Synthesis of nitriles from acetonitrile and methanol in the presence of oxide catalysts

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The promoting effect of potassium included in Cr/MgO catalysts for the synthesis of nitriles from acetonitrile and methanol was found. The 5% Cr—0.5% K/MgO catalyst exhibited the highest activity in the synthesis of nitriles.

Key words: nitriles, acrylonitrile, propionitrile, acetonitrile.

It is known[1] that the reaction of acetonitrile with methanol in the presence of Cs_2CO_3/NaY as a catalyst results in formation of propionitrile. Earlier, we have shown that acrylonitrile (**1**) and propionitrile (**2**) can be synthesized from MeCN and MeOH in the presence of catalytic systems containing oxides of alkaline metals.[2]

In the present work, the activity of catalysts Cr/MgO in the synthesis of **1** and **2** from MeCN and MeOH and the promoting action of potassium included in this catalyst were studied.

Experimental

Catalysts Cr_xO_y/MgO were prepared by impregnating MgO with aqueous $Cr(NO_3)_3$ solutions. The precise formula of chromium oxide incorporated into the catalyst was not determined, and only the chromium content converted to metal is given. The content of potassium was estimated analogously. Systems of 5% Cr—(0.5—1.5%) K/MgO were prepared by impregnating MgO with aqueous KOH and $Cr(NO_3)_3$ solutions. The catalysts were dried in air at 80 °C for 24 h and then heated in an air flow at 400 °C for 4 h.

Table 1. The influence of the Cr content in the catalyst on the nitrile yields

Content of Cr (wt.%)	*T* /°C	Yield (% converted to MeCN)			C_2H_3CN : EtCN
		C_2H_3CN	EtCN	PrCN	
—	425	2.5	1.9	—	1.3
1	400	2.4	1.2	—	2.0
3	450	5.7	4.6	—	1.2
5	450	6.2	5.6	—	1.1
8	450	5.9	5.2	0.6	1.0*
10	450	4.0	3.2	—	1.3

* The C_2H_3CN : (EtCN + PrCN) ratio.

Note. MeCN : MeOH = 1 : 2 (mol.); $\upsilon = 0.5\ h^{-1}$, Cr_xO_y/MgO.

Experiments were carried out at 400—500 °C, atmospheric pressure, volume velocity 0.5 h^{-1}, and molar ratio of MeCN to MeOH = 1 : 2.

Liquid products were analyzed by GLC on a Biokhrom-1 chromatograph with a Porapak Q column and He as the carrier gas. Temperature increase was programmed from 60 to 195 °C with a rate of 8 deg min^{-1}. MeCN, **1**, and **2** were identified by retention times of individual compounds and using a Finnigan MATINCOS-50 chromatomass-spectrometer with a capillary column filled with RSL-200 (30 m). The masses of characteristic molecular ions: 41 for MeCN, 53 for **1**, and 55 for **2**. Traces of CO, CO_2, H_2, and CH_4 were detected along with the liquid products.

Results and Discussion

It is known that chromium oxide catalysts are active in dehydrogenation processes and, in some cases, in hydrogenation as well.[3] We have shown these reactions proceed during the interaction of MeCN with MeOH catalyzed by Cr/MgO containing 1—10% of chromium (Table 1).

For the catalysts studied, at the optimal temperature (given in Table 1) of the synthesis, increasing the chromium content in the catalytic system by 5% elevates the overall yield of nitriles converted to the passed MeCN (from 3.6 to 11.8%), while a further increase by a value from 5 to 10% decreases it (from 11.8 to 7.2%). Thus, the maximum yield of compound **1** (6.2%) can be attained when a catalyst with 5% Cr is used.

The dependences of the yields of **1** and **2** on the reaction temperature in the presence of 5% Cr/MgO catalyst are given in Table 2. An increase in the reaction temperature involves an increase in the yield of compound **2** converted to the passed MeCN from 1.2 to 8.4%. The yield of **1** increases from 4.5 to 6.3% at 475 °C, then decreases to 2.5% at 500 °C. The simultaneous formation of butyronitrile (**3**) in a yield of 0.4% at

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Table 2. The influence of reaction temperature on the nitrile yields in the presence of a 5% Cr/MgO catalyst

T /°C	Yield (% converted to MeCN)			C_2H_3CN : EtCN
	C_2H_3CN	EtCN	PrCN	
400	4.5	1.2	—	3.8
425	5.1	2.5	—	2.0
450	6.2	5.6	—	1.1
475	6.3	7.2	—	0.9
500	2.5	8.4	0.4	0.3*

* The C_2H_3CN : (EtCN + PrCN) ratio.

Note. MeCN : MeOH = 1 : 2 (mol.); v = 0.5 h^{-1}, Cr_xO_y/MgO (5% Cr).

Table 3. The influence of the potassium content in the 5% Cr—K/MgO catalytic system on the yields of nitriles

K content (wt.%)	Yield (% converted to MeCN)		C_2H_3CN : EtCN
	C_2H_3CN	EtCN	
—	6.2	5.6	1.1
0.5	9.7	7.3	1.3
0.75	8.8	6.5	1.4
1.0	5.5	10.5	0.5
1.25	4.3	9.9	0.4
1.5	3.8	8.4	0.5

Note. MeCN : MeOH = 1 : 2 (mol.); v = 0.5 h^{-1}, 450 °C.

Table 4. The influence of reaction temperature on the nitrile yields in the presence of 5% Cr—0.5% K/MgO

T /°C	Yield (% converted to MeCN)		C_2H_3CN : EtCN
	C_2H_3CN	EtCN	
400	2.2	1.5	1.5
425	5.2	4.5	1.2
450	9.7	7.3	1.3
475	4.5	8.8	0.5
500	3.2	11.3	0.3

Note. MeCN : MeOH = 1 : 2 (mol.); v = 0.5 h^{-1}.

500 °C should be noted. Compound **1** was obtained in the maximum yield (6.2%) at 450 °C when the best combination of the overall yield (11.8%) of nitriles and the ratio of **1** to **2** (1.1) is observed.

The introduction of potassium into the chromo-alumina oxide systems promotes their catalytic action in dehydrogenation of paraffin hydrocarbons.[3] We assumed that the introduction of potassium into the chromo-magnesium catalytic oxide system also increases its dehydrogenative activity in our process because dehydrogenation is one of the stages.

The influence of potassium additives of 0.5—1.5 wt. % to the Cr/MgO system on the synthesis of nitriles was studied in the presence of a catalyst optimal with respect to the content of chromium (5%) and at an optimal reaction temperature (Table 3).

The introduction of 0.5% potassium into the Cr/MgO catalyst increases the overall yield of **1** and **2** up to 17%. A further increase in the potassium content (to 1%) increases, at first, the yield of compound **2** to 10.5% but then (1.5% K) decreases it to 8.4%. This is also accompanied by a decrease in both the yield of **1** (to 3.8%) and the overall yield of nitriles (to 12.2%) as well as the **1** : **2** ratio (to 0.5).

The influence of temperature on the activity of 5% Cr—(0.5—1.5%) K/MgO samples in the synthesis of the nitriles was studied. In the presence of a catalyst containing 0.5% K, the increase in temperature from 400 to 500 °C increases the yield of **2** converted to the passed MeCN from 1.5 to 11.3% and decreases the **1** : **2** ratio from 1.5 down to 0.3 (Table 4). In this temperature range, the yield of **1** increases at first to 9.7% (450 °C), then decreases to 3.2% (500 °C). The best combination of the catalytic activity (the yields of the nitriles were 9.7% (**1**) and 7.3% (**2**)) and the selectivity (the **1** : **2** ratio was 1.3) was observed at 450 °C. Similar dependences of the nitrile yield on temperature were obtained for all the Cr—K/MgO catalysts studied.

The introduction of oxides of alkaline metals exerts[4] an activating action on chromo-alumina catalysts involved in dehydrogenation. We demonstrated for the first time that the introduction of potassium similarly affects Cr/MgO catalysts in the synthesis of nitriles from MeCN and MeOH.

When comparing the results obtained for Cr catalysts with data concerning the synthesis of nitriles in the presence of catalytic systems studied earlier,[2] which contain metal oxides (Na_2O, K_2O, Rb_2O, Cs_2O) and are applied onto MgO, one can conclude that chromium-containing catalysts exhibited a higher activity. The overall yield of the nitriles at 450 °C was 10.3, 11.8, and 11.7% for samples containing 3, 5, and 8% Cr, respectively, thus increasing by a factor of two. In the presence of a K_2O/MgO catalyst, the overall yield of the nitriles amounted to 4.6%, while the **1** : **2** ratio was 0.8.

It should be noted that, on Cr—Mg catalysts, compound **1** is formed in an equal amount with **2** and the **1** : **2** ratio changes from 2 to 1, *i.e.*, the content of nitrile **1** in the reaction products increased considerably.

The introduction of potassium into chromo-magnesium oxide catalysts also exerts an activating action. The addition of even 0.5% K to a catalyst markedly increases the overall yield of the nitriles, which amounted to 11.8% for the 5% Cr—MgO system and 17.0% for the 5% Cr—0.5% K/MgO system.

One can assume that under conditions on oxides systems proposed by us MeOH can undergo dehydrogenation to give formaldehyde

$$\mathrm{MeOH} \longrightarrow \mathrm{CH_2O} + \mathrm{H_2}. \qquad (1)$$

A further interaction of the formaldehyde with MeCN leads to formation of **1**

$$\mathrm{MeCN} + \mathrm{CH_2O} \longrightarrow \underset{\mathbf{1}}{\mathrm{CH_2{=}CHCN}} + \mathrm{H_2O}. \qquad (2)$$

Earlier,[5] we demonstrated experimentally the possibility of reaction (2) on oxide systems.

Propionitrile (**2**) can be obtained either directly from MeCN and MeOH

$$\mathrm{MeCN + MeOH \longrightarrow \underset{\mathbf{2}}{EtCN} + H_2O}, \qquad (3a)$$

or by hydrogenating compound **1** formed at the stage (2) with hydrogen evolved in reaction (1)

$$\mathrm{\underset{\mathbf{1}}{CH_2{=}CHCN} + H_2 \longrightarrow \underset{\mathbf{2}}{EtCN}}. \qquad (3b)$$

Stages (3a) and (3b) call for experimental confirmation, though some information concerning the possible hydrogenation of the double bond on metal oxides has been already published.[6]

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Destruction reactions of some σ-derivatives of vanadium

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The interactions of $(Me_3SiCH_2)_4V$ and $(Me_3SiCH_2)_3V \cdot THF$ with cyclopentadiene have been studied. Me_4Si and Cp_2V were isolated. A scheme of the reactions was proposed which involves formation of unstable monocyclopentadienyl derivatives of vanadium.

Key words: cyclopentadiene, monocyclopentadienyl derivatives of vanadium.

At present, the reactivity of vanadium σ-derivatives of the types R_4V and R_3V ($R = CH_2Ph$, CH_2SiMe_3, C_6F_5, and MeS) has been little studied. The ability to cleave the M—C σ-bonds in the presence of compounds containing a mobile hydrogen is a common property for almost all σ-derivatives of transition metals. These reactions can be described by the general scheme

$$R_nM + nHX \longrightarrow nRH + MX_n.$$

The number of cleaved M—C σ-bonds depends on both the nature of the proton-active agent and the character of the σ-substituent.

Previously, we showed using the reaction of tetrabenzylvanadium with cyclopentadiene as an example that the V—C bond is cleaved to give dicyclopentadienylvanadium.[1] No formation of monocyclopentadienyl derivatives of vanadium was observed in this reaction.

In continuation of our investigations, we studied the interaction of tetrakis(trimethylsilylmethyl)vanadium and tris(trimethylsilylmethyl)vanadium tetrahydrofuranate with cyclopentadiene with different mole ratios of the starting components from 1 : 1 to 1 : 4. Complete disappearance of the vanadium(IV) ESR signal and the appearance of the ESR signal of dicyclopentadienyl derivative Cp_2V were observed as a result of the interac-

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