Synthesis of propionitrile and acrylonitrile from acetonitrile and formaldehyde

A. L. Lapidus,[a] M. V. Tsapkina,[a] E. A. Kravtsova,[b] and E. G. Gorlov[b]*

[a]N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, 47 Leninsky prosp., 117913 Moscow, Russian Federation. Fax: +7 (095) 135 5328
[b]Institute of Fossil Fuel, 29 Leninsky prosp., 117910 Moscow, Russian Federation

We have found previously[1] that the reaction of acetonitrile with methanol in the presence of catalytic systems containing MgO-supported metal oxides results in the formation of propionitrile and acrylonitrile. We have suggested that formaldehyde formed from methanol is an intermediate product in this reaction. Based on this assumption, we have prepared nitriles from acetonitrile and formaldehyde for the first time.

Oxide catalysts M_nO_m/MgO (M = Na, K, Rb, and Cs) were prepared by impregnating MgO with solutions of the corresponding hydroxides and calcinating in an air flow at 400 °C. Acrylonitrile and propionitrile were formed in the presence of these catalysts at a volume velocity of 0.5 h^{-1}, T = 400—450 °C, and atmospheric pressure (Table 1). The products were analyzed by GLC. Formaldehyde was used as an aqueous solution (32 %).

At the optimum temperature of 425 °C, an increase in the basicity of the catalyst results in an increase in the overall yield of propionitrile and acrylonitrile from 3.2 to 5.3 % calculated from the amount of MeCN passed, with a maximum (6.9 %) obtained with the Rb_2O/MgO system. An increase in the basicity of the catalysts results in a decrease in the C_2H_3CN : EtCN molar ratio from 7.6 to 0.3. When formaldehyde is used, the C_2H_3CN : EtCN ratio is 2—9-fold higher than that obtained with methanol.[1]

Table 1. Effect of the nature of M_nO_m/MgO catalysts on the yields of nitriles (T = 425 °C, MeCN : HCHO = 1 : 2 (mol/mol))

M	Yield calculated from MeCN passed (%)		C_2H_3CN/EtCN
	C_2H_3CN	EtCN	
Na	2.8	0.37	7.6
K	4.5	1.0	4.5
Rb	4.7	2.2	2.1
Cs	1.1	4.2	0.3

References

1. A. L. Lapidus, M. V. Tsapkina, E. A. Kravtsova, B. P. Tonkonogov, and O. P. Lykov, in *Dokl. VIII Mezhdunar. konf. po khimicheskim reaktivam* [*Proc. of the VIII Intern. Conf. on Chemical Reagents*], Moscow, 1995, 157 (in Russian).

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