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Oxidation of cyclohexylamine by air to its oxime

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Abstract

The oxidation of cyclohexylamine was studied over tungsten, molybdenum and vanadium oxides containing catalysts supported on silica, γ-alumina or hydrotalcite in the temperature range 170°C–230°C. Depending on the catalyst and reaction conditions, the main products of the reaction are cyclohexanone oxime, cyclohexylidenecyclohexylamine or cyclohexanone. About 70% selectivity of cyclohexanone oxime formation at about 20% conversion of cyclohexylamine is obtained over tungsten catalysts. The activity of the tested catalysts usually passes through a maximum and, then, gradually decreases with time on stream. The deactivation of the catalyst is caused by the formation of tar products on the catalyst surface. The mechanism of oxidation involves formation of oxygen species on the catalyst surface which oxidizes cyclohexylamine.

Keywords: Cyclohexylamine; Cyclohexanone oxime; Cyclohexylidenecyclohexylamine; Cyclohexanone; Tungsten; Molybdenum; Silica; γ-Alumina

1. Introduction

Various oxidizing agents can oxidize cyclohexylamine to its oxime. However, hydrogen peroxide and molecular oxygen are environmentally friendly because in the case of their use, water and not inorganic salts or organic residues are disposed. The oxidation of cyclohexylamine with hydrogen peroxide in the presence of W, Mo or V catalysts and alkali metal salts of nitrilotriacetic acid or ethylenediaminetetraacetic acid is a two-step process [1–4]. In the first step, cyclohexylhydroxylamine is formed, and in the second step, it is oxidized to cyclohexanone oxime. The oxidation of cyclohexylhydroxylamine to oxime is 20–50 times faster than the oxidation of cyclohexylamine to cyclohexylhydroxylamine, which proceeds with the rate constant 0.1 h^{-1} and 2 h^{-1} at 5°C and 40°C, respectively. The activation energy of the former reaction is 56 kJ/mol [1,4]. Lebedev et al. [5] describes the oxidation of amines in the presence of ammonium molybdate or tungstate. The highest yield of cyclohexanone oxime (about 80%) was obtained at a temperature of 15°C–20°C with a combination of ammonium tungstate and Trilon B. Cyclohexanone, formed as a by-product of the reaction, acts as stabilizer of H_2O_2 [2].

The hydroperoxides of cumene, ethylbenzene and isobutane selectively oxidize cyclohexy-

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lamine to its oxime in the presence of V, Mo or Ti naphthenates [6,8], various V, Mo, Ti, Ta, Nb, Re or Se compounds [7], organic or inorganic compounds of Ti, e.g. tetrabutyl-, dibutyl-bis(2,6-di-*tert*-butyl-*p*-cresyl)- or tetra-*o*-cresyl-titanates [8]. Appropriate solvents for this reaction are *tert*-butanol or benzene. For example, with ethylbenzene, the hydroperoxide selectivity of cyclohexanone oxime formation is 74%–86% at a temperature of 90°C–98°C in benzene as solvent. The rate determining step is the same as in the case of oxidation with H_2O_2, i.e. the formation of cyclohexylhydroxylamine, which is rapidly oxidized to cyclohexanone oxime. With tetrabutyl-orthotitanate as catalyst, the reaction is second order and its activation energy is 97.6 kJ/mol [9].

Caro's acid oxidizes cyclohexylamine to nitrosocyclohexane and cyclohexanone oxime. The ratio of these compounds depends on pH. Cyclohexanone oxime is the main product in a neutral or weak alkali medium, but nitrosocyclohexane is preferred in weak acids. In strong acids, colored, oily by-products are formed. In a weak alkalic solution at 30°C, the yield of cyclohexanone oxime is 75%–80% and 85% with regards to hydroperoxide, and cyclohexylamine, respectively. [10–13].

The direct oxidation of cyclohexylamine by air over heterogeneous catalysts is a very attractive way of synthesizing cyclohexanone oxime. Unfortunately, the available literature devoted to this method is very scarce. Over Porasil A, cyclohexylamine was oxidized at 150°C with a mixture of oxygen and helium (20 vol.% of O_2) to cyclohexanone oxime with a selectivity of 60% [14,15].

The presence of WO_3 on silica or γ-alumina supports has a positive effect on cyclohexanone oxime formation. Over the WO_3/γ-alumina catalysts, the oxidation of cyclohexylamine by molecular oxygen at 159°C gives cyclohexanone oxime a selectivity of 54% at 28% conversion [16]. Over the MoO_3/γ-alumina catalyst, the selectivity reaches 64% at a 33% conversion of amine [17].

The aim of our work was to study the selective oxidation of cyclohexylamine by air over various metal oxide catalysts, preferably WO_3 supported on silica, γ-alumina or hydrotalcites.

2. Experimental

2.1. Catalyst preparation

Catalysts were prepared by a slurry impregnation method. Metal oxides were mixed with deionized water and then an appropriate amount of support (particle size 0.3–0.6 mm) was added. Under stirring, water was slowly evaporated at 80°C and the slurry dried at 120°C for 15 h, calcined at 400°C, 500°C or 600°C for 1.5 h with a heating rate of 120°C/h. Silica (407 m^2/g) and alumina (227 m^2/g) used as supports were commercial products. Hydrotalcite was prepared by the co-precipitation method. To the mixture of aqueous solution of Mg and Al nitrates (ratio of Mg/Al = 7:3), a mixture of aqueous solution of KOH and K_2CO_3 was added at constant $pH = 10 \pm 0.5$. The resulting slurry was crystallized at 75°C at vigorous stirring for 18 h, filtered, washed with water and dried at 70°C. After drying, the solid was pelletized, crushed and sieved to a particle size fraction of 0.3–0.6 mm.

2.2. Catalyst characterization

The temperature programmed reduction of the catalyst was performed in pure hydrogen in a conventional apparatus with a thermal conductivity detector. The heating rate of a catalyst, which contained about 25 mg of reducible metal oxides, was 10°C/min in a temperature range from 20°C to 650°C. Then, the process proceeded isothermally until the reduction of catalyst was finished. The flow rate of hydrogen was 30 cm^3/min. The composition of effluent gases from the TPR apparatus was checked by a Quadrex 200 mass spectrometer (Leybold).

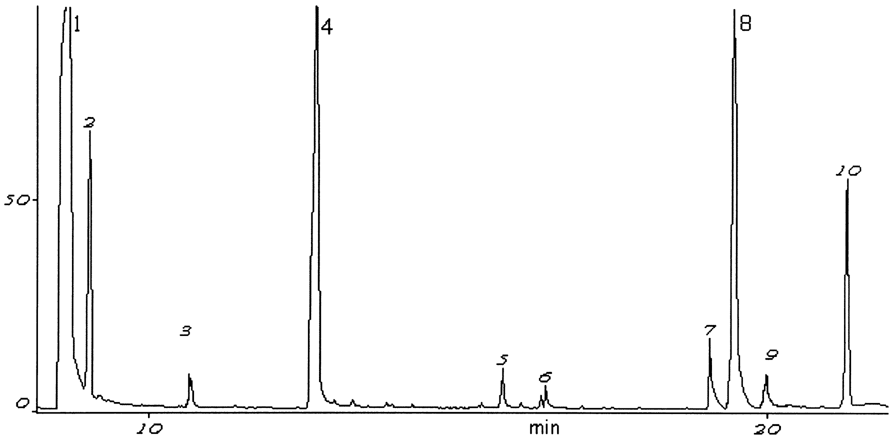

Fig. 1. Chromatogram of the reaction products.

No.	Compound	No.	Compound
1	Cyclohexylamine	6	Cyclohexylacetamide
2	Cyclohexanone	7	Dicyclohexylamine
3	Impurity in cyclohexylamine	8	Cyclohexylidenecyclohexylamine
4	Cyclohexanone oxime	9	Unknown product
5	Cyclohexylformamide	10	Cyclohexylaniline

The specific surface area of the supports was measured at -196°C using the Pulse Chemisorb 2700 apparatus (Micromeritics) with nitrogen as an adsorbed gas.

2.3. Oxidation of cyclohexylamine

The catalysts were tested in a tubular steel reactor with i.d. 8.4 mm containing 2 g of catalyst. Cyclohexylamine was oxidized by air at atmospheric pressure, in the temperature range 150°C–230°C, at a space velocity of amine 0.5–1 h^{-1}, and a flow rate of air 1–1.5 dm^3/h. The reaction products were analyzed by gas–liquid chromatography (Chrompack 9000) with FID using a glass column packed with 10% Carbowax 6000 + 2.5% KOH on Chromatone NAW DMCS (0.125–0.16 mm). 1-Octanol was used as an internal standard and methanol for the dilution of samples. The reaction products were identified by the GC/MS method using a GCMS-QP5000 apparatus (Shimadzu). This apparatus was equipped with a capillary column HP-1 (50 m $\times 0.2$ mm $\times 0.33$ μm). The flow rate of the carrier gas (He) was 1 cm^3/min. A typical chromatogram of a reaction mixture is given in Fig. 1.

3. Results and discussion

Experimental results show that the oxidation of cyclohexylamine to cyclohexanone oxime by molecular oxygen is not a typical heterogeneous redox reaction. An untypical feature is that this reaction is catalyzed by SiO_2 and γ-Al_2O_3, which are not common redox catalysts [17]. In addition, the activity of almost all tested catalysts increases in the first 2–8 h of time on stream and after reaching the maximum, it decreases. For the catalyst preparation we have chosen SiO_2, γ-Al_2O_3 and hydrotalcite, which have different acid–base properties. However, all these supports contain surface OH groups, which can adsorb cyclohexylamine. Armor et al. [17] found that classical oxidation catalysts are not selective for the oxidation of cyclohexylamine to its oxime. Strong acids (e.g. aluminosilicates), bases (MgO) and α-Al_2O_3 are also inactive for this oxidation.

Table 1
Oxidation of cyclohexylamine over various supports. Space velocity, 0.5 h^{-1}; air, 24 cm^3/min; temperature, 181°C

Time on stream (h)	Conversion of CHA (%)			Selectivity of CHO (%)		
	SiO_2^a	γ-$Al_2O_3^b$	HT^c	SiO_2	γ-Al_2O_3	HT
1	1.6	1.7	2.7	5.8	0	1.6
2	6.3	3.9	1.2	28.3	13.1	4.5
3	14.5	10.7	1.3	25.8	14.6	7.3
4	19.2	13.9	1.1	24.2	21.4	9.0
5	–	14.7	1.0	–	25.5	7.2
6	18.1	12.9	1.7	18.7	22.6	10.8

[a] Specific surface area, 407 m^2/g; particle size, 0.3–0.6 mm.
[b] 222 m^2/g, 0.3–0.6 mm.
[c] 175 m^2/g, 0.3–0.6 mm.
CHA — cyclohexylamine, CHO — cyclohexanone oxime.

As we have observed, the activity and the selectivity of SiO_2 and γ-Al_2O_3 depend on the method of their preparation. Over the hydrotalcites, a very low conversion and poor selectivity were achieved (Table 1).

Over the catalyst 10 wt.% MoO_3/SiO_2 prepared by impregnation, oxidation of cyclohexylamine gives, in the first 3 h of time on stream, only cyclohexanone and cyclohexylidenecyclohexylamine (Schiff base of cyclohexanone with cyclohexylamine). Cyclohexanone oxime formation, with the selectivity of about 20%, is observed at a longer time on stream (Table 2). The presence of MoO_3 on γ-Al_2O_3 increases the activity and the selectivity of γ-Al_2O_3, but MoO_3 supported on hydrotalcite has a comparable activity as the support. The selectivity of oxime formation is in the presence of MoO_3, higher than the hydrotalcite alone.

Table 2
Oxidation of cyclohexylamine over the catalyst containing 10% of MoO_3 on the support. Space velocity, 0.5 h^{-1}; air, 24 cm^3/min; reaction temperature, 181°C

Time on stream (h)	Conversion of CHA (%)			Selectivity of CHO (%)		
	SiO_2	γ-Al_2O_3	HT	SiO_2	γ-Al_2O_3	HT
1	9.8	5.5	1.9	0	20.1	41.8
3	14.1	23.6	1.6	0	35.7	40.8
5	12.1	18.7	0.5	20.8	45.1	42.1
7	15.5	–	0.5	16.3	–	46.5

Table 3
Oxidation of cyclohexylamine over the catalyst containing 10% of V_2O_5 on the support. Space velocity, 0.5 h^{-1}; air, 24 cm^3/min

Support	Reaction temperature (°C)	Time on stream (h)	Conversion of CHA (%)	Selectivity of CHO (%)
SiO_2	180	2	6.3	0
		4	23.2	0
		6	18.7	0
γ-Al_2O_3	165	2	9.2	0
		4	10.9	0
		6	18.2	0
	180^a	2	12.7	0
		4	15.5	0
		6	15.0	0

[a] Reaction with the same catalyst next day.
CHA — cyclohexylamine, CHO — cyclohexanone oxime

The presence of 10 wt.% V_2O_5 on SiO_2 or γ-Al_2O_3 has a small effect on the conversion of cyclohexylamine but totally suppresses the formation of cyclohexanone oxime (Table 3).

The selectivity of cyclohexylamine oxidation to its oxime is significantly higher on the above mentioned supports impregnated with WO_3 (Table 4). However, the effect of WO_3 on the conversion of cyclohexylamine is low. The highest selectivity of oxime formation (60%–70%) at about 9%–18% conversion of cyclohexylamine was obtained over the WO_3/γ-Al_2O_3 catalyst (Table 4). In comparison with

Table 4
Oxidation of cyclohexylamine over the catalyst containing 10% of WO_3 on the support. Space velocity, 0.5 h^{-1}; air, 24 cm^3/min; temperature, 180°C

Time on stream (h)	Conversion of CHA (%)			Selectivity of CHO (%)		
	SiO_2	γ-Al_2O_3	HT	SiO_2	γ-Al_2O_3	HT
1	8.8	19.1	2.9	36.6	60.3	33.8
2	14.5	18.7	–	39.5	67.9	–
3	20.6	15.7	2.8	32.1	65.9	48.8
4	–	13.4	–	–	71.3	–
5	16.2	11.0	3.3	40.5	70.8	49.5
6	–	9.0	–	–	74.7	–
7	–	6.4	–	–	69.8	–
8^a	–	5.6	–	–	66.0	–
9	–	3.6	–	–	63.4	–
10	–	3.4	–	–	62.0	–
11	–	3.0	–	–	66.0	–

[a] Reaction with the same catalyst next day.

γ-Al_2O_3 alone, it is an almost three times higher increase of selectivity. However, after 8–10 h of time on stream, this catalyst is strongly deactivated. By the analysis of deactivated catalysts, the formation of tar products on the catalyst surface was confirmed. After flushing the deactivated catalyst with alcohol, a part of the deposit is dissolved and the activity of the catalyst is renewed. However, the washed catalyst never reaches the original activity.

In order to prolong the lifetime of the catalyst by stripping the by-products from its surface, oxidation of cyclohexylamine was carried out in the presence of a solvent or water vapor. The results summarized in Table 5 show that in the presence of solvent, the lifetime of the catalysts is obviously at least twice longer than in their absence. Especially in the presence of isopropanol, the selectivity of oxidation to cyclohexanone oxime is in the first period of reaction, more than 80% at about 13% conversion. These results indicate that lower boiling by-products are probably stripped from the catalyst surface. Higher boiling products, however, remain on the surface of the catalyst and block its active sites.

The presence of water in the reaction system not only strips lower molecular products from the catalyst surface but probably also decomposes tar products by hydrolysis. As it follows from the data in Table 6, by increasing the concentration of water, the selectivity of cyclohexylamine oxidation to its oxime decreases. However, the lifetime of the catalyst is significantly longer (up to 6 days). The increase of the reaction temperature in the range 170°C–190°C has practically no effect on the conversion of cyclohexylamine. At higher temperatures, the catalyst is very rapidly deactivated by tar products and the formation of cyclohexanone oxime cannot be increased by increasing temperature.

In order to get a better insight into the mechanism of the reaction, some experiments were carried out at standard reaction conditions in nitrogen atmosphere. First, the catalyst was heated several hours in air, and after a short flushing the reactor with nitrogen, cyclohexylamine in nitrogen stream was injected into the reactor. After 7 h of passing cyclohexylamine over the 10% WO_3/SiO_2 catalyst, 0.61 mol of cyclohexanone oxime, 0.15 mol of cyclohexanone and 0.04 mol of cyclohexylidenecyclohexylamine were formed per mole of WO_3 present in the catalyst. Over the 10% WO_3/γ-Al_2O_3 catalyst at the same conditions and after 5 h of time on stream, 0.5 mol of cyclohexylamine per mole of WO_3 reacted to cyclohexanone oxime (0.063 mol), cyclohexylidenecyclohexylamine (0.072 mol), dicyclohexylamine (0.005 mol), cyclohexanone (0.135 mol)

Table 5
Oxidation of cyclohexylamine over 10% WO_3/γ-Al_2O_3 in the presence of a solvent (20 wt.%). Space velocity, 0.5 h^{-1}; air, 24 cm^3/min; temperature, 180°C

Time on stream (h)	Conversion of CHA (%)				Selectivity of CHO (%)			
	Dioxane	MeOH	*i*-PrOH	*n*-Hexanol	Dioxane	MeOH	*i*-PrOH	*n*-Hexanol
1	13.3	5.9	11.8	14.1	31.0	48.2	28.0	31.1
2	14.0	19.4	15.6	14.8	64.2	52.0	41.4	46.2
3	13.1	19.0	13.4	12.9	68.3	67.0	52.8	59.0
4	–	18.1	13.8	14.4	–	69.6	66.5	63.9
5	17.0	11.0	15.6	14.8	61.8	–	66.9	66.2
6	17.6	–	–	16.3	–	–	–	56.8
7	–	–	15.4	–	–	–	64.0	–
9[a]	14.1	15.0	–	12.9	56.9	64.0	–	55.6
11	–	–	–	7.8	–	–	–	70.8
13	–	–	–	9.4	–	–	–	66.0
16	–	–	–	8.9	–	–	–	58.7

[a] Reaction with the same catalyst next day.

Table 6
Oxidation of cyclohexylamine over 10% $WO_3/\gamma\text{-}Al_2O_3$ in the presence of water. Space velocity, 0.5 h^{-1}; air, 24 cm^3/min

Water wt.%	Reaction temperature (°C)	Time on stream (h)	Conversion of CHA (%)	Selectivity of CHO (%)
5	170	2	7.2	59.5
		3	8.6	70.7
		5	12.5	59.6
	180	9[a]	10.3	70.2
		11	8.7	62.7
		13	10.4	57.8
10	170	2	7.7	37.6
		4	5.1	52.6
		6	7.7	51.5
	180	9[a]	8.0	53.6
		11	8.2	54.1
		13	7.1	53.1
20	170	2	7.4	34.0
		4	7.6	49.0
		6	8.0	48.2
	182	10[a]	12.6	43.3
		12	14.1	44.0
		16	15.5	46.3
	190	18[a]	10.3	49.4
		20	17.8	44.2
		22	14.9	46.8
		24	11.6	47.1
	210	26[a]	16.3	41.0
		28	14.1	42.2
		30	13.7	40.5
	220	34[a]	16.3	18.4
		36	10.3	19.7
		38	12.7	17.6
		40	10.1	10.0
	230	42[a]	7.1	11.7
		44	6.1	8.3
		48	5.6	7.3
30	170	1	5.9	6.5
		3	7.8	35.2
		5	10.6	31.8
	185	9[a]	14.0	49.4
		11	8.3	44.9
		13	9.0	46.5
	215	17[a]	17.5	36.3
		19	14.4	36.1
		21	13.8	35.9
		23	11.8	35.7

[a] Reaction with the same catalyst next day.

and benzene (0.137 mol). Whereas, before the reaction, 10% $WO_3/\gamma\text{-}Al_2O_3$ catalyst was flushed only with nitrogen and not with air after 5 h of passing cyclohexylamine over this catalyst at the same reaction conditions as in the previous experiment. Formation of cyclohexanone oxime and benzene was lower by one order of magnitude (0.004 and 0.012 mol per mole of WO_3, respectively). The amount of formed cyclohexanone and its Schiff base was nearly the same, but the amount of dicyclohexylamine was almost five times higher.

When the same catalyst was mixed with cyclohexylamine (0.5 g amine/g catalyst) in a sealed tube and heated for 20 min to 150°C under nitrogen atmosphere, after cooling and extraction of the reaction mixture with diethylether, the same compounds were found in the extract as in the previous gas-phase experiment. After reaction in nitrogen atmosphere, the catalyst retained the original color. It indicates that tungsten oxide was not reduced by cyclohexylamine during the experiment in nitrogen atmosphere. Hence, a very small decrease of the oxidation number of tungsten intensively changes the color of WO_3 [18].

Schiavello et al. [19] found that the amount of reversibly adsorbed oxygen on WO_3 practically does not depend on the temperature in the range 100°C–500°C. This is in agreement with our finding that during the heating of the 10% $WO_3/\gamma\text{-}Al_2O_3$ catalyst (previously saturated with oxygen) from 50°C–450°C, practically any desorption maximum of oxygen was observed. By the analysis of the effluent gas from the reactor by mass spectrometry, it was found out that in the nitrogen atmosphere at standard reaction temperature (180°C), oxygen was desorbed from the catalyst, but only very slowly. When a catalyst saturated with oxygen was placed into the reactor, and the reactor was flushed with nitrogen (150 ml/min, containing 0.02 vol.% of oxygen), the concentration of oxygen was 0.028 vol.%. After decreasing the flow rate of nitrogen to 15 ml/min, the concentration of oxygen increases to 0.125 vol.%. However, during the next 3 h this value decreases very slowly.

From the experiments made in nitrogen atmosphere, it follows that cyclohexylamine is probably oxidized to its oxime by adsorbed oxygen species and not by WO_3, because dur-

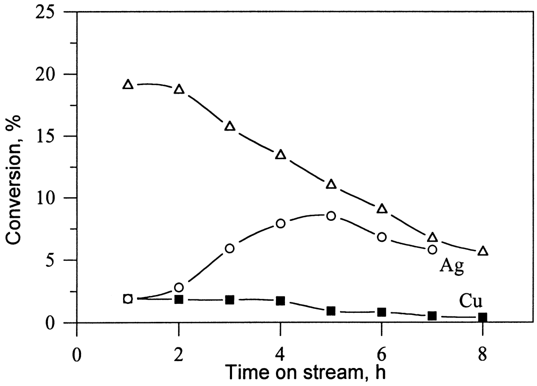

Fig. 2. Conversion of cyclohexylamine over $WO_3/\gamma\text{-}Al_2O_3$ catalyst (Δ) and doped with 1 mol% of Ag or Cu; standard reaction conditions.

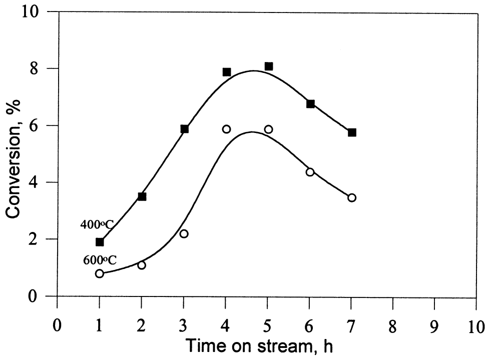

Fig. 4. Influence of temperature of catalyst calcination on the conversion of cyclohexylamine over $WO_3/\gamma\text{-}Al_2O_3$ catalyst doped with 1 mol% of Ag; standard reaction conditions.

ing the reaction, WO_3 is not reduced and, moreover, with decreasing amounts of adsorbed oxygen, the yield of cyclohexanone oxime markedly decreases. The amount of dicyclohexylamine in the reaction mixture is very low. However, the fact that its yield increases with decreasing amount of oxygen on the catalyst surface is very interesting. Since the formation of dicyclohexylamine is an acid catalyzed reaction, it suggests that at a higher concentration of oxygen species on the catalyst surface, these sites are probably occupied by oxygen.

Very interesting is the formation of benzene, which was not found in experiments carried out in the presence of oxygen. The amount of formed benzene very rapidly decreases with time on stream, i.e. by decreasing the amount of adsorbed oxygen. Thus, in the mechanism of oxidation of cyclohexylamine on the catalyst surface, the oxygen species plays an important role.

The blank experiment without catalyst (the reactor was filled with small glass balls) carried out in the absence of oxygen shows that depending on the reaction conditions, up to 30% of cyclohexanone oxime is converted to cyclohexanone or cyclohexylidenecyclohexylamine when it is passed through the reactor as a 10 wt.% solution in cyclohexylamine. Also interesting is the fact that under constant reaction conditions, the conversion of cyclohexanone oxime increases with time on stream. After several hours, the formation of a solid deposit was observed

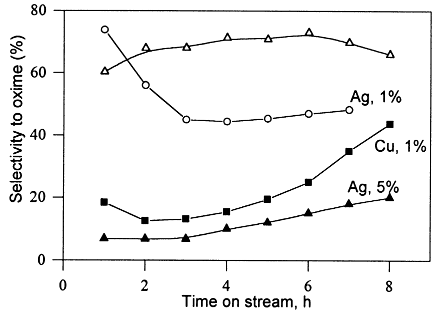

Fig. 3. Selectivity of cyclohexanone oxime formation over $WO_3/\gamma\text{-}Al_2O_3$ catalyst (Δ) and doped with Ag or Cu; standard reaction conditions.

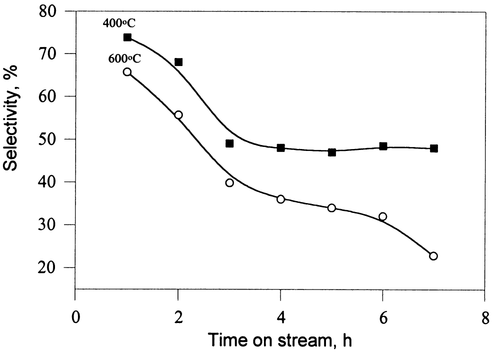

Fig. 5. Influence of temperature of calcination on the selectivity of cyclohexanone oxime formation over $WO_3/\gamma\text{-}Al_2O_3$ catalyst doped with 1 mol% of Ag; standard reaction conditions.

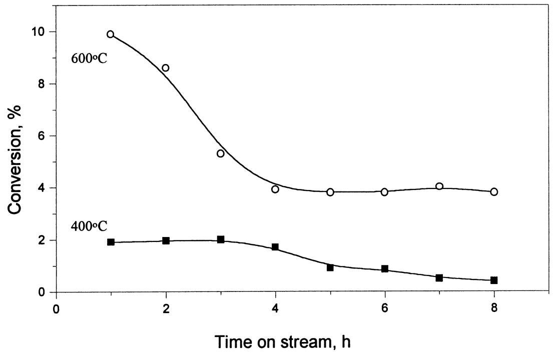

Fig. 6. Influence of temperature of calcination on the conversion of cyclohexylamine over $WO_3/\gamma\text{-}Al_2O_3$ catalyst doped with 1 mol% of Cu; standard reaction conditions.

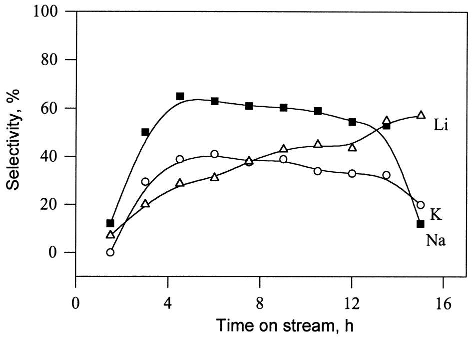

Fig. 8. Selectivity of cyclohexanone oxime formation over $WO_3/\gamma\text{-}Al_2O_3$ catalyst doped with 50 mol% of Li, Na or K; standard reaction conditions.

on the glass balls. This indicates that solid by-products also participate in the transformation of cyclohexanone oxime.

Because both the acidity and redox properties of the catalyst influence its activity and selectivity, some prepared tungsten catalysts were doped with alkali metals, Ag, Cu or Mo. As can be seen in Figs. 2 and 3, both the activity and the selectivity of the catalyst 10 wt.% $WO_3/\gamma\text{-}Al_2O_3$ doped with Ag or Cu decreased with increasing concentration of these metals in the catalyst. For example, 1 mol% of Cu (calculated on the content of WO_3) already significantly suppresses the oxidation of cyclohexylamine and formation of its oxime. Instead of oxime, cyclohexanone and its Schiff base are the main products.

The preferred calcination temperature of monometallic tungsten catalyst is about 600°C. At lower calcination temperatures, the activity of almost all prepared catalysts is lower. However, the influence of calcination temperature on the studied reaction is more complex, especially when the tungsten catalyst is doped with Ag or Cu. The conversion of cyclohexylamine is higher than the catalyst doped with silver and calcined at 400°C instead of 600°C. The calcination temperature has an opposite effect on the selectivity of oxidation to oxime, which, moreover, very rapidly decreases with time on stream. The tungsten catalyst doped with Cu has an opposite behavior (Figs. 4–6).

The presence of alkali metals in the catalyst also suppresses the formation of oxime, but for

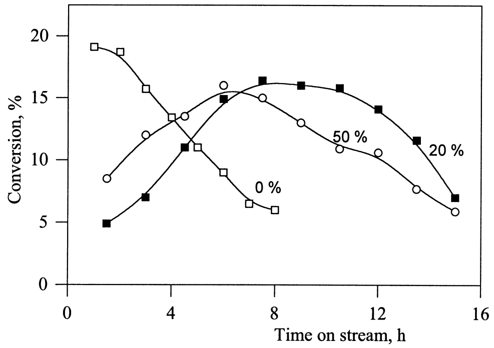

Fig. 7. Conversion of cyclohexylamine over $WO_3/\gamma\text{-}Al_2O_3$ catalyst doped with sodium; standard reaction conditions.

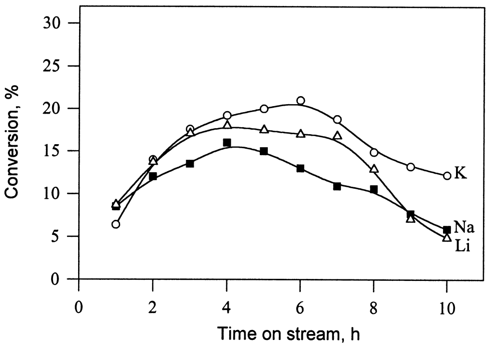

Fig. 9. Conversion of cyclohexylamine over $WO_3/\gamma\text{-}Al_2O_3$ catalyst doped with 50 mol% of Li, Na or K; standard reaction conditions.

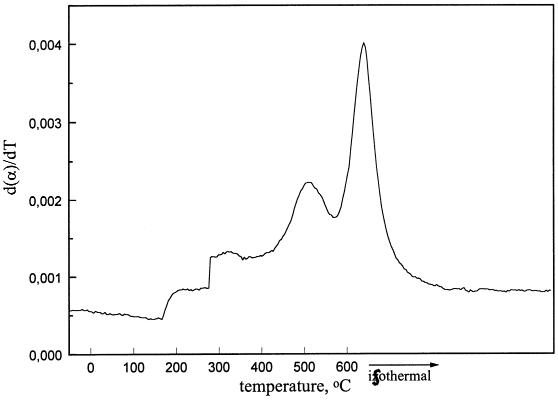

Fig. 10. TPR curve of 10 wt.% of WO_3/γ-Al_2O_3 catalyst doped with 1 mol% of Cu; catalyst, 50 mg; rise of temperature, 10°C/min from 20°C to 650°C; at 650°C isothermal for 30 min.

achieving the same influence as in the case of Ag and Cu, alkali metals have to be present in about 10-fold excess (Fig. 7). The catalysts doped with alkali metals are more stable against deactivation (the lifetime is nearly twice longer). The highest selectivity of cyclohexylamine oxidation to its oxime was observed over the tungsten catalyst doped with sodium (Figs. 8 and 9).

The TPR study of tungsten catalysts shows that, in agreement with the literature data [18], WO_3 is reduced with hydrogen at temperatures above 500°C. This temperature is independent of the support and the alkali metal used. It means that at temperatures of cyclohexylamine oxidation, WO_3 is not reduced. However, catalysts doped with Cu and Ag are already partially reduced at temperatures of around 200°C (Fig. 10). Reduction and oxidation of Cu or Ag ions probably prefer the formation of cyclohexanone. It is known that WO_3 is a semiconductor and the presence of alkali metals in the structure of the formed tungsten bronzes increases the amount of free electrons and the conductivity of bronzes [18]. The conductivity of WO_3 also increases in the presence of oxygen, amines or other donors of electrons after their adsorption on the surface of WO_3. Thus, electrons of alkali metals can lead to a decrease of adsorption of amines and oxygen on WO_3, and decrease the formation of cyclohexanone oxime.

On the basis of the above mentioned results, we suggest that the oxidation of cyclohexylamine to oxime is not a typical redox reaction. It is a process where a specific adsorption of oxygen and amine plays a key role.

4. Conclusions

The oxidation of cyclohexylamine over tungsten and molybdenum oxides containing catalysts supported on silica or γ-alumina gives mainly cyclohexanone oxime, cyclohexylidenecyclohexylamine or cyclohexanone in the temperature range 170°C–230°C. About 70% selectivity of cyclohexanone oxime formation at about 20% conversion of cyclohexylamine is obtained over the tungsten catalysts. The deactivation of the catalyst is caused by the formation of tar products on the catalyst surface. The mechanism of oxidation involves the formation of oxygen species on the catalyst surface which oxidizes cyclohexylamine. Oxidation of cyclohexylamine to oxime is not a typical redox reaction. It is a process where a specific adsorption of oxygen and amine plays a key role.

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