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Oxidation of amines over alumina based catalysts

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ABSTRACT

Amines were oxidized by molecular oxygen in the vapor phase at atmospheric pressure over alumina and silicotungstic acid/alumina catalysts. The study is focused on the influence of structure of amine and catalyst properties on the composition of the main reaction products and byproducts. Coating of γ-Al_2O_3 with silicotungstic acid or its semisalt can significantly enhance its catalytic activity in amine oxidation. The adsorption of amine on weak acidic sites of catalyst is essential for its oxidation to main reaction products. Cycloalkylamines are oxidized mainly to cyclic oximes (selectivity up to 64%) and Schiff bases of appropriate cycloalkanone and cycloalkylamine (selectivity up to 38%). Mainly nitriles (selectivity up to 55%) and appropriate Schiff bases (selectivity up to 54%) were observed in the oxidation products of primary alkylamines. Their molar ratio depends on the catalyst acidity and reaction conditions. 1,6-Hexanediamine is oxidized mainly to caprolactam (yield 48%) and other cyclic lactames and Schiff bases as well as to dinitrile (yield 13%).

1. Introduction

The oxidation of amines is a fundamental reaction for the synthesis of *o*-containing amine derivatives and both industry and academia have paid considerable attention to them. Depending on amine, catalytic system, reaction conditions and oxidizing agent different oxidation products are formed. Catalytic system for selective aerobic oxidation of amines to imines or nitriles involves copper(I) or copper(II) chloride as catalyst, toluene as solvent, and molecular sieve 3A as dehydrating agent under atmospheric pressure of oxygen [1]. Using this system variety of amines can be oxidized by molecular oxygen to corresponding nitriles (up to 97% yield; TON up to 60 from primary amines) or to imines (up to 90% yield; TON up to 45 from secondary amines) [1]. Lu and Xi oxidized primary aromatic amines by air to azo derivatives, anils, and/or quinone anils over Cu-chloride catalyst [2].

The molybdenum acetylide oxo–peroxo complex obtained in situ was used as an efficient catalyst for selective N-oxidation of primary amines to nitroso derivatives. Very high amine conversion (up to 100%) and selectivity for nitroso compounds (99%) have been obtained using 30% hydrogen peroxide as an oxidant. The oxo–peroxo Mo(VI) complex was also very active in the oxidation of various substituted primary aromatic amines with electron donating as well as electron withdrawing substituents on the aromatic ring [3].

Bifunctional gold–titania catalytic system was reported by Klitgaard et al. [4] to facilitate the oxidation of amines by molecular oxygen into amides with high selectivity. High catalytic activity of Ru/Al_2O_3 catalyst was observed at the oxidation of amines by molecular oxygen in liquid phase at atmospheric conditions [5].

Catalysis with heteropoly compounds has been widely studied in recent decades. For their acidic and redox properties they can be used as catalysts in gas–solid as well as in liquid–solid reactions. The oxidations of anilines with 30% H_2O_2 catalyzed by Preyssler catalysts ($H_{14}[NaP_5W_{30}O_{110}]$) in various solvents with different molar ratio of amine to oxidant, have been investigated by Bamoharram et al. [6]. It has been recognized that a major drawback of used heteropolyacid is its low surface area (1–10 m^2/g), separation problem from the reaction mixture and low thermal stability when applied at high temperature [7]. Although the

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thermal stability depends on the structure and composition of heteropolyacid [8], heteropolyacids can get high surface area and also thermal stability by supporting them onto suitable support.

Recently a facile, efficient and substrate-selective oxidation of benzylamine with NaClO as oxidant catalyzed by β-cyclodextrin (β-CD) was reported [9]. Primary amines, which could form host-guest complexes with β-cyclodextrin were oxidized to nitriles with excellent yields (98%) at ambient temperature (50 °C).

The oxidation of cyclohexylamine by H_2O_2 or molecular oxygen produces mainly cyclohexanone oxime and N-cyclohexylidene-cyclohexylamine, the condensation product of cyclohexanone and cyclohexylamine [10,11]. Cyclohexanone oxime is also formed by ammoxidation of cyclohexanone by H_2O_2 [12]. In both oxidations the catalytic system contains alumina or silica supported hetero-polymetalates of tungsten.

In the present work we have investigated vapor phase oxidation of amines by molecular oxygen (air) as an oxidizing agent at atmospheric pressure over alumina and silicotungstic acid containing catalysts. This process with cheap oxidizing agent without solvent and inorganic byproducts allows simple separation of the used heterogeneous catalyst and unused components of oxidizing agent after condensation of reaction products. The influence of silicotungstic acid (STA) and its sodium salt on catalytic activity and selectivity of alumina in the oxidation of various amines with molecular oxygen was also evaluated and compared.

2. Experimental

2.1. Catalysts preparation

All catalysts were made from γ-Al_2O_3 (Alfa Aesar, $S_{BET} = 211\ m^2\ g^{-1}$, $Vp = 0.6\ cm^3\ g^{-1}$, acidity = 0.7 mmol g^{-1}). 0.3 g of polyoxomatelate ($Na_nH_{4-n}[Si(W_3O_{10})_4]$, $n = 0$ for silicotungstic acid and $n = 2$ for its sodium salt, Lachema Brno) was dissolved in 100 ml of deionised water. Then 2 g of alumina was added and mixed for 1 h at ambient temperature. After impregnation all catalysts were dried at 110 °C for 8 h and calcined with a ramp 4 °C/min for 2 h, then kept at constant temperature 500 °C for 1 h.

2.2. Catalysts characterization

The BET surface areas and pore volumes were determined from nitrogen adsorption–desorption isotherm data obtained at −196 °C on a Micromeritics ASAP 2020 apparatus. The pore volumes were determined at relative pressure (p/p_0) of 0.99. The samples were degassed at $p = 2$ Pa, $T = 350$ °C for 12 h before measurement. The pore size distributions in samples were determined by BJH method, calculated assuming cylindrical pore model [13].

The total amount of acidic sites of the catalyst was determined by temperature programmed desorption of ammonia (NH_3-TPD). The eventually adsorbed compounds were desorbed or decomposed from the surface of all catalysts in He just before saturation by NH_3 with the same temperature program as during NH_3-TPD. Thus about 0.1 g of the sample was initially flushed with He (flow rate 24 $cm^3\ min^{-1}$) at temperature 600 °C for 1 h to eliminate adsorbed impurities. Then it was cooled to 100 °C under He and saturated with NH_3. After NH_3 exposure the sample was purged with He during 12 h at 100 °C to remove the not chemisorbed initial excess of NH_3. The sample with stabilized amount of ammonia was heated from 100 °C to 600 °C by a ramp 10 °C $min^{-1}$and kept at 600 °C for 1 h. To monitor the effluent content of ammonia thermal conductivity detector was employed. The measured values were recorded as a function of temperature.

Modified titration method [14] was also used to compare the acidity of solid catalyst. In a blank experiment 50 ml of acetonitrile was titrated with titrating agent (0.1 M ethylamine in acetonitrile) to record the baseline of titration. In normal titrations 1 g of catalyst sample and 0.05 ml of titrating agent were added to 50 ml of acetonitrile. After agitation for 0.5 h and stabilization of apparent pH the suspension was titrated with mentioned solution of ethylamine. The titrating agent was added regularly every 5 min in 0.5 ml doses and the pH was recorded just before adding next dose, i.e. at the end of time interval. The change in pH during last minute of time intervals was less than ±0.01 pH. Hannah HI223 pH meter and combined glass/SCE electrode were used for measuring pH. Before each titration the pH meter was adjusted by buffer solution (pH 7.04) and after adjustment the electrode was rinsed by distilled water.

Shimadzu IRAffinity-1 FT-IR equipment with Specac Golden Gate ATR accessory was used to obtain the FT-IR spectra of catalysts in a wave number range of 4000–600 cm^{-1}.

2.3. Catalytic test

All chemicals were purchased from commercial source (Fluka) and used without further purification.

The oxidation process of amines was performed in a fixed bed glass reactor with 1.6 cm inner diameter which contains 2 g of catalyst. The space velocity of amines was 0.7 h^{-1}. The gas leaving the reactor was passed through a cool trap in order to condense the formed products. The oxidation was carried out by air with increased content of oxygen (32 vol.%) at atmospheric pressure and at temperature range of 180–185 °C. The flow rate of air was 24 $cm^3\ min^{-1}$.

The reactions were monitored during first 6 h of time on stream of a given catalyst. The samples of the reaction mixture were withdrawn from the reactor periodically in 1 h intervals and were analyzed on Shimadzu GC 2014 equipped with FID and CP-SIL 5CB capillary column (25 m × 0.53 mm × 1.0 μm). The used temperature program was: 60 °C (3 min), then ramp 9 °C min^{-1} up to 240 °C. For quantitative analysis the method of the external standard was used.

The reaction products were identified on GC/MS QP5000 (Shimadzu) with EI and capillary column (HP-1, 50 m × 0.2 mm × 0.33 μm), carrier gas was helium (1 ml/min); temperature program: from 60 °C with ramp 9 °C min^{-1} up to 240 °C.

3. Results and discussion

3.1. Properties of modified alumina

The textural properties of commercial γ-Al_2O_3, alumina modified by 15 wt% of silicotungstic heteropolyacid or its sodium salt (catalysts: C, CH and CHN, respectively) are shown in Table 1. The surface area, pore volume and pore diameter of the calcined alumina are found to be 211 $m^2\ g^{-1}$, 84 Å and 0.6 $cm^3\ g^{-1}$, respectively. After loading of 15 wt% of heteropolyacid (HPA) on the surface of alumina these properties moderately decrease. There is a further very mild decrease of mentioned properties after partial neutralization of silicotungstic acid by NaOH.

The pore size distribution curves of all catalysts are narrow, symmetric and centered around 4.1 nm (Fig. 1). From the mentioned results follows that the pores of alumina are not clogged by HPA or its Na salt. Moreover, the contribution of HPA to BET surface and pore volume is positive, because the content of alumina in alumina-supported HPA is reduced by 15 wt%, however, the BET surface and pore volume only by 5.7% and 6.7%, in the case of HPA salt by 7.5% and 10%, respectively.

Table 1
Textural properties and acidity of tested catalysts.

Catalyst	BET surface area ($m^2 g^{-1}$)	Pore diameter (Å)	Pore volume ($cm^3 g^{-1}$)	Amount of adsorbed NH_3 ($mmol\,g^{-1}$)
C	211	82	0.60	0.71
CH	199	84	0.56	1.18
CHN	195	70	0.54	0.75

TPD-NH_3 curves of tested catalysts are shown in Fig. 2 and the total amounts of chemisorbed ammonia (acidity of catalyst) derived from them are in Table 1. For commercial alumina three desorption peaks of ammonia centered at 223 °C, 355 °C and 551 °C were found. In the case of catalyst containing 15 wt% of HPA sodium salt one broad desorption peak of ammonia centered at 229 °C followed by a small peak at 600 °C was observed. The highest peaks were found in the case of alumina-supported HPA. The first peak is centered at 227 °C and the second broad one around 300 °C. In the TPD-NH_3 curves of tested catalysts the first desorption peak around 220 °C belongs to sites with the weakest acidity on the boundary of physisorbed and chemisorbed ammonia. HPA, supported on alumina increased the intensity of the first peak and of broad peak between 250 °C and 450 °C. Partial neutralization of HPA reduced this broad peak, which belongs to sites with mild acidity.

The dependence of pH on the amount of titrant (ethylamine) in the suspension of catalysts is shown in Fig. 3. In the blank titration the equilibrium between the hydrated surface of glass electrode and amount of ethylamine was checked and recorded as a dependence of apparent pH on the amount of added ethylamine to 50 ml of acetonitrile. Acetonitrile was chosen as a solvent, because solvents with active proton can react with ethylamine or surface of alumina. For example, at the presence of water gelatinous alumina is formed after addition of ethylamine at higher pH. Before each titration the used glass electrode was rinsed by distilled water for cleaning and rehydration of its surface. After addition of 1 g of a given catalyst increased acidity of the formed suspension (containing also 5 μmol of ethylamine in 50 ml of acetonitrile) was observed. The measured apparent pH decreased as a result of new protolytic equilibrium between acidic centers of catalyst, ethylamine and surface of glass electrode. In this initial step of the titration of catalysts C, CH and CHN apparent initial pH values equal to 7.7, 6.7 and 6.1, respectively, were measured. Thus the highest initial acidity was achieved by partially neutralized heteropolyacid. It is known, that in same partially neutralized HPA the acidic strength of protons can be higher as in HPA [7,15]. To get the same apparent pH value as in the blank titration at the presence of 5 μmol of ethylamine in 50 ml of acetonitrile (0.1 mmol(EA) dm^{-3}, app. pH 9.55) it was necessary to add to the suspension of catalyst C, CH and CHN 0.67 mmol, 1.6 mmol and 1.44 mmol of extra ethylamine, respectively. The first derivative of titration curves of catalyst shows maximum (equivalent point of titration) at pH around 10. The apparent pH 10 in the blank titration was achieved after addition of 0.2 mmol ethylamine (4 mmol(EA) dm^{-3}). To get the same pH in the titration of catalysts C, CH and CHN an extra ethylamine is necessary in the amount of 0.85 mmol, 2.95 mmol and 2.15 mmol, respectively. The above mentioned amounts of extra ethylamine may be interpreted as its adsorbed amount on the surface of 1 g of catalyst C, CH and CHN at concentration of free ethylamine 0.1 mmol dm^{-3} (apparent pH 9.55) or at 4 mmol dm^{-3} (apparent pH 10), respectively. The presence of sites with very low acidity (equivalent point around apparent pH 10) is the reason, why in the TPD-NH_3 experiment is not possible to distinguish between physisorbed and chemisorbed ammonia. The total amount of H^+ in catalyst CH and CHN originated from the used amount of HPA should be 0.2 mmol and 0.1 mmol, respectively. Because the differences between adsorbed amounts of ethylamine by catalyst C, CH and CHN are higher, HPA is decomposed on the surface of alumina to components with weaker acidity which can adsorb more ethylamine (have higher total acidity).

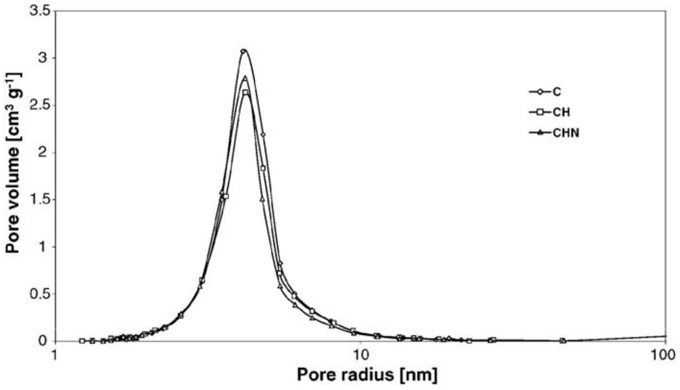


Fig. 1. Pore size distributions determined by BJH method: (C) γ-alumina (Alfa Aesar); (CH) γ-alumina-supported HPA (15 wt% $H_4[Si(W_3O_{10})_4]$); (CHN) γ-alumina-supported neutralized HPA (15 wt% $Na_2H_2[Si(W_3O_{10})_4]$).

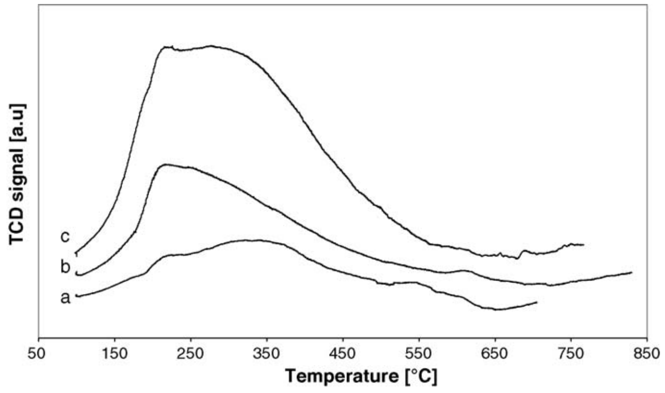


Fig. 2. NH_3-TPD profiles of γ-alumina: (a) without heteropolyacid; (b) γ-alumina-supported neutralized HPA (15 wt% $Na_2H_2[Si(W_3O_{10})_4]$); (c) γ-alumina-supported HPA (15 wt% $H_4[Si(W_3O_{10})_4]$).

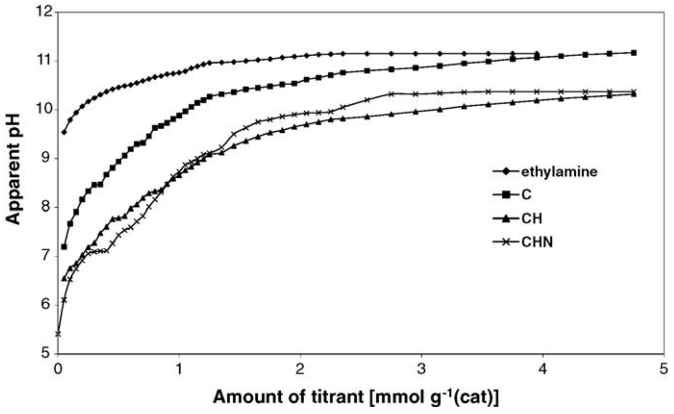


Fig. 3. Titration curves of catalysts by 0.1 M ethylamine in acetonitrile: (C) γ-alumina (Alfa Aesar); (CH) γ-alumina-supported HPA (15 wt% $H_4[Si(W_3O_{10})_4]$); (CHN) γ-alumina-supported neutralized HPA (15 wt% $Na_2H_2[Si(W_3O_{10})_4]$).

Fig. 4 shows the FT-IR spectra of non-calcined and calcined alumina-supported silicotungstic acid. The tungsten oxygen bonds

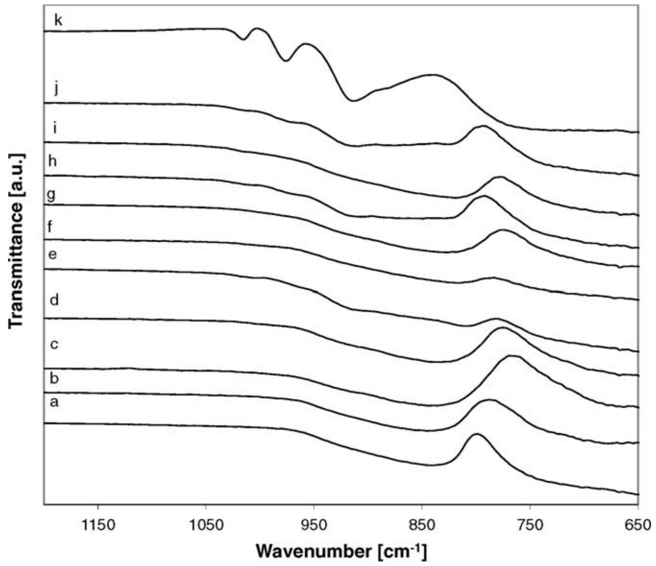


Fig. 4. FT-IR spectra of (a) γ-alumina (Alfa Aeser); other spectra: γ-alumina-supported HPA calcined at 500 °C, HPA content: (b) 5 wt%; (c) 15 wt%; (d) 23 wt%; (f) 33 wt%; (g) 40 wt%; (i) 50 wt%; spectra measured before calcination; HPA content: (e) 33 wt%; (h) 40 wt%; (j) 50 wt%; (k) HPA mechanically mixed with γ-alumina (1:2).

(W–O_e–W, W–O_c–W, W=O_t), and Si–O bond for pure heteropolyacid or mechanical mixture with alumina appear at 730, 906, 976 and 1016 cm^{-1}, respectively, which are the fingerprints of STA in the region between 500 and 1600 cm^{-1} [14–16]. These bands are recognizable only before calcination and at concentration of STA over 30% (lines e, h and j, Fig. 4). The intensity of peaks is very low in comparison with peaks in the mechanical mixture containing 33% of STA (line k, Fig. 4). According to Mizuno and Misono, alumina tends to decompose STA [15]. Thus, the bonds W–O–W, W=O and Si–O are reorganized, but part of silicotungstic acid at very high concentrations retains the Keggin structure before calcination. During calcination new bonds are formed between alumina and tungsten which are not optically active at the measured region of FT-IR (4000–600 cm^{-1}). The formed surface compounds significantly increased the amount of active sites with mild acidity. FT-IR spectra of original alumina and of alumina-supported STA with content of STA 5, 15 and 23 wt% were the same before and after calcination, i.e. without characteristic bands of STA.

3.2. Oxidation of cycloalkylamines

The oxidation of amines was carried out at temperature 180–185 °C, which was found as optimal in our previous works [10,11] for the oxidation of cyclohexylamine. The main products of the oxidation of cycloalkylamines (C_5, C_6 and C_8) were oximes and N-cycloalkylidene-cycloalkylamines (Table 2). The last compound is a condensation product (Schiff base) of cycloalkanones and cycloalkylamines. Between minor byproducts we found appropriate nitrocycloalkane, bis-cycloalkyl-amine and cycloalkene. On the surface of all used catalyst carbonaceous deposits were formed with initial dark yellow color, which was gradually changed by time on stream through dark brown up to black. The rate of deposits formation was increasing by increasing molecular weight of oxidized amine. Part of deposits was soluble in alcohols. All deposits could be removed in the presence of molecular oxygen at temperatures over 500 °C.

The FT-IR spectra of catalyst with mentioned deposits (Fig. 5) contain bands which are typical for alkyl- and cycloalkylamines. In both amines bands around 2920, 2850, 1450, 1260, 840 and 780 cm^{-1} are assigned to $–CH_2–$ groups. The IR spectrum of N-octylamine contains also bands assigned to $–CH_3$ group and the spectrum of cyclohexylamine bands assigned to –CH– group and ring deformation. The same bands nearly at the same wave numbers were found in the spectra of used catalysts, which beside mentioned bands and broad bands of alumina contain also unknown bands. In the region, where N–H bonds of amines absorb, the spectra of deposits and amines are different. In the spectra of both amines, bands around 3330, 3250, 1575 and 1035 cm^{-1} assigned to $–NH_2$ group and –C–N bond were found. The bands around 3300 cm^{-1} in the spectrum of catalyst used for cyclohexylamine oxidation are overlapped by a broad band assigned to the amine adsorbed on acidic centers by different acidity. This broad band in the spectrum of catalyst used for N-octylamine oxidation is superimposed by band with wave number 3298 cm^{-1}, which probably belong to secondary amine (for example, di-octylamine). We could not recognize differences in the FT-IR spectra of used alumina and used alumina-supported STA catalyst.

Table 2
Conversion of cycloalkylamines and selectivity of formation of appropriate oxime and Schiff base over γ-alumina: (C) without heteropolyacid (HPA); (CH) γ-alumina-supported HPA (15 wt% $H_4[Si(W_3O_{10})_4]$); (CHN) γ-alumina-supported neutralized HPA (15 wt% $Na_2H_2[Si(W_3O_{10})_4]$). *Reaction conditions*: $T = 180$ °C, atmospheric pressure, results at 2 h time on stream.

Amine	Catalyst	Conversion (%)	Selectivity (%)	
			Oxime	Schiff base
Cyclopentylamine	C	36	21	35
	CH	42	30	32
	CHN	54	37	38
Cyclohexylamine	C	21	54	30
	CH	26	64	20
	CHN	30	63	23
Cyclooctylamine	C	19	58	12
	CH	23	64	13

Next minor byproducts of studied oxidation are specific for oxidized cycloalkylamine. The oxidation of cyclopentylamine

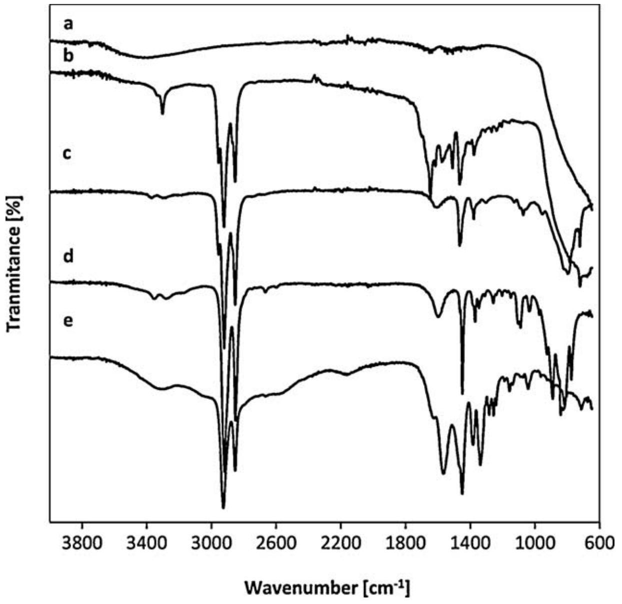
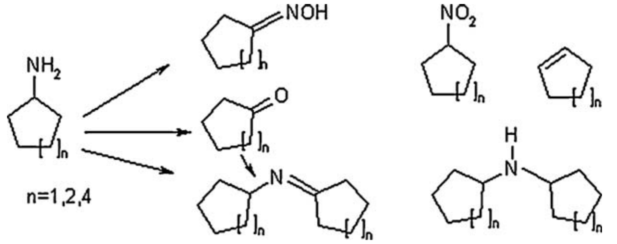


Fig. 5. FT-IR spectra of (a) γ-alumina (Alfa Aesar), (b) used γ-alumina (Alfa Aesar) from oxidation of N-octylamine, (c) pure N-octylamine, (d) pure cyclohexylamine and (e) used γ-alumina (Alfa Aesar) from oxidation of cyclohexylamine.



Scheme 1. Products of cyclopentylamine oxidation over catalyst C, CH and CHN.

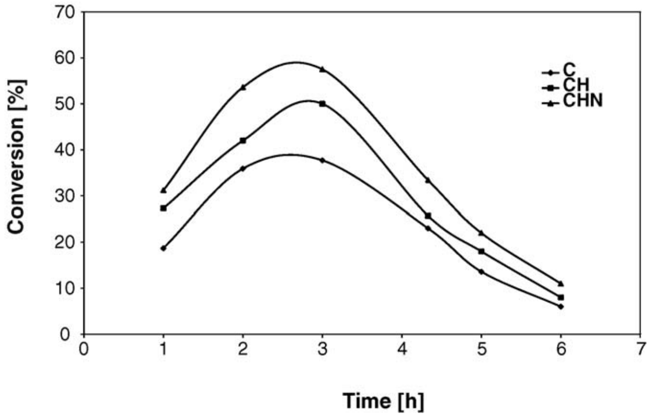


Fig. 6. Conversion of cyclopentylamine during its oxidation over γ-alumina: (C) without heteropolyacid; (CH) γ-alumina-supported HPA (15 wt% $H_4[Si(W_3O_{10})_4]$); (CHN) γ-alumina-supported neutralized HPA (15 wt% $Na_2H_2[Si(W_3O_{10})_4]$) [T = 180 °C at atmospheric pressure].

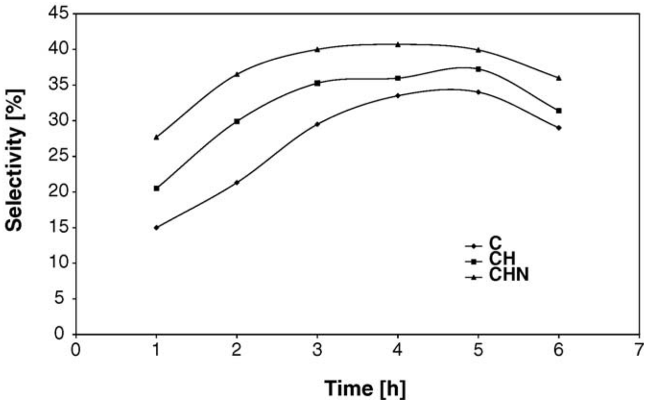


Fig. 7. Selectivity of cyclopentanone oxime formation during oxidation of cyclopentylamine over γ-alumina: (C) without heteropolyacid; (CH) γ-alumina-supported HPA (15 wt% $H_4[Si(W_3O_{10})_4]$); (CHN) γ-alumina-supported neutralized HPA (15 wt% $Na_2H_2[Si(W_3O_{10})_4]$) [T = 180 °C at atmospheric pressure].

produced a small amount of pyridine (up to 7 wt%). This product of ring isomerization and aromatization was not found in the oxidation products of other amines. Benzene and N-cyclohexylaniline were found in the oxidation product of cyclohexylamine (yields <0.5%, respectively, <2%), i.e. cyclohexene and N-cyclohexylidene-cyclohexylamine were partially dehydrogenated and aromatized. The driving force of formation of mentioned aromatic compounds is most probably the energy of aromatization. In the reaction products of cyclooctylamine we did not found products of

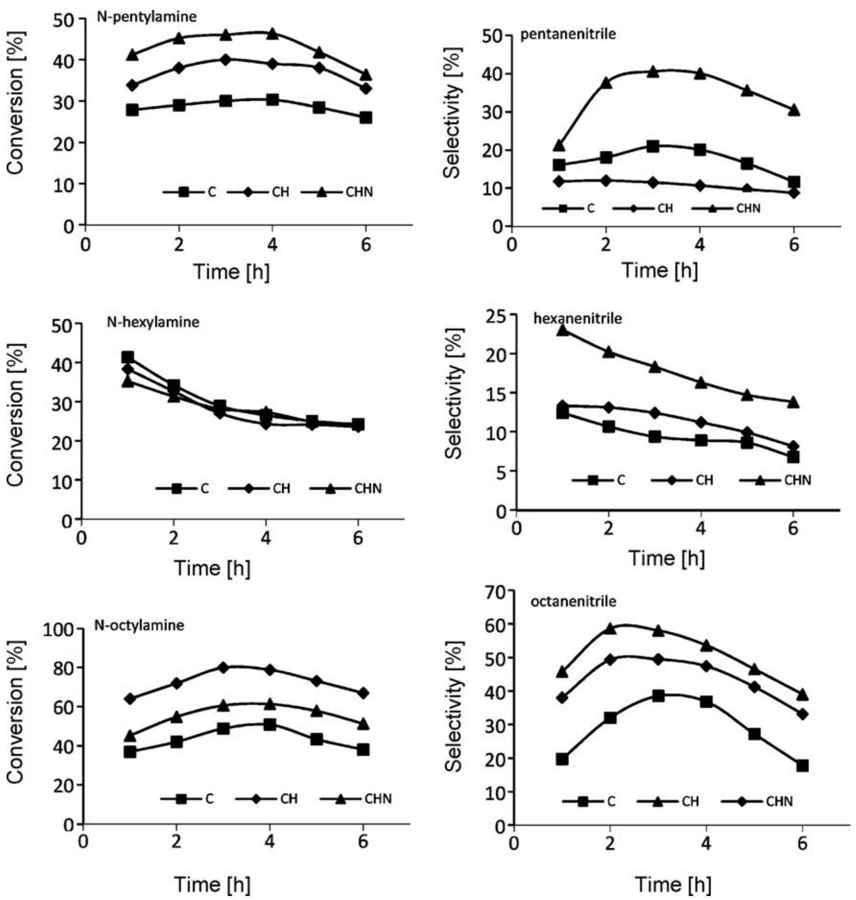


Fig. 8. Conversion of N-alkylamines and selectivity of formation of their main reaction products over γ-alumina (Alfa Aeser): (C) without heteropolyacid; (CH) γ-alumina-supported HPA (15 wt% $H_4[Si(W_3O_{10})_4]$); (CHN) γ-alumina-supported neutralized HPA (15 wt% $Na_2H_2[Si(W_3O_{10})_4]$) [T = 180 °C at atmospheric pressure].

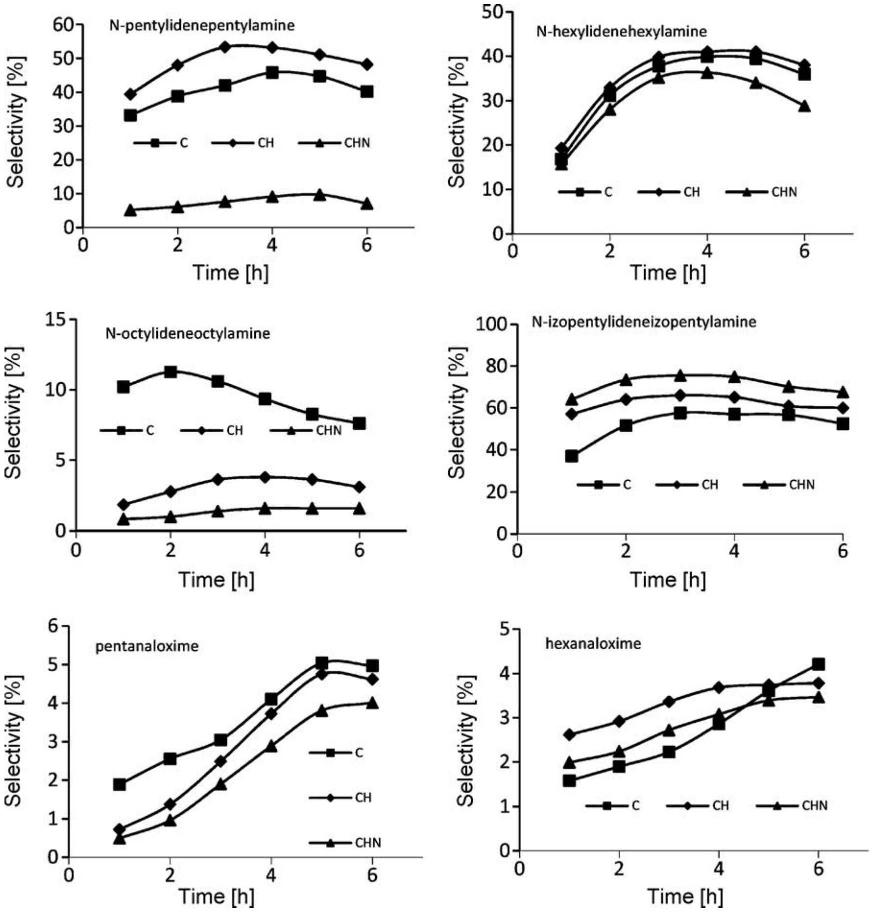


Fig. 9. Selectivity of formation of main products of oxidation of N-alkylamines and isopentylamine over γ-alumina (Alfa Aesar): (C) without heteropolyacid; (CH) γ-alumina-supported HPA (15 wt% $H_4[Si(W_3O_{10})_4]$); (CHN) γ-alumina-supported neutralized HPA (15 wt% $Na_2H_2[Si(W_3O_{10})_4]$) [$T = 180\,^{\circ}C$ at atmospheric pressure].

aromatization. On the other side, we found products of potential hydrogenation, for example, in the case of cyclohexylamine we found cyclohexanol [11]. In all cases we found bis-cycloalkylamine (yields <1%), which can be formed by hydrogenation of appropriate Schiff base or by alkylation of amine by cycloalkene (Scheme 1).

Generally the conversion of cycloalkylamines during first 2 h of time on stream was decreasing by increasing molecular weight. In the same direction the selectivity of oxime formation increased and the selectivity of Schiff base formation decreased (Table 2). After impregnation of alumina by HPA or its semisodiumsalt the conversion of cycloalkylamines and selectivity of oxime formation mostly increased or stayed on the same level within experimental error. Carbonaceous deposits formed during first 2–3 h of time on stream deactivate the catalyst and the observed conversions of cycloalkylamines after a maximum began to decrease by increasing time on stream (Figs. 6 and 7).

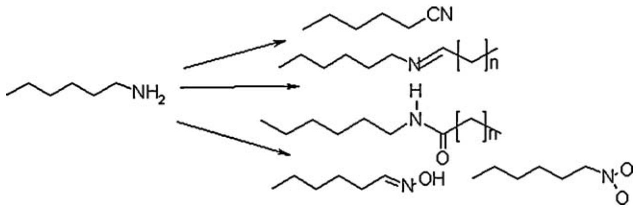
3.3. Oxidation of N-alkylamines

During oxidation of linear aliphatic amines (N-pentyl, N-hexyl, and N-octylamine) over catalysts C, CH and CHN in the gas phase the main oxidation products were nitriles (selectivity up to 55%) and Schiff bases (selectivity up to 56%, Figs. 8 and 9).

Oximes, aldehydes, nitro compounds and alkyl amides were also observed in the reaction products, as minor byproducts (selectivity <5%). In the reaction products besides dominating Schiff bases and amides with original length of alkyl chain, also series of Schiff bases and amides with shortened length of alkyl chain were found in low concentrations. The concentration of mentioned Schiff bases and amides gradually decreases by decreasing length of alkyl chain. However, during oxidation of N-octylamine almost the same amount of N-hexylideneoctylamine and N-octylideneoctylamine was formed. The selectivity of N-octylideneoctylamine was significantly lower in comparison with full length Schiff bases formed from N-pentyl-, isopentyl- and N-hexylamine (Fig. 9). The alkyl chains were shortened only in the part of molecules originated from the aldehydes and acids, i.e. the shortening of alkyl chain was a result of oxidative decomposition of aldehydes. In these cyclic reactions aldehyde is oxidized to acid. The acid is decarboxylated to alkyl radical with shortened alkyl chain, which is quickly oxidized by molecular oxygen to aldehyde (Scheme 2).

The influence of STA and its semisalt on the conversion of pentylamine is the same as in the case of cycloakylamines. STA and its semisalt have practically no influence on the conversion of hexylamine. In the case of octylamine STA significantly enhanced its conversion. The influence of semisalt was mild.

The formation of nitriles is preferred and the formation of Schiff bases was suppressed by semisalt of STA at all linear amines. The influence of STA on the formation of nitriles is not so clear. In the case of N-pentylamine had negative; in the case of N-hexyl- and N-octylamine had mostly positive effect. STA and its semisalt have positive effect on the formation of Schiff base in the case of isopentylamine.



Scheme 2. Products of N-hexylamine oxidation over catalyst C, CH and CHN.

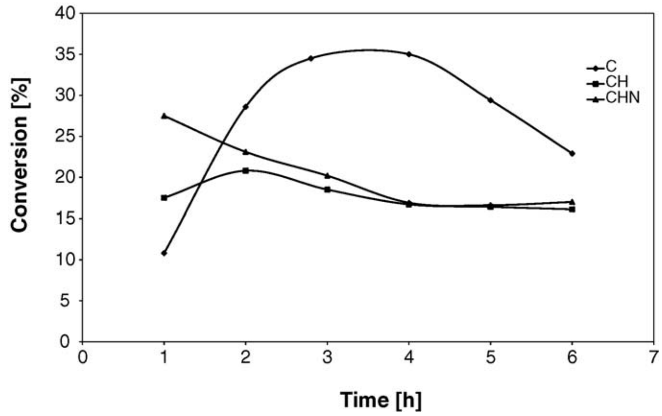


Fig. 10. Conversion of isopentylamine during its oxidation over γ-alumina (Alfa Aesar): (C) without heteropolyacid; (CH) γ-alumina-supported HPA (15 wt% $H_4[Si(W_3O_{10})_4]$); (CHN) γ-alumina-supported neutralized HPA (15 wt% $Na_2H_2[Si(W_3O_{10})_4]$) [T = 180 °C at atmospheric pressure].

Oxime was found only in the case of N-pentylamine and N-hexylamine on the levels up to 5 wt%. The influence of STA and its semisalt in this case is mostly in the range of experimental error.

3.4. Oxidation of isoalkylamines

The oxidation of isobutyl- and isopentylamine also produces high amount of Schiff base (selectivity up to 65%). In the reaction products N-isopentylformamide and N-isopentylacetamide were observed as a minor byproduct, too. As shown in Fig. 10, conversion of isopentylamine was the highest on alumina (maximum at 30%). Modification by STA and its semisalt had negative effect on the formation of Schiff base.

The isobutylamine was more resistant to the selective oxidation than isopentylamine. Reaction products contained only traces of nitriles and imines.

3.5. Oxidation of 1,6-hexanediamine

From the group of diamino-compounds we oxidized 1,6-hexanediamine. Specially, we studied the possibility of ε-caprolactam production in the gas phase. Klitgaard et al. [4] reported that ε-caprolactam is formed by oxidation of 1,6-hexanediamine by molecular oxygen in a liquid phase over gold-titania catalyst. For the reaction we used 1 M of 1,6-hexanediamine in methanol, which is liquid and we were able to oxidize it at the same conditions as other amines, i.e. at atmospheric pressure and at different temperatures (170–230 °C). The results of these experiments are shown in Figs. 11 and 12. It is seen that by increasing temperature the conversion of 1,6-hexanediamine increases of up to 85%, but the formation of byproducts also increases. The highest selectivity to ε-caprolactam (45%) was observed at lower temperatures (170–180 °C). Moreover, the same trend was observed in the case of the selectivity to adiponitrile, which is the main byproduct. At the beginning of the oxidation process the amount of adiponitrile is higher, however, by increasing of time on stream the selectivity to ε-caprolactam increases. After 6 h of time on stream the activity of catalyst decreased and the conversion reached only 10%. One of the reasons can be the enhancement of carbonaceous tar formation on the catalyst surface. Besides main reaction products (ε-caprolactam and hexanedinitrile), several minor reaction byproducts were found: butyrolactam, valerolactam, cyclic Schiff bases with 6, 5 and 4 carbon in the ring, pentanedinitrile, pyridine, tetrahydropyridine and 5-cyano-valeric acid methyl ester (methyl-5-cyanopentanoate).

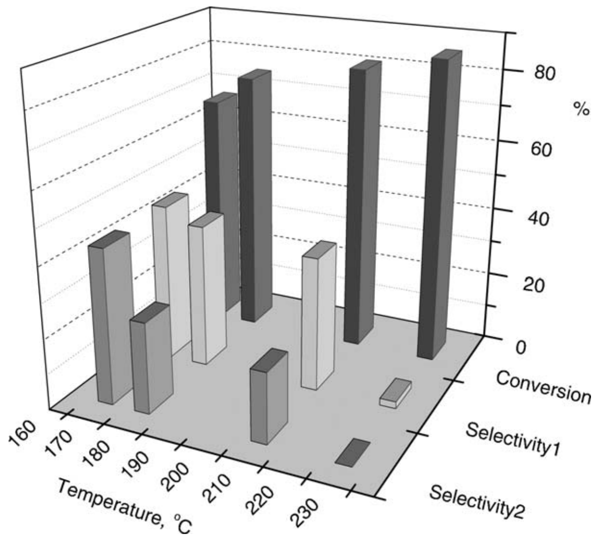


Fig. 11. Results of oxidation of 1,6-hexanediamine over γ-alumina at different temperatures: conversion of 1,6-hexanediamine, selectivity of (1) ε-caprolactam formation and (2) adiponitrile formation, respectively. *Reaction condition*: atmospheric pressure, results at 3 h time on stream.

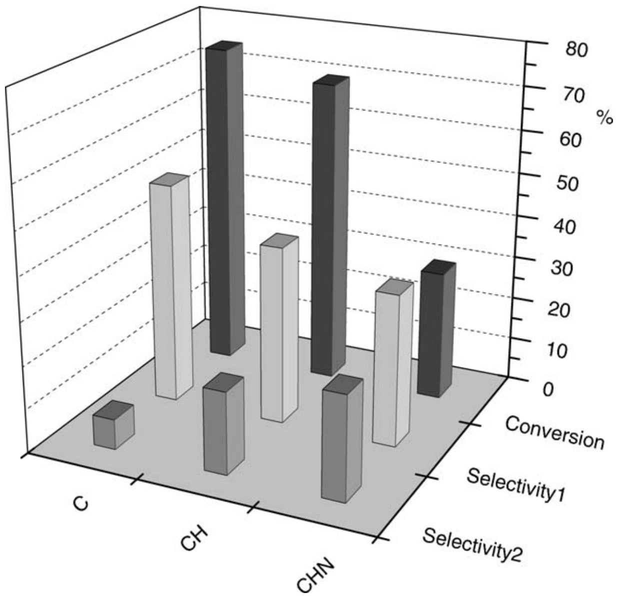
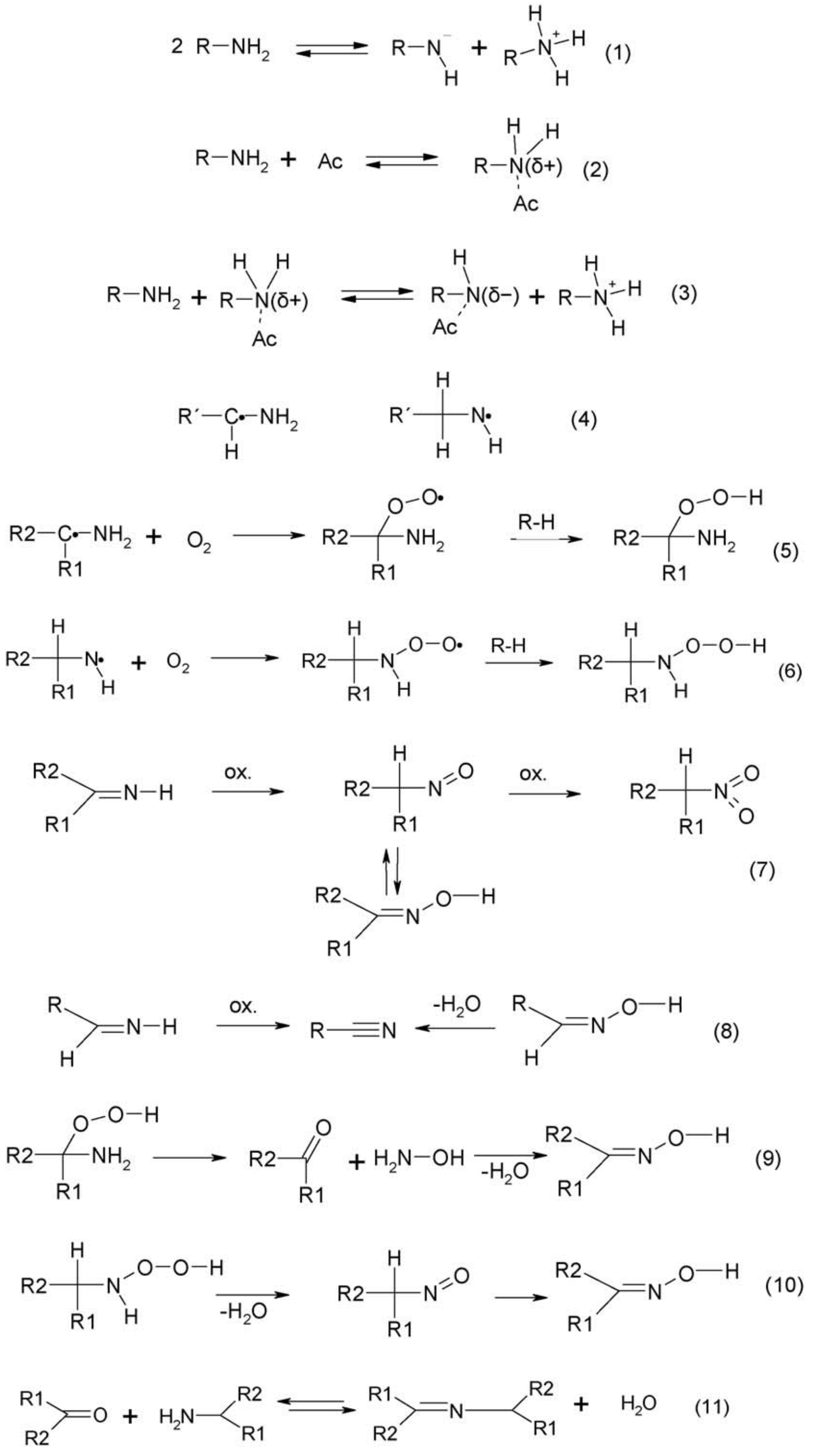


Fig. 12. Results of oxidation of 1,6-hexanediamine over catalysts γ-alumina (Alfa Aesar): (C) without heteropolyacid; (CH) γ-alumina-supported HPA (15 wt% $H_4[Si(W_3O_{10})_4]$); (CHN) γ-alumina-supported neutralized HPA (15 wt% $Na_2H_2[Si(W_3O_{10})_4]$). Conversion of 1,6-hexanediamine, selectivity of ε-caprolactam formation (1) and selectivity of adiponitrile formation (2), respectively. *Reaction conditions*: atmospheric pressure, temperature range 180–185 °C, results at 3 h time on stream.



Scheme 3. Reaction pathways of amines oxidation.

The results of the influence of catalyst acidity are shown in Fig. 12. The acidity of catalyst in the oxidation of amine plays an important role [10,11]. The best results of 1,6-hexanediamine oxidation were reached over pure alumina. Conversion of 1,6-hexanediamine reached 75%. The observed selectivity of ε-caprolactam formation increased up to 52%, but the selectivity of adiponitrile stayed at low level (7%). The alumina-supported HPA (15 wt%) had negative effect to both, conversion of 1,6-hexanediamine and selectivity of ε-caprolactam formation. Moreover, the alumina-supported HPA semisalt (15 wt%) had the worst catalytic activity. The conversion of 1,6-hexanediamine decreased to 32%. On the other hand the selectivity of adiponitrile formation increased three times (up to 23%) in comparison to pure alumina.

3.6. Reaction pathway of oxidation of amines in gas phase over alumina and alumina partially covered by STA or its semisalt

From the composition of oxidation products of different amines and acidity measurements of catalyst follows the next set of processes and reactions:

1. Amine should be adsorbed on the acidic surface before oxidation. (Amine was not oxidized in the gas phase and overneutralized or basic alumina, where amine was practically not adsorbed [11].) The acidity of protons of adsorbed amine was higher in comparison with free amines, i.e. the autoprotolytic equilibrium of amines at the presence of acidic sites is shifted to the right side (reactions (1)–(3)) (Scheme 3).

   The increased concentration of $R–NH_3^+$ was detected as increased acidity of the solution of amine at the presence of catalyst during titration of its slurry by amine in comparison with acidity of blank solutions. If Ac (acidic centers) is a strongly acidic proton, then the last step of equilibrium represents only an exchange of proton between molecules of amine, practically without further significant change. However, if amine is adsorbed on a weak acid site, after exchange of proton the electron density on nitrogen or α-carbon of amine is increased to the level between density of electrons on mentioned atoms in original amine and RNH^- ion. By increasing electron density the sensitivity of amine to oxidation increases. On the other side, the formed $R–NH_3^+$ with significantly lowered electron density on nitrogen and α-carbon is practically insensitive to oxidation. Thus the protonized part of amine is blocked against oxidation. However, an equivalent part is oxidized more easily. This effect, which depends on the acidity of site, can increase the rate of oxidation of amine, i.e. to catalyze it.
2. The autooxidation of amines in liquid phase is initiated on the α-C–H group or N–H group [17]. We suppose that in the initiation step of oxidation of adsorbed amine also two radicals are formed (reaction (4)).

   The formed radicals by the reaction with molecular oxygen and extraction of hydrogen can form hydroperoxides (reactions (5) and (6)). When instead of substance R–H the originally formed radicals react, imines are formed, which can by easily overoxidized to nitroso and nitro compounds. The nitroso derivative is mostly isomerized to oxime. When R1 or R2 is hydrogen, the imines are oxidized to nitriles (reactions (7) and (8)). Oximes and carbonyl compounds can be also formed by direct decomposition of hydroperoxides ((9) and (10)).

   From the known experimental data is not clear, what is the main route of the oxime formation. The most probable way is through imine, because in the case of alkylamines, which have two hydrogen atoms on the α-carbon, nitriles belong to the main product. On the other side, in the case of cycloalkylamine with one hydrogen atom on α-carbon, oxime belongs to the main products, because the formation of nitrile from imine is not possible. The formation of oxime by the reaction of carbonyl compounds and hydroxylamine is less probable because of high concentration of free amine in the system, which by the reaction with carbonyl compounds easily forms Schiff bases (reaction (11)). Schiff bases belong to the main reaction products of all amines. An addition of water to amine shifts this equilibrium to the left, but does not change the total amount of formed carbonyl compound [10], i.e. the eventual formation of carbonyl compounds by hydrolysis of imines is not significant. In the case of diamines volatile cyclic Schiff bases are formed. Probably the linear Schiff bases form part of carbonaceous deposits on the surface of catalyst by oligomerization of double bond or in the case of diamines by repeated condensation of carbonyl and $–NH_2$ group.
3. Formation of amides

   The formed carbonyl compounds at the oxidation of primary alkylamines were aldehydes, which at the used conditions were easily oxidized to carboxylic acids. Carboxylic acids were decarboxylated or react with amines to amides. The radicals formed by decarboxylation were easily oxidized to aldehydes and again to carboxylic acids with shortened alkyl chain, down to acetic and formic acids and its amides, which were found in the oxidation products of practically all amines including cycloalkylamines. In parallel by the formation of amides with shortened alkyl chain also Schiff bases are formed by the reaction of intermediate aldehydes with shortened alkyl chain and original amine.
4. Alkenes as minor byproducts were formed by deamination. On the strong acidic sites these alkenes could form dialkylamines by the reaction with amines. These dialkylamines were found in the reaction mixture of some amines. The formation of some minor aromatic compounds (pyridine, cyclohexylaniline and benzene) was powered by the energy of aromatization. Because this aromatization was connected by dehydrogenation of intermediate products, the formed hydrogen could be consumed by hydrogenation of other compounds, for example, hydrogenation of cyclohexanone to cyclohexanol, Schiff base to dialkylamine, cyclohexene to cyclohexane. These compounds were recognized in some reaction products at low concentrations.

4. Conclusion

It was found that modification of alumina by polyoxometalate ($Na_nH_{4-n}[Si(W_3O_{10})_4]\cdot xH_2O$ ($n = 0$ or 2)) had only little effect to the specific surface and also the pore volume size of catalyst, but the total acidity of catalyst markedly increased. This modification of alumina markedly changes its activity and selectivity of formation of main and byproducts in the oxidation of amines.

In the oxidation of cycloalkylamines the main products are appropriate oximes and Schiff bases (formed by condensation of cycloalkylamine and cycloalkanone). Between minor byproducts appropriate nitrocycloalkane, bis-cycloalkyl-amine and cycloalkene were found. Products of ring decomposition were not observed in the reaction products.

During oxidation of aliphatic primary amines the main oxidation products were nitriles and Schiff bases. Between minor byproducts oximes, alkylamines and Schiff bases with shortened alkyl chain were found. Isobutylamine was more resistant to the oxidation than isopentylamine or linear amines. In the oxidation products of 1,6-hexanediamine were identified the similar compounds, but in the cyclic form, the aminic and aldehydic or acidic ends of intermediate products form cyclic lactames or Schiff bases.

Acknowledgement

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