



Short communication

Low temperature liquid phase catalytic oxidation of aniline promoted by niobium pentoxide micro and nanoparticles



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ABSTRACT

A microwave-assisted hydrothermal method was employed to synthesis Nb₂O₅ (niobium pentoxide) nanoparticles and the effects of synthesis conditions on the physical-chemical properties were evaluated. The catalytic activity of the prepared samples in the liquid phase oxidation of aniline with aqueous hydrogen peroxide as oxidizing agent was also studied. The nanoparticles showed hexagonal structure and rounded shape covered by nanoneedles. The results evidenced high catalytic activity with total conversion of aniline at ambient condition. Aniline conversion and product selectivities depended on the experimental parameters, particularly the oxidizing agent concentration, the nature of the solvent, type of the catalyst and reaction time.

1. Introduction

The oxidation of aniline to its corresponding derivatives, such as phenylhydroxylamine, nitrosobenzene, nitrobenzene, azobenzene and azoxybenzene, has been investigated over the past few decades due to the potential applications of these products in several processes important to the chemical and pharmaceutical industries. These oxidations products are valuable intermediates in industry and are used to produce pharmaceuticals, dyes, reducing agents, polymer stabilisers, food additives and as liquid crystals in electronic displays [1–5]. Selective oxidation of aromatic amines is one of the most challenging reactions for heterogeneous catalysis. Achieving a highly selective catalytic process with reasonable substrate conversion is hampered by competitive over-oxidation and condensation reactions (Scheme 1).

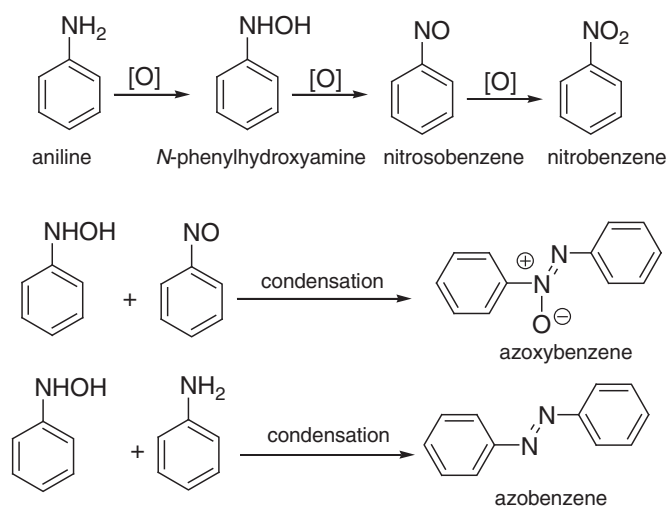
Hydrogen peroxide is a reasonable environmentally friendly oxidant for satisfying the ideals of green chemistry given that it does not produce any toxic waste. Methodologies utilizing heterogeneous catalysts and hydrogen peroxide have been developed for the oxidation of aromatic amines. Examples include: rhenium, molybdenum, cobalt oxide, titanium silicate, Au/TiO₂, Ag/WO₃, CuCr₂O₄, dimeric [Ln₄(H₂O)₆(b-GeW₁₀O₃₈)₂]¹²⁻ anions, titanium silicalite-1, titanium (IV) oxide and Cu–CeO₂ [6–16]. Although varying degrees of success in terms of substrate conversion and selectivity's have been achieved, there is

clearly still a demand for reusable and efficient heterogeneous catalysts for the selective oxidation of anilines. There is precedence for the application of niobium catalysts in oxidative processes that employ hydrogen peroxide as oxidant. Most examples involve the epoxidation of alkenes [17], but oxidation of dithioacetals, benzylalcohols, naphthols and sulfides [17–21] have also been reported. Reddy and Sayari demonstrated that vanadium was capable of catalyzing the oxidation of amines in the presence of hydrogen peroxide to afford the corresponding imines and oximes under mild conditions [22]. Given that no examples for the oxidation of aniline by niobium catalysts were encountered in the literature and that niobium bears some similarity in electronic structure and catalytic behavior in oxidation-reduction reactions to vanadium, a niobium catalyzed oxidation of aniline under heterogeneous conditions is described herein for the first time. Niobium pentoxide (Nb₂O₅) exhibits good chemical stability, nontoxicity and commercial availability [23]. This oxide has been reported as a promising material for application in many fields due to its properties, such as high specific surface area and strength of surface acid sites. Nb₂O₅ presents band gap values between 3.4 and 4.2 eV [24], which is another promising property for its application.

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Scheme 1. Illustrative scheme of main possible products of aniline oxidation.

2. Experimental

2.1. Catalyst preparation

Nb_2O_5 nanoparticles were synthesized by following a method reported previously [25], meanwhile microwave radiation was used to accelerate the synthesis. In this synthesis was used ammonium niobium oxalate ($\text{NH}_4[\text{NbO}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot n\text{H}_2\text{O}$), supplied by Companhia Brasileira de Metalurgia e Mineração (CBMM, Brazil), hydrogen peroxide 30% in vol. (LabSynth, Brazil), and distilled water. 2.0 g of $\text{NH}_4[\text{NbO}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2] \cdot n\text{H}_2\text{O}$ were dispersed in 100 mL of distilled water. After the homogenization, hydrogen peroxide (10 mol/mol) was added. The solution was poured into a container of polytetrafluoroethylene, sealed and placed into a microwave oven (Electrolux, MEF41, Brazil), then heated to 160 °C under different times (15, 30 and 60 min). After the cooling until room temperature, the precipitate was collected and washed three times with absolute ethanol (LabSynth, Brazil) and then dried in an oven (DeLeo, A5SE, Brazil) for 24 h at 50 °C. The powders were denominated $\text{Nb}_2\text{O}_5\#15$, $\text{Nb}_2\text{O}_5\#30$ and $\text{Nb}_2\text{O}_5\#60$, according to the synthesis time.

2.2. Catalyst characterization

The Nb_2O_5 powder was analyzed by: X-ray diffraction (XRD; 6000, Shimadzu, Japan) with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Raman analysis (green line ion laser, 514.53 nm, Horiba, LABRAM-HR, Japan). Transmission Electron Microscope (JEOL, JEM 1400, Japan). Field Emission Scanning Electron Microscope (Zeiss, Supra 35, Germany). Brunauer-Emmett-Teller (BET) method using a Surface Area Analyzer (BEL Japan Inc., BELSORP-mini, Japan).

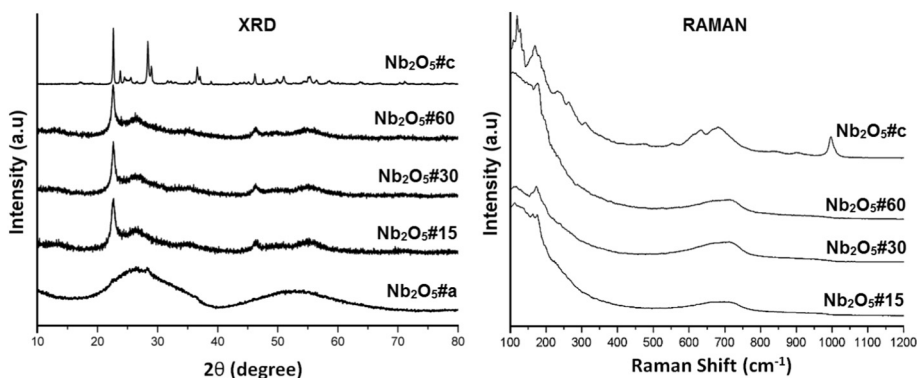


Fig. 1. XRD patterns and Raman spectra of Nb_2O_5 catalysts.

The acidity of the catalysts was determined by titration method. 20 mL of a sodium hydroxide aqueous solution ($0.01 \text{ mol}\cdot\text{L}^{-1}$) was added to the catalyst (10 mg). The mixture was stirred for 24 h at room temperature. Upon separation by centrifugation, the supernatant was then titrated with hydrochloric acid ($0.05 \text{ mol}\cdot\text{L}^{-1}$) aqueous solution using phenolphthalein as indicator. The quantity of acid sites within the catalysts was determined by: number of acid sites = [initial quantity of NaOH added (moles) – quantity of HCl consumed (moles)] \times Avogadro constant.

2.3. Catalytic tests

The liquid phase oxidation of aniline was carried out in a one necked round bottom flask (10 mL batch reactor) maintained at 25 °C on a hotplate stirrer with an oil bath. To the flask was added catalyst (10 mg), specific solvent (3 mL), aniline (0.10 mL) and finally the drop wise addition of H_2O_2 (0.15–1.0 mL of a 35% aq. solution) and the reaction allowed to stir at 25 °C for 3–24 h. Regarding the solvent, water, chloroform, ethanol, acetone, tetrahydrofuran and acetonitrile were evaluated. Upon completion, the reaction was quenched by the addition of a saturated aqueous solution of NaHCO_3 (10 mL) and then taken up in to a separatory funnel and extracted with chloroform ($2 \times 10 \text{ mL}$), the organic extractions were combined, dried over anhydrous sodium sulphate, filtered and made up to 25 mL in a volumetric flask with chloroform. This solution was injected in to the GC for analysis. Analysis was performed on Gas Chromatograph (Shimadzu, GC-2014) connected with Rtx-Wax capillary column and flame ionization detector (FID). Aniline conversion and product formation were quantified with calibration curves which were obtained by manually injecting authentic samples of known concentrations. Conversion of aniline was calculated by: [moles of reactant reacted] / [initial moles of reactant used] $\times 100$ and selectivity of products were calculated by: [total moles of product formed] / [the sum of total moles of all oxidation products formed] $\times 100$. The obtained products were also confirmed by GC-MS (Shimadzu, GCMS-QP2010).

3. Results and discussion

3.1. Characterization of the catalysts

In this study, three groups of Nb_2O_5 nanoparticles were synthesized and each group was differentiated by the exposure time during the microwave-assisted hydrothermal synthesis (MHS). The synthesized nanoparticles were also compared to commercially available micro-particles ($\text{Nb}_2\text{O}_5\#c$) and amorphous Nb_2O_5 ($\text{Nb}_2\text{O}_5\#a$). The XRD patterns of samples are shown in Fig. 1. The peaks of the synthesized Nb_2O_5 could be indexed to the hexagonal phase (JCPDS No. 28-0317) [26,27]. The peaks of the $\text{Nb}_2\text{O}_5\#c$ could be attributed to the orthorhombic phase (JCPDS No. 27-1003) [26,28]. The broad peak of the synthesized Nb_2O_5 formed at 26° is relative to the hydrated niobium oxide. The weak bands present in the synthesized Nb_2O_5 may be due to

the low temperature used in the synthesis, which may have influenced its crystallinity. The formation of more crystalline materials can be managed by increasing the synthesis temperature [29]. The Nb₂O₅#15, Nb₂O₅#30, and Nb₂O₅#60 samples exhibited crystallographic orientation of 8 nm, 10 nm, and 12 nm, respectively, while the Nb₂O₅#c sample is microcrystalline. XRD confirms that Nb₂O₅#a is amorphous.

The Raman spectra of the Nb₂O₅ samples are shown in Fig. 1. The Raman shift presented typical chemical groups of Nb₂O₅ compounds. The spectra of the pseudohexagonal (TT phase) and orthorhombic (phase T) phases have almost identical structures [30]. Broad bands between 650 and 750 cm⁻¹ are assigned to the symmetric stretching mode of the Nb–O polyhedra (presence of disordered NbO₆, NbO₇, and NbO₈) [24,31]. The vibration mode at 226 cm⁻¹ is assigned to the stretching of the Nb–O–Nb bonds. Synthesized Nb₂O₅ has a broad peak at 649 cm⁻¹, which is characteristic of hydrated niobium oxide (Nb₂O₅·nH₂O), and the poorly defined shoulder at 712 cm⁻¹ is characteristic of the orthorhombic phase. This indicates that the sample has higher proportion of Nb₂O₅·nH₂O than the orthorhombic phase [29]. The commercial Nb₂O₅ shows a transition from the orthorhombic phase (phase T) to the monoclinic phase (phase H) due to the emergence of a weak peak at 902 cm⁻¹ and the average peak at 996 cm⁻¹ [31].

Morphology of the samples is shown in Fig. 2. Synthesized Nb₂O₅ showed shape of nanoneedles aggregates in 3D nanostructures in the form of nanoflowers [32]. Commercial Nb₂O₅ showed irregular and large particles. Fig. 3 shows that the synthesized Nb₂O₅#30 has homogeneous particle size and average diameter of 85.83 nm.

The N₂-physorption results are shown in Table 1. As observed, the synthesized Nb₂O₅ samples have greater specific surface area and pore volume than Nb₂O₅#c. For Nb₂O₅#60, the specific surface area was much higher (151.6 m²/g) than Nb₂O₅#c (6.3 m²/g). Also, the increasing of the synthesis time contributed to the formation of particles with larger surface area and higher pore volume.

The amount of acid sites of the Nb₂O₅ samples was determined by the titration method in aqueous solutions (Table 1). The Nb₂O₅#c catalyst had 30.1 × 10²⁰ H⁺ sites/g, presenting lower values than the other Nb₂O₅ samples which presented values in the range of 74.3 × 10²⁰–91.3 × 10²⁰ H⁺ sites/g [33,34].

3.2. Catalytic reactions

In order to investigate the catalytic behavior of the Nb₂O₅, liquid

phase aniline oxidation reactions were carried out under different conditions. Control experiments were conducted without catalyst under the test conditions. No consumption of aniline was observed in all cases, indicating the necessity of the catalyst for the process. It could be observed that Nb₂O₅ were very active and the results revealed that aniline conversion and product selectivity's were influenced by the nature of the catalyst and experimental conditions employed (Figs. 4 and 5). Nitrobenzene and phenylhydroxylamine were detected as the major products, nitrosobenzene as a minor product whereas only traces of azobenzene were observed, for which the selectivity was always less than 2%. Fig. 4 presents the catalytic activity of Nb₂O₅ samples in the aniline oxidation reaction, using water as solvent. All catalysts practically promoted the complete conversion of aniline, however significant differences in product selectivity's could be observed. The selectivity towards nitrobenzene decreased and the formation of phenylhydroxylamine increased when the specific surface area and pore volume within the prepared Nb₂O₅ nanoparticles catalysts were greater. Nb₂O₅#15 catalyst provided the highest selectivity towards nitrobenzene (71.1%) and the lowest selectivity to phenylhydroxylamine (28.3%). It is interesting to observe that Nb₂O₅#c catalyst had an opposite trend presenting a poor selectivity to nitrobenzene (25.7%). This catalyst possesses irregular and larger particles indicating that the size and form could influence the reactivity of the catalyst towards the advanced oxidation product (nitrobenzene) since its surface sites can be less accessible towards aniline molecules owing to their lower surface/volume ratio compared to that of the Nb₂O₅ synthesized nanoparticles [11,12]. Furthermore, in this study both crystalline and amorphous niobium oxide compounds as well as compounds with intermediate states between the two extremes were evaluated in order to determine if these properties affect catalytic performance. Although Nb₂O₅#c demonstrated high catalytic activity, Nb₂O₅#a was significantly more selective towards nitrobenzene (58.2%). These findings are similar to the results described in an important study carried out by Ziolek et al. [35,36] which demonstrated the high ability of the amorphous Nb₂O₅ to form superoxo, peroxy, and hydroxyl reactive oxygen species upon contact with hydrogen peroxide in the epoxidation and oxidation reactions. Differences in the interaction between amorphous and crystalline Nb₂O₅ with H₂O₂ were dependent on the level of surface hydroxylation. The more effective interaction of amorphous Nb₂O₅ with H₂O₂ could be attributed to the higher content of free hydroxyl groups present on the catalyst surface (niobic acid) which is comparatively not

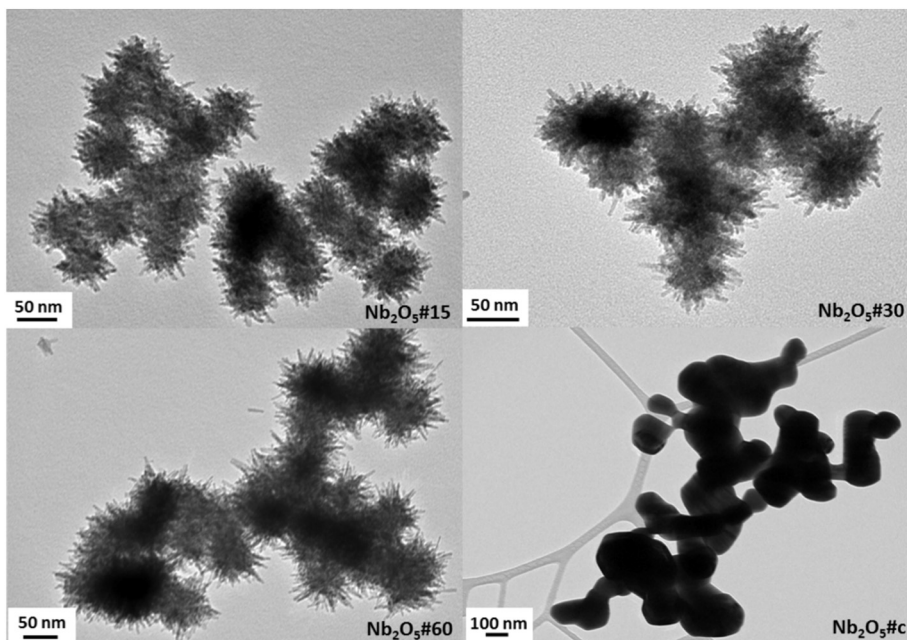


Fig. 2. TEM images of Nb₂O₅ catalysts.

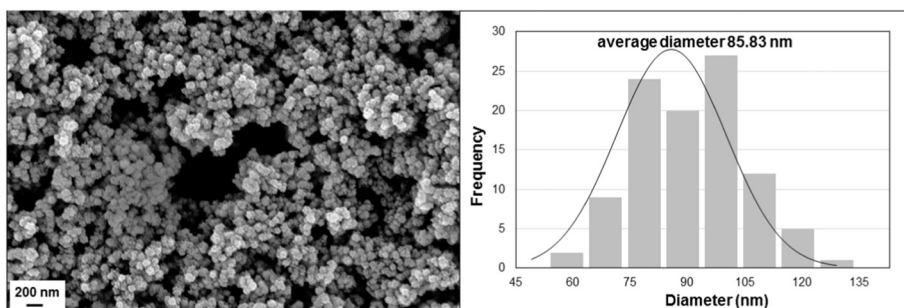


Fig. 3. FE-SEM image and histogram of size distribution of $\text{Nb}_2\text{O}_5\#30$ catalyst.

Table 1

Textural properties measured by N_2 -physorption and acid sites amount determined by a titration method, for the Nb_2O_5 catalysts.

Catalyst	S (m^2/g)	V (cm^3/g)	D (\AA)	Acid sites (H^+ sites/g)
$\text{Nb}_2\text{O}_5\#c$	6.3	0.003	20.84	30.1×10^{20}
$\text{Nb}_2\text{O}_5\#60$	151.6	0.074	19.43	91.3×10^{20}
$\text{Nb}_2\text{O}_5\#30$	109.4	0.053	19.43	74.3×10^{20}
$\text{Nb}_2\text{O}_5\#15$	97.3	0.047	19.28	90.3×10^{20}
$\text{Nb}_2\text{O}_5\#a$	–	–	–	75.2×10^{20}

S: specific surface area; V: pore volume; D: pore diameter.

as readily available on crystalline Nb_2O_5 . According to Ziolk and Pietrzyk, amorphous Nb_2O_5 is more efficient in generating peroxy radicals and so exhibits high ability to form radical peroxy species which are the source of active oxygen species. Thus, since the peroxy groups replace the acid group on the surface [34], from the data presented in Table 1 can speculate that the lower hydroxylation level of $\text{Nb}_2\text{O}_5\#c$ surface gives rise to decrease in surface concentration of those peroxy species [34–36]. Ziolk and Pietrzyk also suggest that amorphous Nb_2O_5 is beneficial since they act as a sponge for trapping $\text{O}_2^{\cdot-}$ and O_2^{2-} , shifting the electroprotic equilibrium towards $\cdot\text{OH}$ radical formation. The greater efficiency of amorphous niobium oxides to generate these species may be conducive to faster consumption of aniline and also limiting the possibility of under oxidation, leading to higher conversions to nitrobenzene.

The effect that the amount of hydrogen peroxide had on conversion and product distribution are presented in Fig. 4. At the lowest H_2O_2 amount (0.15 mL), 70.8% of aniline conversion was achieved and the reaction proceeds via the formation mainly of phenylhydroxylamine and nitrosobenzene, with 88.1% phenylhydroxylamine, 9.6% nitrosobenzene and 2.3% nitrobenzene selectivities, respectively. Interestingly when increasing the H_2O_2 amount up to 0.50 mL, complete aniline conversion was achieved and phenylhydroxylamine selectivity dropped to 41.8% with a considerable increase in the nitrobenzene formation (58.2%). On increasing the H_2O_2 amount up to 1.0 mL, aniline conversion rate remained almost the same, however the catalyst was very selective towards nitrobenzene formation (92.5%). This indicates that the oxidation of phenylhydroxylamine to nitrobenzene was favored due to the higher amount of oxidizing agent present in the reaction mixture.

It is known that the catalyst performances depend on the nature of the solvent used in these reactions [14]. The $\text{Nb}_2\text{O}_5\#30$ catalyst was used to investigate the effect of different solvents on the aniline oxidation reactions (Fig. 5). In almost all cases, the solvents used were able to reach aniline conversion above 90%, except with ethanol, in which the aniline conversion was, around 48.4%. The selectivity of the products varied according to the solvent employed. Using ethanol as solvent, only phenylhydroxylamine was obtained indicating that phenylhydroxylamine oxidation to nitrosobenzene and further to nitrobenzene is probably inhibited in ethanol solvent. In the presence of acetone and THF, phenylhydroxylamine selectivity was high (92.8%

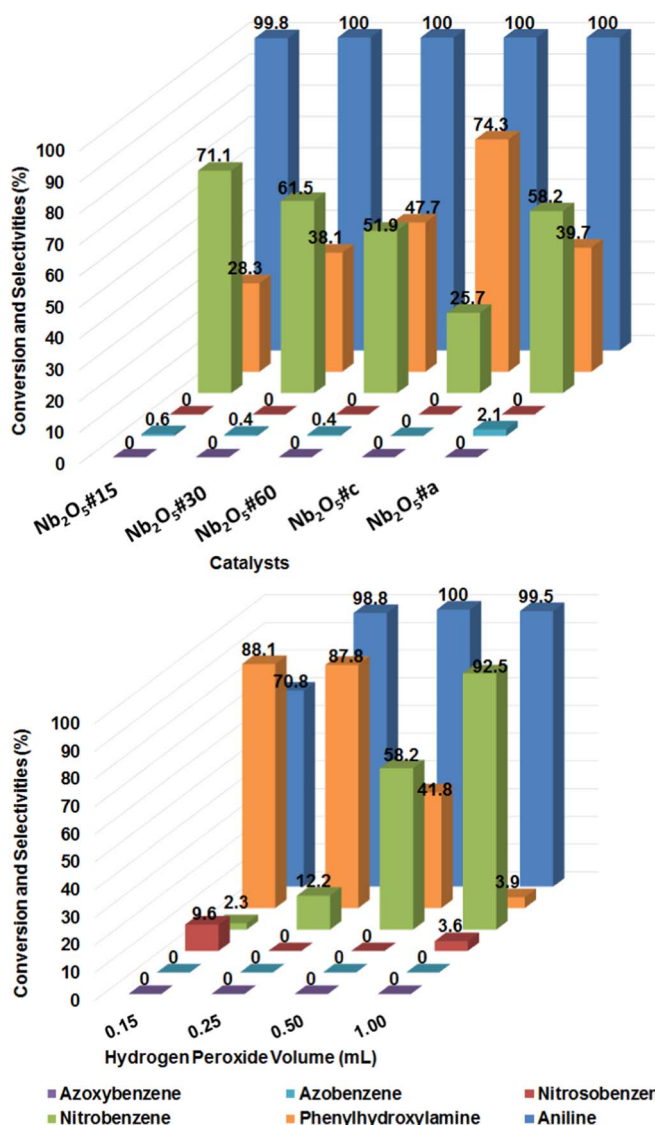


Fig. 4. Aniline oxidation catalyzed by different Nb_2O_5 catalysts (with 0.5 mL of H_2O_2 and water as solvent) and effect of H_2O_2 volume on oxidation of aniline over $\text{Nb}_2\text{O}_5\#60$ catalyst (with acetonitrile as solvent).

and 94.3%, respectively) and less nitrobenzene being formed (5.4% and 4.3%, respectively). On the other hand, selectivities to nitrobenzene and nitrosobenzene in the ranges of 20–30% and 11–13%, respectively, in both chloroform and acetonitrile were observed. The amount of nitrosobenzene is found to be very similar in these two solvents. It is interesting to observe that low amounts of azobenzene were detected and nitrosobenzene was not detected in the final products when acetone and THF were used as solvents. This result suggests that most probably, phenylhydroxylamine reacted with unreacted aniline leading to the

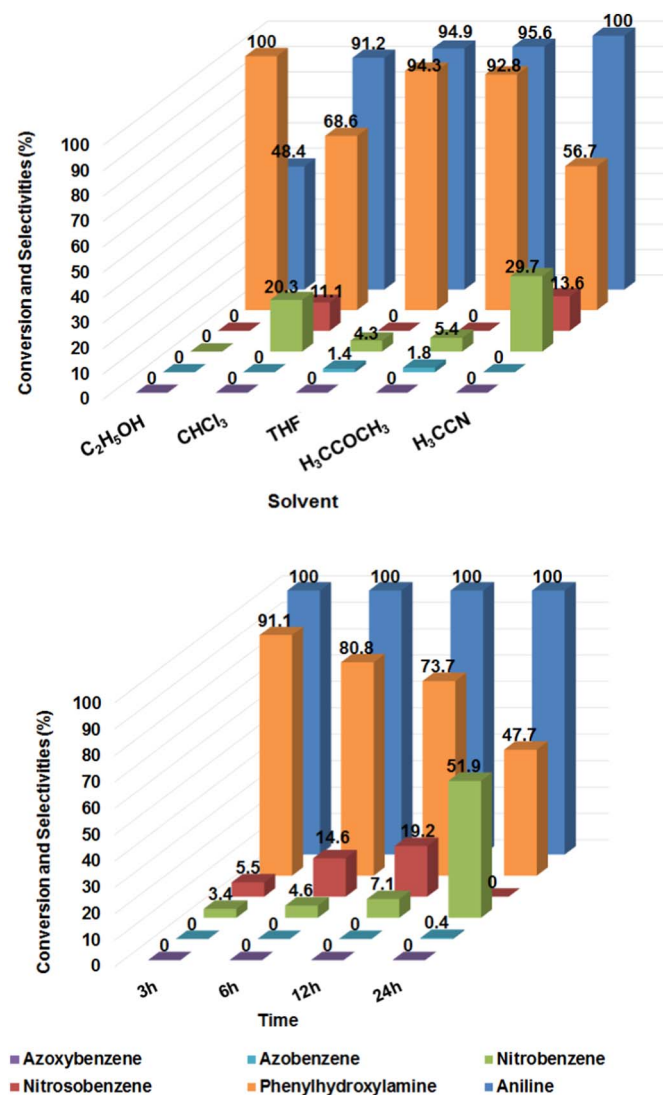


Fig. 5. Effect of solvent on oxidation of aniline over Nb₂O₅#30 catalyst (with 0.5 mL of H₂O₂) and effect of reaction time on oxidation of aniline over Nb₂O₅#60 catalyst (with 0.5 mL of H₂O₂ and acetonitrile as solvent).

formation of azobenzene [9].

Fig. 5 presents the formation of the products in the course of the reaction over Nb₂O₅#60 catalyst, with 0.5 mL of H₂O₂ and acetonitrile as solvent. Phenylhydroxylamine, which can be obtained by direct oxidation of aniline, was formed in high conversion at the early stages of the reaction and slowly disappeared with time, achieving 41.8% of selectivity after 24 h of reaction. Concomitantly, the amount of nitrosobenzene and nitrobenzene increased continuously with time. At the end of the run (24 h), phenylhydroxylamine and nitrobenzene were the only products indicating that initially formed nitrosobenzene from phenylhydroxylamine is converted to nitrobenzene. Furthermore, the oxidation of nitrosobenzene to nitrobenzene is significantly faster than the conversion of phenylhydroxylamine to nitrosobenzene.

4. Conclusions

In this study we have investigated the effect of various parameters on the liquid phase oxidation of aniline over synthesized Nb₂O₅ nanoparticles and commercial Nb₂O₅ microparticles. The influence of the oxidant amount, nature of solvents and reaction time on the oxidation of aniline was evaluated. To our knowledge, the use of Nb₂O₅ has not yet been reported to promote this reaction. It should be highlighted that

the results showed that the prepared catalysts could be very active in the proposed reaction even at mild reaction conditions (ambient temperature and pressure). The process could be made selective towards the formation of phenylhydroxylamine when employing ethanol as solvent and utilizing smaller amounts of H₂O₂ or favour the formation of nitrobenzene in the presence of excess H₂O₂ and acetonitrile as solvent.

Acknowledgments

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