merization reaction and the amount of aluminum are observed on nickel-containing amorphous and crystalline aluminosilicates. In the NiO-mordenite catalyst, the same as in the NiO-amorphous aluminosilicate catalyst, the active center for C2H4 dimerization is probably formed via the involvement of Ni4+ and the acid sections.

CONCLUSIONS

When the amount of aluminum in a nickel-containing mordenite with variable degree of dealumination is increased the total acidity of the zeolite increases, the concentration of the electron-acceptor centers, recorded by the EPR method, passes through a maximum, while the degree of ethylene conversion varies within narrow limits.

LITERATURE CITED


N–NITROSATION OF SECONDARY AMINES


Nonacidic nitrosating agents (N2O4, NOCl, NOBF4) react with tertiary amines (trialkyamines, dialkylarylamines) and pyridine in aprotic solvents to give unstable complexes of types (I) and (II) [1-6]:

\[ [R_3N \cdot NO]^+ \cdot \cdot \cdot X^- \quad \text{(I)} \]

\[ \text{[}] N \cdot NO \text{[} X^- \quad \text{(II)} \]

\[ R \text{=} \text{Alk, Ar; } X \text{=} \text{NO}_2^- \text{, Cl}^- \text{, BF}_4^- \]

The literature data on the ability of complexes (I) and (II) to transfer the nitroso group to the N atom of secondary amines is scanty. Only one example of the N-nitrosation of amino acids, containing a secondary amino group, via the use of (II) \((X = BF_4^-)\) is known [7].

The N-nitrosation of secondary amines via the reaction of \(N_2O_4\) complexes with triethylamine (Ia) and pyridine (IIa) (paths A and B, respectively) is described in the present paper:

\[ \text{NH} + [R_3N \cdot NO]^+ \cdot \cdot \cdot \text{NO}_2^- \quad \text{A} \quad \text{C} \quad \text{NH} + R_3N + N_2O_4 \]

\[ \text{R} \quad \text{R} \quad \text{R} \quad \text{R} \]

N–N–NO

The synthesized N-nitrosamines (III) and their yields are given in Table I. The physico-
chemical and spectral characteristics of the obtained (III) compounds agree with the litera-
ture data.

The (III) compounds were also obtained by treating secondary amines with N₂O₄ in the
presence of triethylamine (path C) or pyridine (path D). Also in this case, the N-nitrosation
most probably proceeds via the intermediate formation of complexes (Ia) and (IIa).

As can be seen from Table I, the nitrosation of secondary amines using (Ia) and (IIa)
made it possible to obtain nitrosamines (IIia-d) in high yields. Here (IIId) was obtained
previously by known methods [8, 9] in 3-14% yield.

**EXPERIMENTAL**

**General Method for N-Nitrosation of Secondary Amines Using Complexes (Ia) and (IIa)
(Methods A and B).** To a solution of 0.05 mole of triethylamine or pyridine in 10 ml of dry
CH₂Cl₂, at −60°C, in an inert gas stream, was added in drops a solution of 0.05 mole of N₂O₄
in 15 ml of CH₂Cl₂, followed by the addition of a solution of 0.05 mole of the secondary
amine in 10 ml of CH₂Cl₂ at the same temperature, after which the reaction mixture was al-
lowed to warm up to 20°C, recooled to 0°C, and 10 ml of water was added. The obtained product
was isolated and purified in conventional manner.

**General Method for N-Nitrosation of Secondary Amines with N₂O₄ in Presence of Tertiary
Amines or Pyridine (Methods C and D).** To a solution of 0.05 mole of secondary amine and 0.05
mole of triethylamine or pyridine in 15 ml of dry CH₂Cl₂, at −60°C, in an inert gas stream,
was added in drops a solution of 0.05 mole of N₂O₄ in 15 ml of CH₂Cl₂. Then the reaction
mass was allowed to warm up to 20°C, recooled to 0°C, and 10 ml of water was added. The ob-
tained product was isolated and purified in conventional manner.

**CONCLUSIONS**

A method was proposed for the N-nitrosation of secondary amines using N₂O₄ complexes in
combination with tertiary amines or pyridine.

**LITERATURE CITED**