REDUCTIVE AMINATION OF DIETHYLENE GLYCOL TO MORPHOLINE OVER SUPPORTED NICKEL CATALYSTS: ZEOLITES AS CATALYST ADMIXTURES*

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Received September 13, 1991
Accepted October 22, 1991

The effect of HZSM-5, H-silicalite and amorphous silica admixtures on the surface properties of nickel catalysts as well as on their activities, selectivities and stabilities in the reductive amination of diethylene glycol was studied. It was found that, in comparison with amorphous silica, zeolites do not positively affect the catalytic properties of nickel catalysts. In addition, the acidity of the zeolites, the dispersity of the nickel phase, changes in the chemical composition during the reaction and adsorption of the reaction components or intermediates on the surface and consequent blocking of the zeolite surface played a role.

Synthesis of morpholine by reductive amination of diethylene glycol (DEG) at atmospheric pressure and over supported nickel catalysts proceeds via a system of consecutive steps[1] (dehydrogenation, amination, condensation, hydrogenation) with 2-amino-2'-hydroxydiethyl ether as a reaction intermediate. Further reaction of diethylene glycol with morpholine can lead to the production of molecules with higher molecular weights which decrease the selectivity of the reaction, foul the catalyst surface and decrease its stability. Obviously, in order that the formation of morpholine be sufficiently fast and selective, the catalyst should increase the rates of both hydrogenation and acid catalyzed reactions. Of all the metals, nickel[2] is recommended most often for ensuring sufficiently fast dehydrogenation and hydrogenation reaction steps. Various supports have been recommended for enhancing the catalytic action of nickel: alumina[3], titania[4], chromia[5], zirconia[6]. These supports differ in their properties[7,8] and therefore, their influence on the properties of the resulting catalyst can vary, even when the recommended content of nickel in the catalyst for morpholine formation is rather high – $\geqq 50$ wt.% NiO.

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* Presented as a poster at the *International Symposium "Zeolite Chemistry and Catalysis", Prague, September 8–13, 1991.*

This work was carried out to evaluate the effect of two crystalline admixtures (supports) – ZSM-5 zeolites (designated as HZSM-5 and H-silicalite) with different Si/Al ratios and, therefore, the effect of the acidity on the activity, selectivity and stability of the resulting nickel catalyst. A nickel catalyst supported on amorphous silica together with an unsupported nickel phase and (in some cases) nickel on titania, alumina, zirconia and niobia were used for comparison.

EXPERIMENTAL

Two samples of ZSM-5 zeolites were supplied by the Research Institute for Oil and Hydrocarbon Gases, Bratislava, in their Na form. They were converted into the H form by treatment with 0·5M HNO_3. The residual amount of Na_2O was lower than 0·1 wt. % for both samples of zeolites. The Si/Al ratio of sample HZSM-5 was 13·6 while that of H-silicalite was 600. The silica used in this work was the commercial product of Tonaso Neštěmice (Czechoslovakia). Its chemical composition was as follows (in wt. %): SiO_2 97·4, Al_2O_3 0·74, CaO 0·89, Fe_2O_3 0·09, SO_3 0·88, Si/Al = 112.

Nickel catalysts in the oxidic form (about 70 wt.% NiO) were prepared by mixing the carrier in the form of a fine powder with a solution of basic nickel carbonate in aqueous ammonia. The same nickel solution was used for the preparation of unsupported nickel oxide. All the supported catalysts and the unsupported catalyst were dried at 120°C and calcined at 370°C for 3 h. Before reaction, the catalysts were reduced at 270°C for 2 h.

Surface area of the supports and the catalysts was determined with Digisorb 2600 Instrument (Micromeritics, U.S.A.) using BET method. Argon sorption capacities of the supports and catalysts were determined at −195°C and 13 kPa.

Temperature programmed desorption of ammonia in the range 20 to 400°C was used for characterization of acidity of the supports and the catalysts. The sample in an amount of 20 to 30 mg was dried in a helium stream with a linear heating rate of 15°C . min^{-1} up to 400°C at which it was kept till the signal did not decrease to zero (about 1 h). After cooling to ambient temperature, the catalyst surface was oversaturated with ammonia, then excess ammonia was removed, the dosing loop was calibrated and finally, the temperature-programmed desorption of ammonia was started under the following conditions: helium stream 50 ml min^{-1}, heating rate 15°C min^{-1} with temperature stop at temperature of 100, 200, 300 and 400°C. The amount of ammonia desorbed was evaluated from the areas of the peaks corresponding to the appropriate temperature ranges.

The IR spectra of the samples (supports, calcined and freshly reduced catalysts and catalysts after the reaction) were recorded on an Nicolet MX — 1E FT-IR spectrometer. Various functional groups including hydroxyls were detected on the basis of the IR spectra (i) of selfsupporting platelets 5—7 mg cm^{-2} in thickness and (ii) of the samples in KBr matrix (concentration 0·1 wt. %). IR spectroscopy was also employed for identification of strongly acidic hydroxyls and Lewis acidic sites using pyridine adsorption and desorption (for a detailed description see ref.[9]).

The catalytic activity of the catalysts in the reaction of diethylene glycol with ammonia was measured in an integral flow reactor with a fixed catalyst bed (molar ratio of reaction components DEG : NH_3 : H_2 = 1 : 5 : 10) at a reaction temperature of 190°C. The procedure is given in detail elsewhere[10]. The catalytic activity was evaluated from the dependences of the DEG content in the organic phase of the liquid reaction product on the reaction time. The pseudo first-order rate constants k, $\mathrm{l\,mol^{-1}\,h^{-1}\,kg_{cat}^{-1}}$, of the decrease in the concentration of diethylene glycol related to the unit catalyst mass were taken as a measure of the catalyst activity and the rate constants of catalyst deactivation k_d, $\mathrm{l\,h^{-1}\,mol^{-1}}$, were taken as a measure of the catalyst stability. Both values were evaluated[11] from the equation $\ln\ln(c_0/c) = \ln(k\tau) - k_d t$, where k is the rate constant of diethylene glycol disappearance, $\mathrm{l\,mol^{-1}\,h^{-1}\,kg_{cat}^{-1}}$; k_d is the rate constant of deactivation, $\mathrm{l\,h^{-1}\,mol^{-1}}$; t time, h; τ space velocity Wc_0F^{-1}; c_0 initial concentration of diethylene glycol $\mathrm{mol\,l^{-1}}$; c is the concentration of diethylene glycol in the organic phase of reaction product obtained at time t. Selectivity of the reaction was determined as the amount of morpholine in the organic phase of liquid reaction product at a diethylene glycol content of 20% in this product.

RESULTS AND DISCUSSION

Characterization of the Supports and the Catalysts

Considering the Si/Al ratio of the HZSM-5 zeolite to be equal to 13·6, the zeolite after dehydration at 400°C should contain 1·12 $\mathrm{mmol\,g^{-1}}$ of bridging OH groups. This value corresponds well to that determined by pyridine adsorption: 1·15 mmol . . $\mathrm{g^{-1}}$. In the IR spectrum, these hydroxyls are represented by a band at 3 610 $\mathrm{cm^{-1}}$ (Fig. 1). The number of Lewis acid sites determined by pyridine adsorption[9] is equal to 0·07 $\mathrm{mmol\,g^{-1}}$. The HZSM-5 sample also contains SiOH groups which vibrate at 3 745 $\mathrm{cm^{-1}}$ and AlOH groups vibrating at 3 800 $\mathrm{cm^{-1}}$.

The H-silicalite sample has a very high Si/Al ratio (600) so that the number of strongly acidic bridging OH groups calculated from the composition of the sample

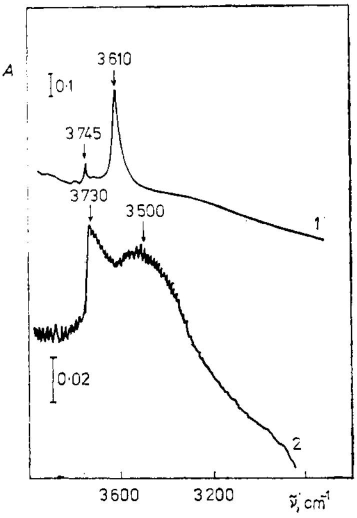

FIG. 1

IR spectra of pyridine adsorbed on the zeolites HZSM-5 (curve 1) and H-silicalite (curve 2) is equal to 0·025 mmol OH g^{-1}. The numbers of both proton donor sites and strong Al electron accepting sites (Lewis sites) were below the detection limit of the pyridine adsorption method. The IR spectrum of H-silicalite provides evidence for SiOH groups of various types (bands at 3 730 cm^{-1} and broad band at 3 500 cm^{-1}). It is evident from TPD measurements (Table I) that the highest total amount of desorbed ammonia and consequently, the highest amount of potentially active sites was found for the HZSM-5 sample – 1·476 mmol g^{-1}, three times less for silica – 0·568 and the least for the H-silicalite – 0·285 mmol g^{-1}. The values of the partial amounts of ammonia desorbed in chosen temperature ranges (see column A – D in Table I) show that ammonia is desorbed most easily from the H-silicalite. Silica exhibited the presence of sites from which ammonia was desorbed in the interval 300 – 400°C, although this is somewhat in contradiction with the data given in the literature[12]. In this case ammonia is most probably desorbed from Al cations which are present in the support material (see its composition in Experimental).

The acidity of the supports should affect the amount of ammonia desorbed from the oxidic nickel catalysts as they contain about 30 wt. % of this admixtures in the catalytic mass. It is evident from Table I that the total and partial amounts of ammonia desorbed from the catalysts differ from those determined for the supports. However, the total amount of ammonia desorbed is not equal to the sum of the ammonia portions corresponding to the relative amount of catalyst components. It thus follows that there is always some interaction between the supports and the nickel phase. For zeolites, the amount of ammonia desorbed is lower than the value expected, probably as a result of blocking of the zeolite surface by the nickel phase. On the other hand, the amount of ammonia desorbed from the NiO/SiO_2 catalyst is much greater than expected, probably because of higher dispersion of nickel in the catalyst or because of the formation of new crystallic phases.

Reduction of the nickel catalysts leads to a further decrease in the total amount of ammonia desorbed, but the differences are not great (Fig. 2). As a result of the reduction procedure, a substantial decrease in the amount of ammonia desorbed at high temperatures was observed for all the reduced catalysts (see column D in Table I).

Activity and Selectivity of the Catalysts

The results of the catalyst tests are given in Table II. It follows that the most active catalyst is Ni/SiO_2 with $k = 11{\cdot}8\ l\ mol^{-1}\ kg_{cat}\ h^{-1}$ and the least active is unsupported nickel and the Ni/ZrO_2 and Ni/Nb_2O_5 catalysts with $k \approx 0{\cdot}6 - 0{\cdot}9\ l\ .\ mol^{-1}\ kg_{cat}\ h^{-1}$. Catalysts containing zeolites exhibited a mean activity of about $4 - 7\ l\ mol^{-1}\ kg_{cat}\ h^{-1}$, similarly to catalysts containing alumina and titania. As the nickel surface area is the most important factor for achieving high catalyst activity in the amination of diethylene glycol[10], the catalysts with zeolites must have a lower nickel surface area than the Ni/SiO_2 catalyst. Part of nickel phase is probably located in the zeolite channels and thus it is less accessible to the reaction components. Moreover, the HZSM-5 zeolite with high amount of surface hydroxyls

TABLE I

The surface area and the amounts of ammonia desorbed from the support and nickel catalysts in various temperature ranges (A 20–100, B 100–200, C 200–300, D 300–400°C)

Support	S_{BET}	Amount of desorbed ammonia, mmol NH_3 g_{cat}^{-1}				
		total	A	B	C	D
HZSM-5	–	1·476	1·023	0·266	0·059	0·118
H-silicalite	–	0·285	0·256	0·018	0·011	0
SiO_2	94	0·568	0·469	0·087	0·004	0·008
		Oxidic catalysts				
NiO/HZSM-5	187	0·689	0·350	0·083	0·110	0·146
NiO/H-silicalite	204	0·114	0·068	0·012	0·002	0·032
NiO/SiO_2	199	0·564	0·305	0·136	0·056	0·067
NiO	89	0·166	0·058	0·035	0·011	0·062
		Reduced catalysts				
Ni/HZSM-5	–	0·572	0·440	0·073	0·034	0·025
Ni/H-silicalite	–	0·122	0·109	0·010	0·003	0
Ni/SiO_2	–	0·347	0·239	0·051	0·026	0·031
Ni	–	0·039	0·004	0·035	0	0

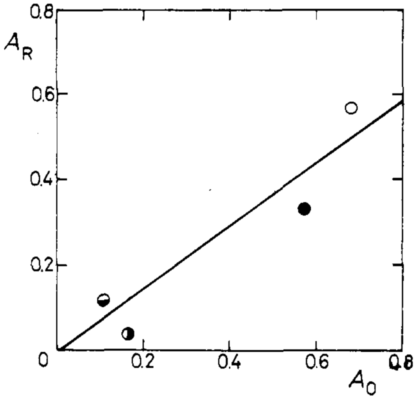

FIG. 2

Relation between the amounts of ammonia, mmol g_{cat}^{-1}, evolved by TPD from calcined (A_O) and reduced (A_R) nickel catalysts with different supports: ○ HZSM-5, ◒ H-silicalite, ● SiO_2, ◑ none probably stabilizes part of the nickel from the Ni solution in the form of nickel ions which are not as easily reducible as bulk NiO particles.

The acidity of the catalyst can play a role in the second step of the reaction, in cyclization of the reaction intermediate, 2-amino-2'-hydroxydiethyl ether, and thus can affect the reaction selectivity and catalyst stability. The data on catalyst selectivity (Table II) indicate that the catalysts with zeolite admixtures do not exhibit substantially higher selectivity for morpholine than the Ni/SiO_2 catalyst or pure nickel phase. In connection with the fact that the acidity of the nickel catalysts containing zeolites differs greatly and the selectivity does not, some other factors must play a role in the reductive amination of diethylene glycol in the presence of catalysts with zeolite admixtures. Their specific porous structure could explain this behaviour. As the selectivity of the reaction is closely connected with the further reactivity of morpholine, possible slower diffusion of reaction intermediates from the zeolite channels could lead to a prolongation of their stay in the interior of the catalyst, making consecutive reactions of reaction intermediates more probable and thus, leading to poorer catalyst selectivity.

Stability of the Catalysts

The rate constants of deactivation k_d of the catalysts examined (Table II) were found to be in the range 0·070–0·280 l mol^{-1} h^{-1}. The catalysts with zeolitic admixtures

TABLE II

Rate constant of diethylene glycol amination k (l mol^{-1} kg_{cat}^{-1} h^{-1}), rate constant of catalyst deactivation k_d (l h^{-1} mol^{-1}) and selectivity of the diethylene glycol reaction to morpholine S_M(%) at 20% content of diethylene glycol in organic phase of liquid reaction product. Reaction temperature 190°C, supported nickel catalysts reduced at 275°C

Catalyst	% Ni	k	k_d	s_M
Ni/HZSM-5	54	5·8	0·128	40
Ni/H-silicalite	56	6·9	0·223	51
Ni/SiO_2	57	11·8	0·066	63
Ni/Al_2O_3	52	4·7	0·281	73
Ni/TiO_2	54	2·8	0·070	41
Ni/ZrO_2	58	0·9	0·103	11 (x = 0·41)[a]
Ni/Nb_2O_5	52	1·0	0·109	13 (x = 0·57)[a]
Ni	100	0·6	0·193	4

[a] x Means conversion.

were deactivated faster than the Ni/SiO_2 catalyst and the unsupported nickel. This phenomenon cannot be simply explained. Comparison of the data in Tables I and II shows that a complex of factors plays a role in deactivation of the catalysts with zeolitic admixtures. The most probable factors have already been mentioned: the differences in the nickel dispersity, the changes in the chemical composition or the decrease in the catalyst porosity caused by fouling of the catalysts with high-molecular compounds. The decrease in the argon sorption capacity of the catalysts

TABLE III

Sorption capacity of fresh and deactivated catalysts, mmol Ar g^{-1}

Catalyst	Fresh	Deactivated	Reaction time, h
HZSM-5	5·3	–	–
H-silicalite	9·61	–	–
Ni/HZSM-5	2·08	1·38	28·5
Ni/silicalite	2·37	1·78	19·5
Ni/SiO_2	2·89	0·72	30

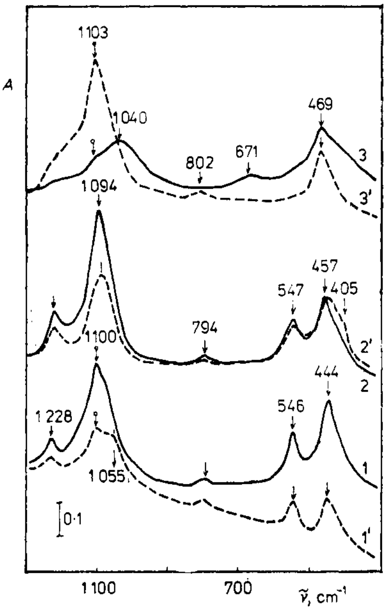

FIG. 3

IR spectra of fresh and deactivated Ni/H-silicalite (1, 1′), Ni/HZSM-5 (2, 2′), Ni/SiO_2 (3, 3′) catalysts. Numbers 1, 2, 3 denote the fresh catalysts, numbers 1′, 2′, 3′ denote the deactivated catalysts after the reaction (Table III) demonstrates that the fouling of the catalysts actually occurs.

The IR spectra of skeletal vibrations of the catalysts before and after the reaction confirm that some changes in the surface structure of the catalysts always occur during the reaction (Fig. 3). The change in the heights of the bands of zeolitic admixtures can be observed (1 220 – 1 230, 1 094 – 1 100, 794, 546, 457 – 444 cm^{-1}), as well as the appearance of new bands (405 cm^{-1} for the HZSM-5 catalyst, probably corresponding to NiO, and 1 055 cm^{-1} for the Ni/silicalite catalyst). Very striking changes were observed for the Ni/SiO_2 system, where a sharp band typical for SiO_2 (1 103 cm^{-1}) appeared after the reaction. Obviously, the effect is closely connected with the reduction of the NiO phase during the reaction. Additional reduction very likely prolongs the life of the NiO/SiO_2 catalyst in comparison with the stability of NiO/zeolites.

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Translated by the author (K.J.).