

## EXAMINATION OF HIGH-LOADED NICKEL CATALYSTS BY IR SPECTROSCOPY: EFFECT OF THE SUPPORT AND Pd ON SURFACE PROPERTIES

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*Dedicated to Dr Miloš Kraus on the occasion of his 65th birthday.*

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Activation of the ammonia molecule and subsequent adsorption of the NH<sub>2</sub> fragment on the surface of the NiO + Pd/TiO<sub>2</sub> catalysts, in contrast to NiO + Pd/SiO<sub>2</sub> catalysts, was demonstrated by IR spectroscopy. The decrease in the NiO + Pd/TiO<sub>2</sub> catalyst acidity was manifested in the higher catalyst stability in reductive amination of diethylene glycol to morpholine.

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Supported nickel compounds are very often used as effective catalysts in amination reactions. The formation of amines from hydroxy compounds proceeds via a system<sup>1</sup> of consecutive steps which includes dehydrogenation of alcohols, amine addition to the carbonyl group, hydrogenation of the imines formed and, finally, elimination of ammonia or water molecules. As the elimination reaction is a reaction with polar intermediates<sup>2</sup>, the acid-base properties of the catalysts can be expected to affect the overall reaction rate when the preceding steps are faster or comparably fast. In general, the acid-base properties of supported metal catalysts with low metal content are significantly affected by the properties of the support used. However, these predictions fail for catalysts with high metal contents (more than 50 wt.%).

This work was carried out to estimate the acidic properties of catalysts containing 50 wt.% or more NiO on SiO<sub>2</sub> or TiO<sub>2</sub> using IR spectroscopic data. It was also considered of interest to determine whether the surface properties of the nickel catalysts are substantially different when the catalysts are modified with small amounts of palladium.

## EXPERIMENTAL

*Supported nickel catalysts* were prepared by mixing the pulverized support (amorphous  $\text{SiO}_2$  or  $\text{TiO}_2$  (anatas)) with basic nickel carbonate dissolved in ammonium hydroxide. The slurry was dried at  $120^\circ\text{C}$  and calcined at  $370^\circ\text{C}$  for 3 h in the air. The amounts of nickel in the oxidic catalysts were 70 or 50 wt.%, respectively. Part of each calcined sample was impregnated with a  $\text{PdCl}_2$  aqueous solution to obtain catalysts modified by 0.1 wt.%  $\text{Pd}^{2+}$ . After the impregnation, the catalysts were dried and calcined under the same conditions as previously.

*IR spectroscopy.* Catalyst samples in the form of thin self-supporting pellets  $10 - 13 \text{ mg cm}^{-2}$  in thickness were used for the IR spectroscopic measurements. Prior to the IR spectra taking, the pellets were thermally treated at  $200^\circ\text{C}$  for 2 h in vacuo ( $P = 0.14 \text{ Pa}$ ). After cooling to ambient temperature, the IR spectrum of the oxidic catalyst sample was recorded at room temperature. In the next step, ammonia (or morpholine) was four times injected in 0.5 ml portions (unless mentioned otherwise) with immediate IR spectra recording on a UR-20 spectrometer (Zeiss, Jena).

*The activity of the catalysts* was examined in the reaction of diethylene glycol (DEG) with ammonia at 190 and  $210^\circ\text{C}$  (the molar ratio of  $\text{DEG} : \text{NH}_3 : \text{H}_2$  was 1 : 5 : 10) in an integral flow reactor with a fixed catalysts bed. The catalytic activity of the freshly reduced catalysts (2 h at  $275^\circ\text{C}$ ) was evaluated from the dependences of the DEG content in the organic phase of the liquid reaction product on the reaction time. When reaction is first-order (fulfilled in our case with respect to the high excess of ammonia) and supposing deactivation to be also first-order and concentration independent, the kinetic data can be evaluated<sup>3</sup> from the relation

$$\ln \ln c_0 / c = \ln [k \tau] - k_d t, \quad (1)$$

where  $k$  is the rate constant for the reaction of DEG ( $\text{l g}_{\text{cat}}^{-1} \text{h}^{-1}$ ),  $k_d$  is the rate constant for the catalyst deactivation ( $\text{l mol}^{-1} \text{h}^{-1}$ ),  $\tau = W c_0 / F$  weight-time ( $\text{g}_{\text{cat}} \text{h l}^{-1}$ ),  $t$  is time on stream (h),  $c$  is concentration of DEG ( $\text{mol l}^{-1}$ ). Subscript 0 means initial time.

## RESULTS AND DISCUSSION

*IR Spectra of Calcined Samples*

The IR spectra of calcined nickel catalysts supported on  $\text{SiO}_2$  and  $\text{TiO}_2$ , respectively, are shown in Fig. 1. In the  $3\,800 - 2\,000 \text{ cm}^{-1}$  region, no substantial absorption bands were found for both catalytic systems except a small band at  $2\,192 \text{ cm}^{-1}$  which could be assigned to  $-\text{CN}$  bond arising very likely from reaction of ammonium carbonate present in the wet catalytic mass. With all supported NiO catalysts, significant absorption bands appeared in the  $1\,500 - 1\,400 \text{ cm}^{-1}$  region which can be assigned very likely to  $\text{NH}_4^+$  ions. Their presence in the calcined catalysts can result from imperfect decomposition of raw materials used in the catalyst preparation. Thus, IR spectroscopy can serve as a useful tool for checking the quality of catalyst heat treatment.

The band in the region of  $1\,300 - 1\,250 \text{ cm}^{-1}$  is the characteristic one for carbonates. It is obvious from Fig. 1 that the NiO/ $\text{SiO}_2$  catalytic system contains considerable amount of carbonates which is substantially lower, practically negligible in the NiO/ $\text{TiO}_2$  catalyst. Very probably, amorphous  $\text{SiO}_2$  with relatively high specific surfa-

ce area (Table I) stabilizes Ni carbonates by their stronger adsorption on the surface. Such stabilization can lead to the higher temperature of decomposition which is necessary for their complete destruction. Similar stabilization was not observed with the catalysts based on  $\text{TiO}_2$  with low surface area. The impregnation of nickel catalysts

TABLE I

Compositions, physical properties of supported nickel catalysts, rate constants  $k$ ,  $\text{l g}_{\text{cat}}^{-1} \text{h}^{-1}$ , in the reductive amination of diethylene glycol and rate constants of catalyst deactivation  $k_d$ ,  $\text{l mol}^{-1} \text{h}^{-1}$

Sample	Support	Composition wt. %			Surface area $\text{m}^2 \text{g}^{-1}$	Kinetic parameters $\cdot 10^3$			
		NiO	Pd	$\text{CO}_3$		190 °C		210 °C	
						$k$	$k_d$	$k$	$k_d$
1	$\text{SiO}_2$	48	0	12	142	14	111	—	—
2	$\text{SiO}_2$	72	0	8	199	12	66	33	157
3	$\text{SiO}_2$	62	0.12	4.5	108	4	219	14	202
4	$\text{TiO}_2$	0	0	0	9	0	0	0	0
5	$\text{TiO}_2$	66	0	2.5	130	5	134	15	109
6	$\text{TiO}_2$	63	0.09	1	157	4	108	4	20

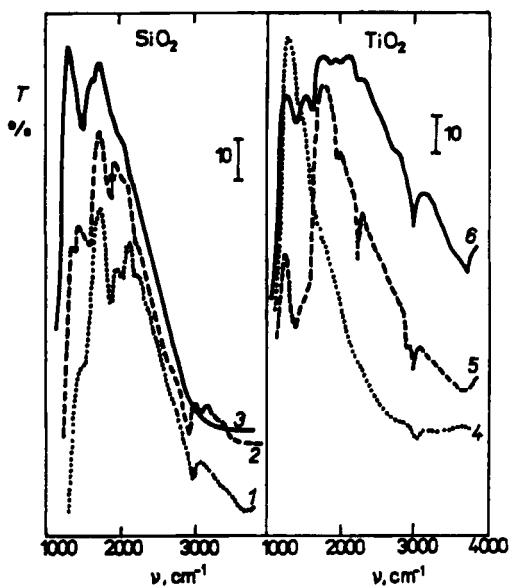


FIG. 1  
IR spectra of calcined nickel catalysts prepared  
on  $\text{SiO}_2$  (curves 1 - 3) or  $\text{TiO}_2$  (curves 4 - 6).  
Description of the samples see Table I

precursors with the palladium chloride solution caused substantial decrease of carbonate content, probably as a result of  $\text{CO}_3$  ion exchange for Cl ion. The presence of carbonates in the catalysts was proved by chemical analysis (Table I).

### IR Spectra of Adsorbed Ammonia

The infrared absorption of ammonium ion is quite distinct from that of ammonia, and this difference has been used to estimate the relative number of Brønsted acid sites (ammonium ions) and coordinated ammonia molecules (Lewis acid sites). Ammonium ions  $\text{NH}_4^+$  have their characteristic bands at  $1\ 440 - 1\ 420\ \text{cm}^{-1}$  and  $1\ 700 - 1\ 680\ \text{cm}^{-1}$ , ammonia molecules coordinated to metal ions have their bands at  $1\ 260 - 1\ 240\ \text{cm}^{-1}$  and  $1\ 640\ \text{cm}^{-1}$ . Ammonia molecules physically adsorbed on solid catalysts show bands at  $1\ 300 - 1\ 100\ \text{cm}^{-1}$  and  $1\ 640\ \text{cm}^{-1}$ . Outline of literature data on the band positions of adsorbed ammonia as well as of ammonia in gas and solid state are given in Table II.

Stepwise titration of the catalyst surface with increasing amount of ammonia makes possible to observe changes in the bands with increasing coverage of the surface with ammonia. Thus, when the  $\text{NiO/SiO}_2$  catalyst sample containing 70 wt.% NiO was titrated with ammonia, IR spectra (given in optical densities) showed distinct band at  $1\ 635\ \text{cm}^{-1}$  which was assigned to physically adsorbed ammonia. The area of this band and consequently, the amount of physically adsorbed ammonia increased with increasing amount of dosed ammonia following Langmuir adsorption isotherm (Fig. 2). This findings confirms correctness of the assignment of this band to the physically adsorbed ammonia.

TABLE II  
Frequencies of observed bands (in the  $1\ 700 - 1\ 200\ \text{cm}^{-1}$  region) for ammonia adsorbed on various oxides

Absorption bands, $\text{cm}^{-1}$	Assignment	Ref.
1 260 - 1 240	Coordinated ammonia $\delta_s$ (Lewis acid sites)	4
1 610	Coordinated ammonia $\delta_{as}$ (Lewis acid sites)	4
1 440 - 1 420	Brønsted acid sites $\delta_{as}\text{NH}_4^+$	4
1 480 - 1 465	Brønsted acid sites $\delta\text{NH}_4^+$	6
1 640	Bending modes of adsorbed ammonia	5
1 552 - 1 550	Si-NH <sub>2</sub>	6
1 556	Al-NH <sub>2</sub>	6
1 510 - 1 500	Al-NH <sub>2</sub>	7
1 650 - 1 510	-R-NH <sub>2</sub>	8
1 628	NH <sub>3</sub> (gas)	4
1 648	NH <sub>3</sub> (solid)	4

In order to ensure comparable conditions in the IR spectroscopy investigation of the effect of catalyst composition on its surface properties, further measurements were done with the same amount of adsorbed ammonia (1 ml  $\text{NH}_3$ ). In Fig. 3, IR spectra of ammonia adsorbed on various  $\text{NiO}/\text{SiO}_2$  catalysts are given. Curves 1 and 2 (catalysts with different NiO content) show that some other bands appeared apart from the band of physically adsorbed ammonia. A band at  $1420\text{ cm}^{-1}$  can be assigned to the protonated ammonia (Brønsted acid sites). Their amounts in the catalysts are not very high what is in accord with the literature<sup>4</sup>. The amount of Brønsted acid sites seems to increase with increasing amount of nickel oxide in the catalyst (compare curves 1 and 2). An impregnation of the  $\text{NiO}/\text{SiO}_2$  catalyst (sample 2) with a solution of  $\text{PdCl}_2$  changed the surface properties of the sample what is evident from IR spectrum of adsorbed ammonia. In this case, the amount of protonated ammonia (Brønsted acid sites) at  $1420\text{ cm}^{-1}$  decreased practically to zero and a slight shoulder of a new band in the region of  $1550 - 1480\text{ cm}^{-1}$  seemed to appear.

IR spectra of ammonia adsorbed on the catalytic system containing  $\text{TiO}_2$  differed a little from those we observed for the  $\text{NiO}/\text{SiO}_2$  system (Fig. 4). Pure  $\text{TiO}_2$  (anatase) did not show any substantial bands at all (curve 1) what indicates its low surface acidity.

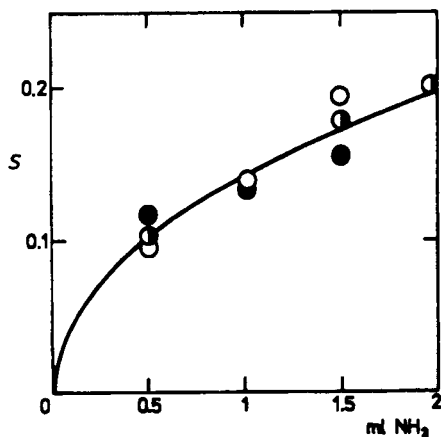


FIG. 2

The dependence of the amount  $S$  of physically adsorbed ammonia (on the  $\text{NiO}/\text{SiO}_2$  catalysts differing in the content of NiO, wt.% :  $\circ$  48,  $\bullet$  72,  $\bullet$  62 + 0.12 wt.% Pd) on the amount of dosed ammonia

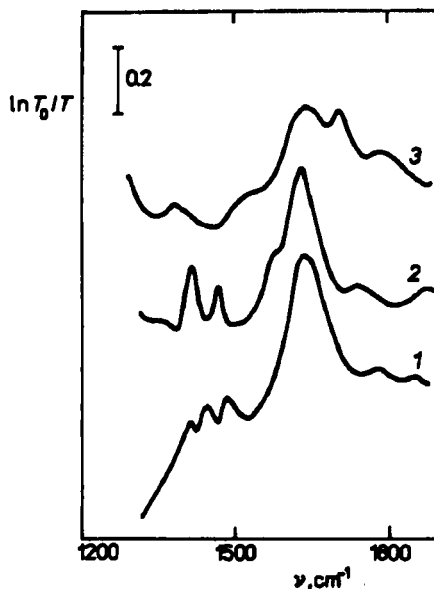


FIG. 3

IR spectra of ammonia adsorbed on the  $\text{NiO}/\text{SiO}_2$  catalysts containing various amount of NiO, wt.%: 1 48, 2 72, 3 62 + 0.12 wt.% Pd

Mixing the  $\text{TiO}_2$  with Ni precursor (resulting in the formation of the  $\text{NiO}/\text{TiO}_2$  catalyst with 66 wt.% NiO) did not increase the amount of Brønsted acid sites very much (Fig. 4, curve 2). Comparison of the curves 2 in Figs 3 and 4 indicates that the  $\text{NiO}/\text{SiO}_2$  catalyst contains a little more Brønsted acidic sites than the  $\text{NiO}/\text{TiO}_2$  system (see the  $1450 - 1410 \text{ cm}^{-1}$  region). Modification of this catalyst with Pd led, similarly as in the case of the  $\text{NiO}/\text{SiO}_2$  catalyst, to the disappearance of the band assigned to the protonated ammonia (Brønsted acid sites). With this catalyst, quite other situation in the IR spectrum of adsorbed ammonia appeared in the region of  $1700 - 1500 \text{ cm}^{-1}$ . IR spectrum revealed great and distinct new band at  $1550 \text{ cm}^{-1}$ . This band can be ascribed to the  $\text{NH}_2$  group combined with the  $\text{TiO}_2$ , Ni or Pd surface atoms. It is very well known from the literature<sup>6-8</sup> that characteristic absorption band of the  $\text{Me}-\text{NH}_2$  bond lies in the  $1556 - 1530 \text{ cm}^{-1}$  region (Table II). Very probably, the presence of Pd on the support surface activates ammonia and causes dissociation of it into the  $\text{NH}_2$  fragments which are subsequently adsorbed on the catalyst surface. Formation of  $\text{Pd}(\text{NH}_2)$  on the catalyst surface is also possible as its existence at 240 K was proved earlier<sup>9</sup>.

#### Catalytic Activity of the Catalysts

In this part of the work we wanted to find whether different surface properties of both the  $\text{Ni}/\text{SiO}_2$  and  $\text{NiO}/\text{TiO}_2$  catalysts examined by IR spectroscopy manifest themselves in various catalytic activity or selectivity in reductive amination of diethylene glycol.

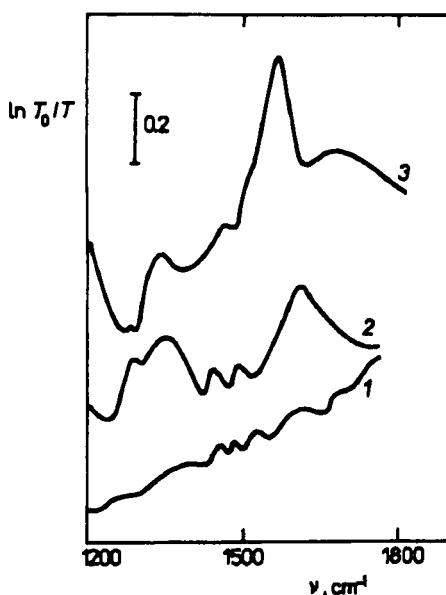


FIG. 4  
IR spectra of ammonia adsorbed on the samples containing  $\text{TiO}_2$ . 1  $\text{TiO}_2$ , 2 66 wt.%  $\text{NiO}/\text{TiO}_2$ , 3 63 wt.%  $\text{NiO} + 0.09 \text{ wt.}\% \text{ Pd}$

Catalytic activities of all samples are summarized in Table I. At 190 °C, the initial activity  $k$  ( $\text{l g}_{\text{cat}}^{-1} \text{h}^{-1}$ ) of the catalyst prepared on  $\text{SiO}_2$  was higher than that of prepared on  $\text{TiO}_2$ . The impregnation of both types of supported Ni catalysts with palladium chloride solution caused a decrease of activity, greater in case of the  $\text{SiO}_2$  supported catalyst. Similar results were also found for the reaction temperature of 210 °C.

Quite different behaviour of the  $\text{Ni/SiO}_2$  and  $\text{Ni/TiO}_2$  systems were observed in their catalytic stability (Table I). Whereas in case of the  $\text{NiO/SiO}_2$  catalyst the modification with palladium increased rate constant of deactivation, the  $\text{NiO/TiO}_2$  catalytic system showed, especially at 210 °C, lower tendency to deactivation and manifested the lowest value of the deactivation rate constant. The explanation can be connected with the IR spectra of the catalyst: In case of the  $\text{NiO/TiO}_2$  system, the presence of palladium enhances the formation of the  $\text{NH}_2$  fragment, which is detectable in the spectrum at  $1550 \text{ cm}^{-1}$ . Amination of the catalyst surface (formation of  $\text{NH}_2$  fragment) decreases the total acidity of the catalyst surface and the result of it is lower formation of high-molecular compounds on the catalyst surface by condensation of reaction intermediates.

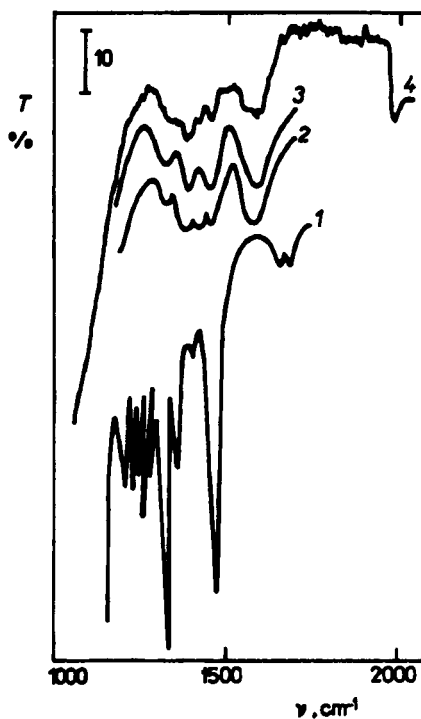


FIG. 5  
IR spectra: 1 morpholine, 2 the oxidic  $\text{NiO} + \text{Pd/TiO}_2$  catalyst, 3 morpholine adsorbed on the previous catalyst, 4 the catalyst with preadsorbed morpholine on which an excess of ammonia was adsorbed

*IR Spectra of Adsorbed Morpholine*

IR spectroscopy can be used for explanation of the way and strength of bond of the reactant to the catalyst surface. We used IR spectroscopy to obtain the answer what is relative strength of morpholine and ammonia bonds to the nickel catalyst surface as in the reaction mixture a great excess of ammonia to morpholine is present.

In the range of  $1750 - 1150 \text{ cm}^{-1}$ , morpholine exhibited typical bands at  $1330$  and  $1470 \text{ cm}^{-1}$  (Fig. 5, curve 1). When morpholine was adsorbed on the NiO + Pd/TiO<sub>2</sub> sample, the bands at  $1325$ ,  $1400$ ,  $1457$ , and  $1579 \text{ cm}^{-1}$  were observed (Fig. 5, curve 3). The comparison of this spectrum with the spectrum of the starting catalyst sample (curve 2) revealed that the intensity of the  $1457$  and  $1330 \text{ cm}^{-1}$  bands slightly increased, very probably, due to morpholine adsorption. An excess of ammonia dosed to the catalyst sample with preadsorbed morpholine did not cause any substantial change of the IR spectrum observed previously (Fig. 5, curve 4). From this follows that adsorbed morpholine is not replaced by ammonia at room temperature. As morpholine is weaker base than ammonia, its adsorption on the catalyst surface must be stronger than ammonia adsorption. Two-point adsorption of the morpholine molecule can be one of the possible explanation of the observed phenomenon.

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