



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 -Al₂O₃ 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%).

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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/Al₂O₃ 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% H₂O₂ catalyzed by Preyssler catalysts (H₁₄[NaP₅W₃₀O₁₁₀]) 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 m²/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 heteropolymetalates 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, $S_{BET} = 211 \text{ m}^2 \text{ g}^{-1}$, $V_p = 0.6 \text{ cm}^3 \text{ g}^{-1}$, acidity = 0.7 mmol g^{-1}). 0.3 g of polyoxometalate ($Na_nH_{4-n}[Si(W_3O_{10})_4]$, $n = 0$ 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 $4 \text{ }^\circ\text{C}/\text{min}$ 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 $-196 \text{ }^\circ\text{C}$ 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 $p = 2 \text{ Pa}$, $T = 350 \text{ }^\circ\text{C}$ 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 $24 \text{ cm}^3 \text{ min}^{-1}$) 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 $10 \text{ }^\circ\text{C min}^{-1}$ 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 $\pm 0.01 \text{ pH}$. 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 $4000\text{--}600 \text{ cm}^{-1}$.

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 $24 \text{ cm}^3 \text{ min}^{-1}$.

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 ($25 \text{ m} \times 0.53 \text{ mm} \times 1.0 \text{ }\mu\text{m}$). The used temperature program was: 60 °C (3 min), then ramp $9 \text{ }^\circ\text{C min}^{-1}$ 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, $50 \text{ m} \times 0.2 \text{ mm} \times 0.33 \text{ }\mu\text{m}$), carrier gas was helium (1 ml/min); temperature program: from 60 °C with ramp $9 \text{ }^\circ\text{C min}^{-1}$ 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 $211 \text{ m}^2 \text{ g}^{-1}$, 84 \AA and $0.6 \text{ cm}^3 \text{ g}^{-1}$, 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.

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