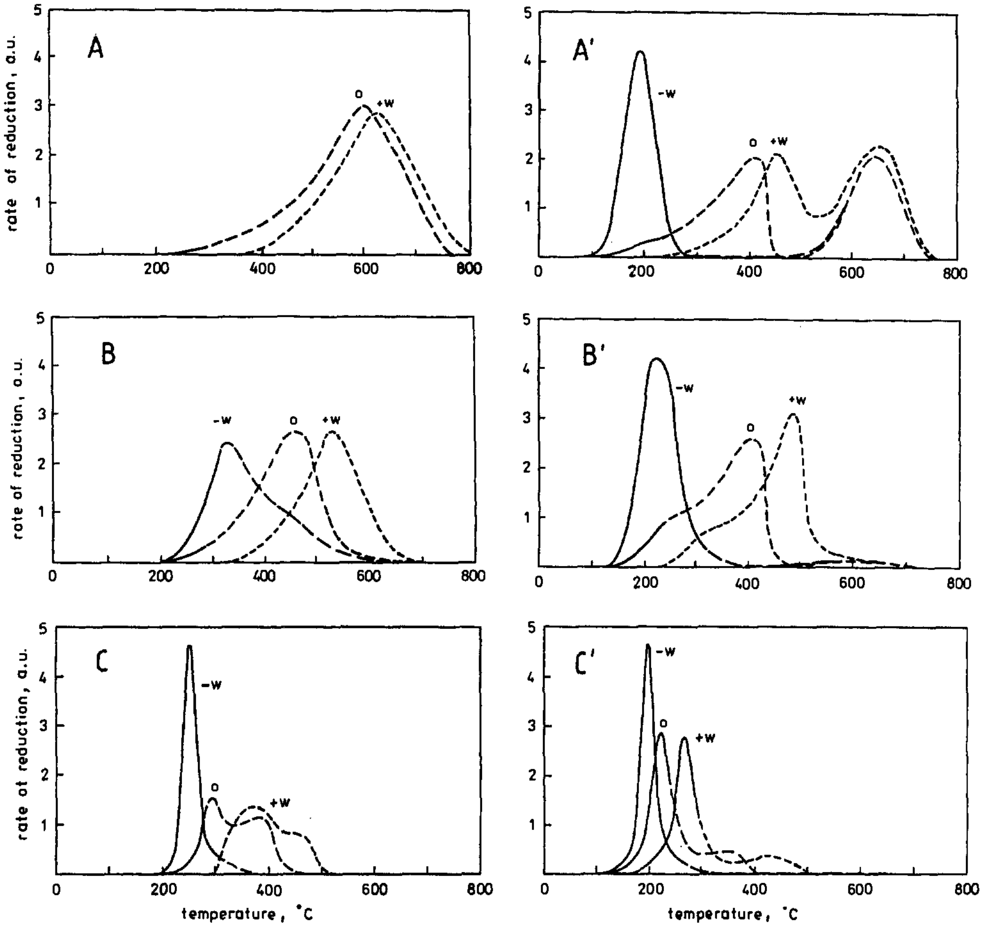

Fig. 1. TPR spectra of NiO/SiO$_2$ specimens.

and 1C′). The TPR^{-w} spectra obtained for these specimens exhibit a peak at ~ 200°C, characteristic of the reduction of unsupported nickel oxide [19], and a profile over 500°C; the profile is large for A′, small for B′, and minimal for C′. The volume of the peak corresponds to the amount of nickel oxide produced during the reoxidation which shows that the oxide is reduced in the same way as unsupported NiO powder, and the profile formed over 500°C is connected with the reduction of NiO species remaining in the prereduced sample. Consequently, these results demonstrate that nickel oxide supported on silica is reduced identically to NiO powder, on condition that the reduction is carried out in the absence of water. In particular, the TPR^{-w} test performed for specimen A′ (fig. 1A′) shows that this finding applies for extremely small NiO crystallites, considerably smaller than the mean size of NiO crystallites in the specimen.

The TPR^{+w} spectra obtained for reoxidized specimens (figs. 1A′, 1B′ and 1C′) exhibit a profile in the 250–550°C range followed by an additional profile at a higher temperature. The volume of the first profile roughly corresponds to the amount of nickel oxide produced during the reoxidation, which shows that the oxide is difficult to reduce in the presence of water. Taking into account the fact that water insignificantly affects reduction of unsupported nickel oxide [19], these results suggest that water and silica jointly interact with nickel oxide, thus retarding the reduction.

Fig. 2 shows XRD examinations. The spectra obtained before reduction agree with those reported previously [11,14,18]: for specimen B the spectrum exhibits a broad profile at 33–48°, composed of overlapping reflections of nickel hydrosilicates and presumably of nickel oxide, and for specimen C, as well as for specimens B′ and C′, the spectrum exhibits merely the reflections of the NiO phase. For each specimen the XRD spectrum gradually transforms with increasing temperature of the reduction, from the pattern recorded before reduction to the pattern characteristic of nickel after the reduction [6,18]. Assuming that a spectrum formed for a partly reduced sample is the linear combination of the initial and final patterns, the spectra taken in the course of the reduction (fig. 2) were used to estimate the degree

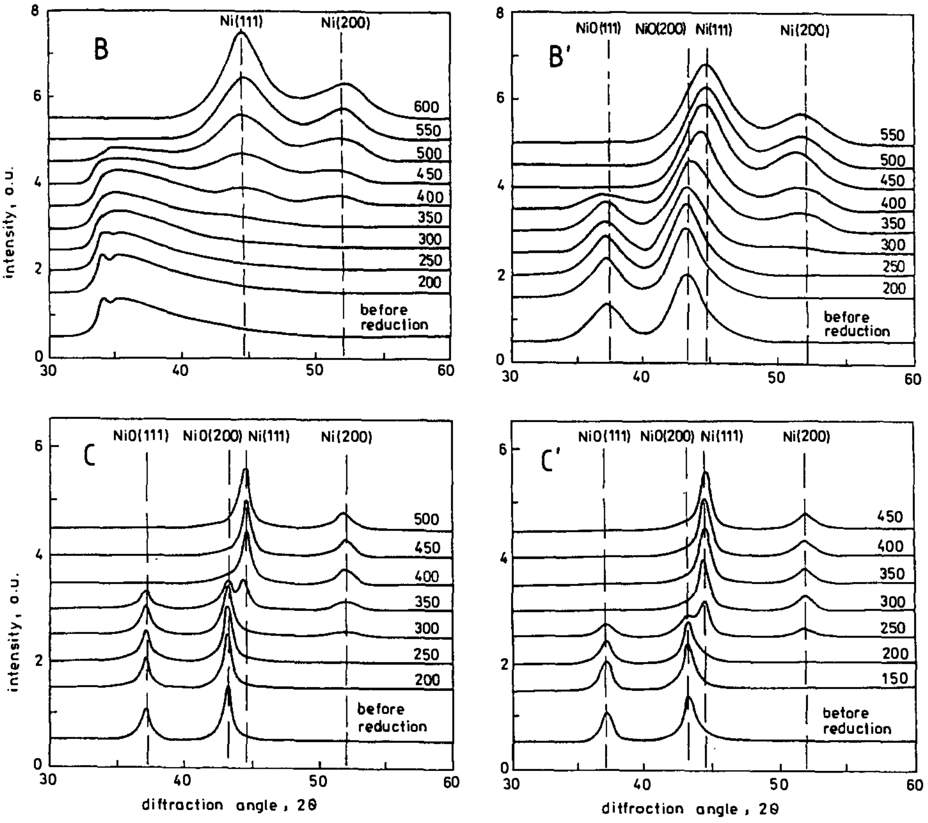

Fig. 2. XRD spectra of NiO/SiO$_2$ specimens; numbers by the curves denote reduction temperature in centigrade.

of the reduction (fig. 3). For each case the estimated degree of the reduction agrees with the value found from the TPR° test (fig. 1), which indicates that the reduction involves mainly crystalline reactants. Moreover, the agreement observed at the middle stage of the reduction suggests that individual crystallites of nickel oxide or nickel silicates quickly turn into nickel crystallites, and that there are no partially reduced particles, consisting of non-reduced and reduced fragments.

A survey of the spectra recorded for specimens C and C′ (figs. 2C and 2C′) shows that the NiO and Ni reflections are peculiarly broad at the bottom. This feature may arise from a strain in NiO and Ni crystallites, but it is more probable that it results from a bimodal distribution of the crystallites. In addition, the spectra recorded before the reduction show that the half-width of the NiO reflections is considerably smaller for specimen C than for specimen C′, which implies that a fraction of nickel in the specimen C exists in the form of XRD amorphous NiO species, and in the specimen C′ in the form of highly dispersed NiO phase.

The XRD spectra presented in figs. 2B′, 2C and 2C′ show that under conditions of the TPR° test crystalline nickel oxide indirectly transforms to nickel and that the reduction occurs at higher temperature than the reduction of NiO powder [19]. The effect is observed for each sample, and it is particularly high for specimen B′: the oxide is transformed to nickel only at 200–500°C, just as in the TPR° test (fig. 1B′), whereas NiO powder is reduced entirely at ~ 200–250°C [19]. This finding leads to the conclusion that NiO crystallites in NiO/SiO_2 materials are covered

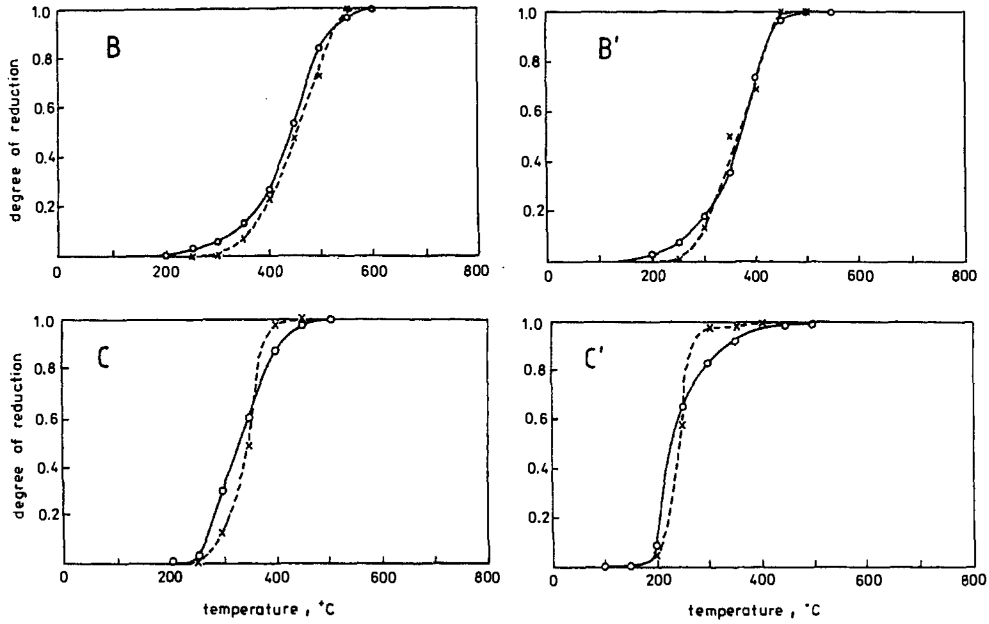

Fig. 3. Degree of reduction of NiO/SiO_2 specimens; solid line: TPR° measurements; dashed line: XRD measurements.

with silica species and these species hinder the reduction. Considering the effect of water on the TPR spectra (fig. 1) it seems that:

– the composition of the covering varies with H_2O concentration in the gas phase according to the schematic equation:

$$NiO + SiO_2 + H_2O = NiO{\cdot}SiO_2{\cdot}H_2O\,, \tag{1}$$

in which SiO_2 and $NiO{\cdot}SiO_2{\cdot}H_2O$ represent silica and nickel hydrosilicate surface species, respectively, and

– the covering by the silica species does not affect the reduction whereas the covering by the hydrosilicate species retards the reduction, and the effect depends on abundance and distribution of species.

In consequence, due to reaction (1) various coverings appear on NiO crystallites in NiO/SiO_2 materials: (i) nickel hydrosilicate species exist in calcined (air, ~ 3 vol% of H_2O) samples, (ii) silica species appear during standard drying and/or during the reduction carried out in the absence of water, and hydrosilicate species exist during the reduction carried out in the presence of water. These transformations are hardly detected by XRD measurements and they are recorded by TPR examinations.

In addition to the above suggestions concerning structure and reactivity of NiO/SiO_2 materials, it seems that, just as has been established for titania and for alumina-supported nickel catalysts [29–32], Ni crystallites in Ni/SiO_2 catalysts are partly covered with support species and this fact has to be considered in the studies of the catalysts.

4. Conclusion

(1) The TPR spectrum recorded for NiO/SiO_2 materials strongly depends on the H_2O concentration in the gas phase, and this fact has to be taken into account when TPR is used to characterize the morphology of the materials.

(2) NiO/SiO_2 materials calcined in air contain nickel in the form of nickel oxide and nickel hydrosilicates, and a part of the oxide particles is covered with the hydrosilicate species. The oxide is reduced in a similar way to unsupported nickel oxide in the absence of water, and in a similar way to nickel hydrosilicates in the presence of water.

(3) Highly dispersed nickel oxide in reoxidized NiO/SiO_2 specimens hardly interacts with silica in the absence of water, and readily interacts with silica in the presence of water. This results in the reduction of the oxide being identical to that of unsupported NiO powder in the absence of water, and similar to that of nickel hydrosilicates in the presence of water.

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