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# Synthesis of Cyclohexylideneacetonitrile on Zeolites

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**Abstract**—Condensation of cyclohexanone with acetonitrile on zeolites with different carcass structures was studied. The highest yield of cyclohexylideneacetonitrile (80 wt %) at a 98% selectivity of the process was attained with NaX zeolite containing 0.5 wt % KOH. Factors responsible for different catalytic activities and selectivities of zeolites are discussed.

Cyclohexylideneacetonitrile (**I**) is used as an intermediate in synthesis of phenylacetonitrile whose derivatives show biological activity [1]. Condensation of carbonyl compounds is usually performed in the liquid phase in the presence of alkali metal amides [2, 3]. A disadvantage of this process is a poor (41%) yield of nitrile **I** and formation of a dimeric by-product. Compound **I** can also be prepared in the presence of a heterogeneous catalyst (35% KOH on $Al_2O_3$ support). The yield of the target product on this catalyst was 78%, and the process selectivity, 98% [1].

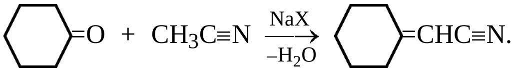
Recently, there has been a trend toward the use of zeolites in fine organic synthesis [4, 5]. The structural features of zeolites and the possibilities of varying in a wide range their molecular-sieve properties allow not only increase in the product yield but also solution of many environmental and service problems in industrial synthesis [6].

In this work we examined the possibility of using zeolites for condensation of cyclohexanone with acetonitrile. We expected that the Na forms of the zeolites, exhibiting the properties of solid bases, would be active in the reaction. Furthermore, we expected that their catalytic effect would be very selective, since these zeolites contain no strong acid centers responsible for occurrence of side reactions. Experiments were performed with samples having different carcass structures and different $SiO_2/Al_2O_3$ ratios.

Here we report the results of the experiments obtained under the following conditions: feed space velocity 0.2 $h^{-1}$, molar ratio cyclohexanone : acetonitrile 1 : 4, temperature 220–280°C. The major reaction product with all the zeolites is nitrile **I**. With respect to the activity, the zeolites can be ranked in the following order: NaX > NaY > NaM > NaTsVM > NaE. With increasing silicate ratio, determining the content of base centers in zeolites, the activity of the catalysts decreases. The zeolites NaX and NaY are characterized by a higher content of these centers than the high-silica zeolite NaTsVM. In the presence of NaX, the yield of **I** at 240°C was 71 wt %, at the reaction selectivity of 89%. With NaTsVM, the reaction under the same conditions was more selective, but the yield of the target product did not exceed 52 wt %. With increasing temperature to 280°C, the conversion of cyclohexanone increased, and the selectivity with respect to nitrile **I** decreased.

In zeolite systems, the chemical transformations occur to a large extent inside crystal cavities. Therefore, the steric factor should be taken into account when developing a selective catalyst. Namely, the critical size of reactant molecules should not exceed the size of the opening of large cavities in the zeolite structure. Our data suggest that the most suitable type of zeolites exhibiting the highest activity in condensation is faujasite in which the size of the zeolite channels is 8–10 Å. Erionite with the channel size of 3–5 Å is unsuitable for this process.

Reaction of cyclohexanone with acetonitrile on zeolite can be represented as follows:



Water released in the reaction is adsorbed by the zeolite. Therefore, the adsorption capacity of zeolite can also affect the yield of nitrile **I**. It is known [7] that the capacity depends on the free volume determined by the amount of water in the fully hydrated crystals. The intracrystalline volume filled with water can amount to 50% of the crystal volume. After dehydration of zeolite, the free volume is filled with molecules of other substances. Among the examined zeolites, faujasite NaX has the largest free volume (0.5 $cm^3\,cm^{-3}$).

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Catalytic activity of zeolites in condensation of cyclohexanone with acetonitrile

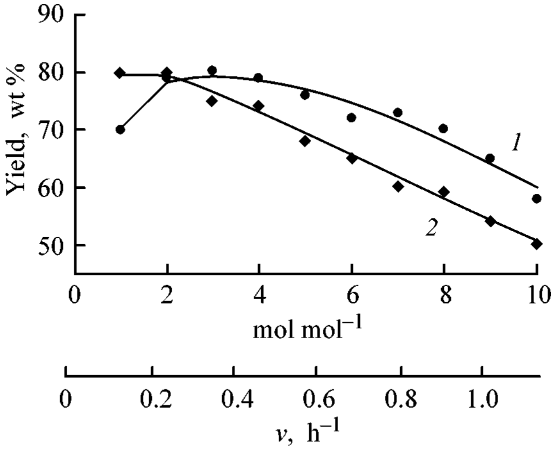
| Catalyst | $SiO_2/Al_2O_3$ | *T*, °C | Conversion of cyclohexanone, wt % | Yield, % | | Selectivity, % |
|---|---|---|---|---|---|---|
| | | | | compound **I** | other products | |
| NaX | 3.0 | 200 | 29 | 26 | 3 | 89 |
| | | 220 | 49 | 43 | 6 | 88 |
| | | 240 | 79 | 71 | 8 | 89 |
| | | 250 | 80 | 68 | 12 | 85 |
| | | 280 | 82 | 66 | 16 | 81 |
| NaY | 4.5 | 220 | 41 | 39 | 5 | 86 |
| | | 240 | 72 | 64 | 8 | 89 |
| | | 250 | 74 | 65 | 9 | 87 |
| NaE | 6.5 | 220 | 3 | 3 | 0.1 | 96 |
| | | 240 | 9 | 9 | 0.3 | 96 |
| | | 250 | 12 | 11 | 0.5 | 95 |
| NaM | 10.0 | 220 | 28 | 20 | 8 | 71 |
| | | 240 | 62 | 48 | 14 | 72 |
| | | 250 | 66 | 50 | 16 | 75 |
| NaTsVM | 33.0 | 220 | 24 | 22 | 1 | 96 |
| | | 240 | 52 | 50 | 2 | 96 |
| | | 250 | 58 | 51 | 3 | 94 |
| 0.1% KOH/NaX | 3.0 | 240 | 77 | 76 | 1 | 98 |
| 0.5% KOH/NaX | | 240 | 81 | 80 | 1 | 98 |
| 1.0% KOH/NaX | | 240 | 87 | 76 | 2 | 97 |

We suggested that replacement in NaX of the $Na^+$ ions (*r* 0.98 Å) by the larger $K^+$ ions (*r* 1.33 Å) would not only enhance the basicity but also affect the molecular-sieve properties and increase the process selectivity. The table shows that introduction of 0.5 wt % KOH into NaX increases the selectivity to 98%. With this catalyst we examined the influence of the reaction mixture composition and feed space velocity on the yield of nitrile **I**. The optimal reaction conditions were found: 240°C, molar ratio cyclohexanone : acetonitrile 1 : 3, feed space velocity 0.1–0.15 $h^{-1}$; under these conditions the yield of **I** was as high as 80 wt % (see figure). Further increase in the KOH content in the zeolite to 1 wt % is not appropriate, since the yield of the target product decreases. Apparently, at a KOH content higher than 0.5 wt % the effective size of the lattice openings decreases, which complicates adsorption of water.

Our results show that with NaX zeolite the condensation of cyclohexanone with acetonitrile can be performed without introducing large amounts of alkali into the catalyst, which will improve the industrial process for production of cyclohexylideneacetonitrile.

## EXPERIMENTAL

As catalysts we used zeolites NaX, NaY, NaM, NaE, and NaTsVM. Catalysts containing 0.1–1.0 wt% KOH/NaX were prepared by application of the calculated amounts of aqueous KOH solutions on NaX zeolite preliminarily calcined at 500°C. For example, 0.15 g of KOH was dissolved in 40 ml of $H_2O$, and a 15-g portion of the zeolite was impregnated with this solution. The mixture was evaporated with stirring under a drying lamp and then dried at 120°C. The catalyst of the composition 1 wt % KOH/NaX was thus obtained. To study the catalytic activity, zeolites



Yield of cyclohexylidineacetonitrile **I** as a function of the (*1*) molar ratio cyclohexanone : acetonitrile and (*2*) feed space velocity *v*.

were pressed in pellets and then crushed to a grain size of 2–3 mm. Experiments were performed in a vertical flow-through catalytic unit. A quartz reactor 20 mm in diameter was charged with 10 ml of the catalyst. Before the experiment, the catalyst sample was activated for 2 h at 500°C in a nitrogen flow. A 22.3-g portion of a mixture consisting of 9.9 g of cyclohexanone and 12.4 g of acetonitrile, placed in a dosing unit, was fed from the top by gravity at a space velocity of 0.15 $h^{-1}$ at atmospheric pressure. The reaction temperature was 240°C. In the course of the experiment, samples were taken for analysis at 30-min intervals. The experiment was performed for 4 h. The results obtained after catalyst operation for 2 h are listed in the table. The reaction products were fractionated in a vacuum. The fraction with bp 73–74°C (5 mm Hg), $n_D^{25}$ 1.4775, $d_4^{20}$ 0.9420 [8], containing 98% nitrile **I**, was isolated.

The purity of the product was determined by GLC with a Chrom-5 chromatograph (2 × 2000-mm glass column, stationary phase Apiezon L on Chromaton N-AW-DMCS, 0.16–0.20 mm).

The IR spectrum of **I** was taken with a Specord M-80 spectrophotometer in the range 400–4000 $cm^{-1}$. The spectrum contains the characteristic absorption bands of the C≡N bond at 2240 $cm^{-1}$ and of the C=CH bond at 1670 $cm^{-1}$.

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