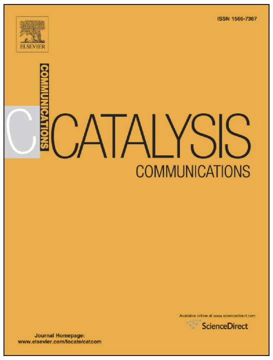


Low temperature liquid phase catalytic oxidation of aniline promoted by niobium pentoxide micro and nanoparticles

Wellington M. Ventura, Daniel C. Batalha, Humberto V. Fajardo, Jason G. Taylor, Natália H. Marins, Bruno S. Noremberg, Tomasz Tański, Neftalí L.V. Carreño

PII: S1566-7367(17)30235-2
DOI: doi: 10.1016/j.catcom.2017.06.004
Reference: CATCOM 5070

To appear in: *Catalysis Communications*

Received date: 3 April 2017
Revised date: 1 June 2017
Accepted date: 8 June 2017

Please cite this article as: Wellington M. Ventura, Daniel C. Batalha, Humberto V. Fajardo, Jason G. Taylor, Natália H. Marins, Bruno S. Noremberg, Tomasz Tański, Neftalí L.V. Carreño , Low temperature liquid phase catalytic oxidation of aniline promoted by niobium pentoxide micro and nanoparticles. The address for the corresponding author was captured as affiliation for all authors. Please check if appropriate. Catcom(2017), doi: 10.1016/j.catcom.2017.06.004

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

Wellington M. Ventura[a], Daniel C. Batalha[a], Humberto V. Fajardo[a,*], Jason G. Taylor[a], Natália H. Marins[b], Bruno S. Noremberg[b], Tomasz Tański[c,d], Neftalí L. V. Carreño[b,**]

[a] Chemistry Department, Institute of Exact and Biological Sciences, Federal University of Ouro Preto, 35400-000, Ouro Preto, MG, Brazil

[b] Graduate Program in Materials Science and Engineering, Technology Development Center, Federal University of Pelotas, 96010-000, Pelotas, RS, Brazil

[c] Institute of Engineering Materials and Biomaterials, Silesian University of Technology, 44-100, Gliwice, Poland

[d] Center for Nanotechnology, Silesian University of Technology, 44-100, Gliwice, Poland

[*] E-mail Corresponding author: hfajardo@iceb.ufop.br

** E-mail Corresponding author: neftali@ufpel.edu.br

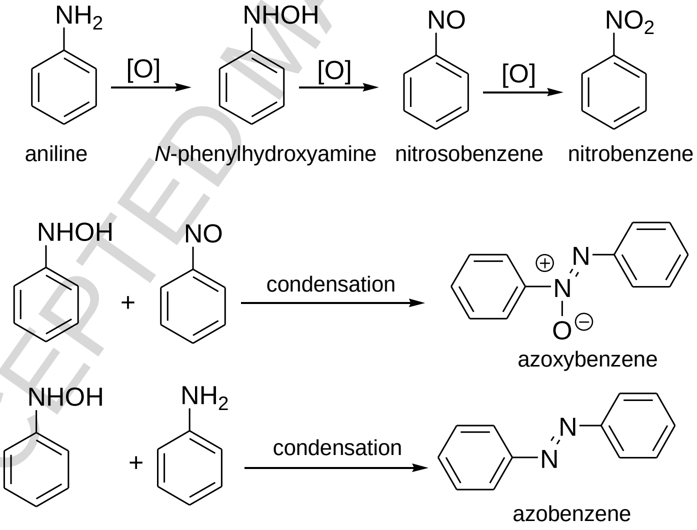
Abstract

A microwave-assisted hydrothermal method was employed to synthesis Nb_2O_5 (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.

Keywords: niobium pentoxide, aniline, oxidation, hydrogen peroxide, nitrobenzene, phenylhydroxylamine.

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).



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

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/TiO_2, Ag/WO_3, $CuCr_2O_4$, dimeric $[Ln_4(H_2O)_6(b\text{-}GeW_{10}O_{38})_2]^{12-}$ anions, titanium silicalite-1, titanium (IV) oxide and Cu–CeO_2 [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 catalysis 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 (Nb_2O_5) 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. Nb_2O_5 presents band gap values between 3.4 and 4.2 eV [24], which is another promising property for its application.

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 ($NH_4[NbO(C_2O_4)_2(H_2O)_2].nH_2O$), supplied by Companhia Brasileira de Metalurgia e Mineração (CBMM, Brazil), hydrogen peroxide 30% in vol. (LabSynth, Brazil), and distilled water. 2.0 g of $NH_4[NbO(C_2O_4)_2(H_2O)_2].nH_2O$ 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 minutes). 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 hours at 50°C. The powders were denominated Nb_2O_5#15, Nb_2O_5#30 and Nb_2O_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 Kα radiation (λ = 1.5418 Å). 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).

The acidity of the catalysts was determined by titration method. 20 mL of a sodium hydroxide aqueous solution ($0.01\ mol.L^{-1}$) was added to the catalyst (10 mg). The mixture was stirred for 24 hours at room temperature. Upon separation by centrifugation, the supernatant was then titrated with hydrochloric acid ($0.05\ mol.L^{-1}$) aqueous solution using phenolphthalein as indicator. The quantity of acid sites with in the catalysts was determined by: number of acid sites = [initial quantity of NaOH added (moles) – quantity of HCl consumed (moles)] x 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 hours. 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 x 10 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] x 100 and selectivity of products were calculated by: [total moles of product formed]/[the sum of total moles of all oxidation products formed] x100. 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 microparticles (Nb_2O_5#c) and amorphous Nb_2O_5 (Nb_2O_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 Nb_2O_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 Nb_2O_5#15, Nb_2O_5#30, and Nb_2O_5#60 samples exhibited crystallographic orientation of 8 nm, 10 nm, and 12 nm, respectively, while the Nb_2O_5#c sample is microcrystalline. XRD confirms that Nb_2O_5#a is amorphous.

The Raman spectra of the Nb_2O_5 samples are shown in Fig. 1. The Raman shift presented typical chemical groups of Nb_2O_5 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 NbO_6, NbO_7, and NbO_8) [24,31]. The vibration mode at 226 cm^{-1} is assigned to the stretching of the Nb-O-Nb bonds. Synthesized Nb_2O_5 has a broad peak at 649 cm^{-1}, which is characteristic of hydrated niobium oxide ($Nb_2O_5 \cdot nH_2O$), and the poorly defined shoulder at 712 cm^{-1} is characteristic of the orthorhombic phase. This indicates that the sample has higher proportion of $Nb_2O_5 \cdot nH_2O$ than the orthorhombic phase [29]. The commercial Nb_2O_5 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 Nb_2O_5 showed shape of nanoneedles aggregates in 3D nanostructures in the form of nanoflowers [32]. Commercial Nb_2O_5 showed irregular and large particles. Fig. 3 shows that the synthesized Nb_2O_5#30 has homogeneous particle size and average diameter of 85.83 nm.

The N_2-physisorption results are shown in Table 1. As observed, the synthetized Nb_2O_5 samples have greater specific surface area and pore volume than Nb_2O_5#c. For Nb_2O_5#60, the specific surface area was much higher (151.6 m^2/g) than Nb_2O_5#c (6.3 m^2/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 Nb_2O_5 samples was determined by the titration method in aqueous solutions (Table 1). The Nb_2O_5#c catalyst had 30.1x10^{20} H^+ sites/g, which was less than that of the other Nb_2O_5 samples which presented values in the range of 74.3 x10^{20}-91.3x10^{20} H^+ sites/g [33,34].

3.2 Catalytic reactions

In order to investigate the catalytic behavior of the Nb_2O_5, 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 Nb_2O_5 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 (Figures 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 Nb_2O_5 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 Nb_2O_5 nanoparticles catalysts were greater. Nb_2O_5#15 catalyst provided the highest selectivity towards nitrobenzene (71.1%) and the lowest selectivity to phenylhydroxylamine (28.3%). It is interesting to observe that Nb_2O_5#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 toward the advanced oxidation product (nitrobenzene) since its surface sites can be less accessible toward aniline molecules owing to their lower surface/volume ratio compared to that of the Nb_2O_5 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 Nb_2O_5#c demonstrated high catalytic activity, Nb_2O_5#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 and Pietrzyk [35,36] which demonstrated the high ability of the amorphous Nb_2O_5 to form superoxo, peroxo, and hydroxyl reactive oxygen species upon contact with hydrogen peroxide in the epoxidation and oxidation reactions. Differences in the interaction between amorphous and crystalline Nb_2O_5 with H_2O_2 were dependent on the level of surface hydroxylation. The more effective interaction of amorphous Nb_2O_5 with H_2O_2 could be attributed to the higher content of free hydroxyl groups present on the catalyst surface (niobic acid) which is comparatively not as readily available on crystalline Nb_2O_5. According to Ziolek and Pietrzyk, amorphous Nb_2O_5 is more efficient in generating peroxo radicals and so exhibits high ability to form radical peroxo species which are the source of active oxygen species. Thus, since the peroxo groups replace the acid group on the surface [34], from the data presented in Table 1 one can speculate that the lower hydroxylation level of Nb_2O_5#c surface gives rise to decrease in surface concentration of those peroxo species [34-36]. Ziolek and Pietrzyk also suggest that amorphous Nb_2O_5 is beneficial since they act as a sponge for trapping $O_2^{-\bullet}$ and O_2^{2-}, shifting the electroprotic equilibrium towards •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 toward 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 Nb_2O_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% 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 formation of azobenzene [9].

Fig. 5 presents the formation of the products in the course of the reaction over Nb_2O_5#60 catalyst, with 0.5 mL of H_2O_2 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 hours of reaction. Concomitantly, the amount of nitrosobenzene and nitrobenzene increased continuously with time. At the end of the run (24h), 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 Nb_2O_5 nanoparticles and commercial Nb_2O_5 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 Nb_2O_5 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 H_2O_2 or favour the formation of nitrobenzene in the presence of excess H_2O_2 and acetonitrile as solvent.

Acknowledgments

This work was supported by the CAPES/PROCAD 2013/2998/2014, UFOP, CNPq and FAPEMIG. Nb_2O_5#c and Nb_2O_5#a samples were kindly supplied by Companhia Brasileira de Metalurgia e Mineração (CBMM, Brazil).

References

[1] S. Gontier, A. Tuel, Liquid-phase oxidation of aniline over various transition-metal-substituted molecular-sieves, J. Catal. 157 (1995) 124–132.

[2] N. Jagtap, V. Ramaswamy, Oxidation of aniline over titania pillared montmorillonite clays, Appl. Clay Sci. 33 (2006) 89–98.

[3] L. Lekha, K. Kanmani Raja, G. Rajagopal, D. Easwaramoorthy, Schiff base complexes of rare earth metal ions: Synthesis, characterization and catalytic activity for the oxidation of aniline and substituted anilines, J. Organomet. Chem. 753 (2014) 72–80.

[4] A. Bordoloi, S.B. Halligudi, Tungsten- and molybdenum-based coordination polymer-catalyzed N-oxidation of primary aromatic amines with aqueous hydrogen peroxide, Adv. Synth. Catal. 349 (2007) 2085–2088.

[5] A. Grirrane, A. Corma, H. Garcia, Gold-catalyzed synthesis of aromatic azo compounds from anilines and nitroaromatics, Science. 322 (2008) 1661–1664.

[6] R.W. Murray, K. Iyanar, J. Chen, J.T. Wearing, Oxidation of organonitrogen compounds by the methyltrioxorhenium-hydrogen peroxide system, Tetrahedron Lett. 37 (1996) 805–808.

[7] A. Defoin, Simple preparation of nitroso benzenes and nitro benzenes by oxidation of anilines with H_2O_2 catalysed with molybdenum salts, Synthesis. 2004 (2004) 706–710.

[8] C.F. Chang, S.T. Liu, Catalytic oxidation of anilines into azoxybenzenes on mesoporous silicas containing cobalt oxide, J. Mol. Catal. A Chem. 299 (2009) 121–126.

[9] T. Selvam, A. V Ramaswamy, A new catalytic method for the selective oxidation of aniline to nitrosobenzene over titanium silicate molecular sieves, TS-1, using H_2O_2 as oxidant, Chem. Commun. (1996) 1215–1216.

[10] S. Fountoulaki, P.L. Gkizis, T.S. Symeonidis, E. Kaminioti, A. Karina, I. Tamiolakis, G.S. Armatas, I.N. Lykakis, Titania-supported gold nanoparticles catalyze

the selective oxidation of amines into nitroso compounds in the presence of hydrogen peroxide, Adv. Synth. Catal. 358 (2016) 1500–1508.

[11] S. Ghosh, S.S. Acharyya, T. Sasaki, R. Bal, Room temperature selective oxidation of aniline to azoxybenzene over a silver supported tungsten oxide nanostructured catalyst, Green Chem. 17 (2015) 1867–1876.

[12] S.S. Acharyya, S. Ghosh, R. Bal, Catalytic oxidation of aniline to azoxybenzene over $CuCr_2O_4$ spinel nanoparticle catalyst, ACS Sustain. Chem. Eng. 2 (2014) 584–589.

[13] G. Trautwein, B. El Bakkali, J. Alcañiz-Monge, B. Artetxe, S. Reinoso, J.M. Gutiérrez-Zorrilla, Dimeric assemblies of lanthanide-stabilised dilacunary Keggin tungstogermanates: A new class of catalysts for the selective oxidation of aniline, J. Catal. 331 (2015) 110–117.

[14] S. Gontier, A. Tuel, Oxidation of aniline over TS-1, the titanium substituted silicalite-1, Appl. Catal. A Gen. 118 (1994) 173–186.

[15] H. Tumma, N. Nagaraju, K.V. Reddy, Titanium (IV) oxide, an efficient and structure-sensitive heterogeneous catalyst for the preparation of azoxybenzenes in the presence of hydrogen peroxide, Appl. Catal. A Gen. 353 (2009) 54–60.

[16] A. Shukla, R.K. Singha, L.N.S. Konathala, T. Sasaki, R. Bal, Catalytic oxidation of aromatic amines to azoxy compounds over a Cu–CeO_2 catalyst using H_2O_2 as an oxidant, RSC Adv. 6 (2016) 22812–22820.

[17] N.E. Thornburg, S.L. Nauert, A.B. Thompson, J.M. Notestein, Synthesis-structure-function relationships of silica-supported niobium(V) catalysts for alkene epoxidation with H_2O_2, ACS Catal. 6 (2016) 6124–6134.

[18] M. Kirihara, T. Goto, T. Noguchi, M. Suzuki, Y. Ishizuka, S. Naito, Niobium (V) chloride catalyzed oxidation of dithioacetals with 30% hydrogen peroxide: a concise preparation of bissulfonylmethylene compounds, Chem. Pharm. Bull. 61 (2013) 460–463.

[19] M.C. Reis, S.D.T. Barros, E.R. Lachter, R.A.S. San Gil, J.H. Flores, M.I. Pais Da Silva, T. Onfroy, Synthesis, characterization and catalytic activity of meso-niobium

phosphate in the oxidation of benzyl alcohols, Catal. Today. 192 (2012) 117–122.

[20] G. Strukul, F. Somma, N. Ballarini, F. Cavani, A. Frattini, S. Guidetti, D. Morselli, The oxidation of 2-methyl-1-naphthol to menadione with H_2O_2, catalyzed by Nb-based heterogeneous systems, Appl. Catal. A Gen. 356 (2009) 162–166.

[21] M. Kirihara, J. Yamamoto, T. Noguchi, A. Itou, S. Naito, Y. Hirai, Tantalum (V) or niobium (V) catalyzed oxidation of sulfides with 30% hydrogen peroxide, Tetrahedron. 65 (2009) 10477–10484.

[22] J.S. Reddy, A. Sayari, Oxidation of primary amines over vanadium silicalite molecular sieve, VS-1, Catal. Letters. 28 (1994) 263–267.

[23] J. Yan, G. Wu, N. Guan, L. Li, Nb_2O_5/TiO_2 heterojunctions: Synthesis strategy and photocatalytic activity, Appl. Catal. B Environ. 152–153 (2014) 280–288.

[24] R. Brayner, F. Bozon-Verduraz, Niobium pentoxide prepared by soft chemical routes: morphology, structure, defects and quantum size effect, Phys. Chem. Chem. Phys. 5 (2003) 1457–1466.

[25] E.R. Leite, C. Vila, J. Bettini, E. Longo, Synthesis of niobia nanocrystals with controlled morphology, J. Phys. Chem. B. 110 (2006) 18088–18090.

[26] R. Shao, Z. Cao, Y. Xiao, H. Dong, W. He, Y. Gao, J. Liu, Enhancing photocatalytic activity by tuning the ratio of hexagonal and orthorhombic phase Nb_2O_5 hollow fibers, RSC Adv. 4 (2014) 26447–26451.

[27] J. He, Y. Hu, Z. Wang, W. Lu, S. Yang, G. Wu, Y. Wang, S. Wang, H. Gu, J. Wang, Hydrothermal growth and optical properties of Nb_2O_5 nanorod arrays, J. Mater. Chem. C. 2 (2014) 8185–8190.

[28] A. Le Viet, M.V. Reddy, R. Jose, B.V.R. Chowdari, S. Ramakrishna, Electrochemical properties of bare and Ta-substituted Nb_2O_5 nanostructures, Electrochim. Acta. 56 (2011) 1518–1528.

[29] O.F. Lopes, E.C. Paris, C. Ribeiro, Synthesis of Nb_2O_5 nanoparticles through the oxidant peroxide method applied to organic pollutant photodegradation: A mechanistic study, Appl. Catal. B Environ. 144 (2014) 800–808.

[30] J.G. Weissman, E.I. Ko, P. Wynblatt, J.M. Howe, High-resolution electron microscopy and image simulation of TT-, T-, and H-niobia and model silica-supported niobium surface oxides, Chem. Mater. 1 (1989) 187–193.

[31] J.M. Jehng, I.E. Wachs, Structural chemistry and Raman spectra of niobium oxides, Chem. Mater. 3 (1991) 100–107.

[32] J.N. Tiwari, R.N. Tiwari, K.S. Kim, Zero-dimensional, one-dimensional, two-dimensional and three-dimensional nanostructured materials for advanced electrochemical energy devices, Prog. Mater. Sci. 57 (2012) 724–803.

[33] A. Onda, T. Ochi, K. Yanagisawa, Selective hydrolysis of cellulose into glucose over solid acid catalysts, Green Chem. 10 (2008) 1033–1037.

[34] L.C.A. de Oliveira, N.T. Costa, J.R. Pliego, A.C. Silva, P.P. de Souza, P.S. Patrício, Amphiphilic niobium oxyhydroxide as a hybrid catalyst for sulfur removal from fuel in a biphasic system, Appl. Catal. B Environ. 147 (2014) 43–48.

[35] M. Ziolek, I. Sobczak, P. Decyk, L. Wolski, The ability of Nb2O5 and Ta2O5 to generate active oxygen in contact with hydrogen peroxide, Catal. Commun. 37 (2013) 85–91.

[36] M. Ziolek, I. Sobczak, P. Decyk, K. Sobanska, P. Pietrzyk, Z. Sojka, Search for reactive intermediates in catalytic oxidation with hydrogen peroxide over amorphous niobium(V) and tantalum(V) oxides, Appl. Catal. B Environ. 164 (2015) 288–296.

Figures

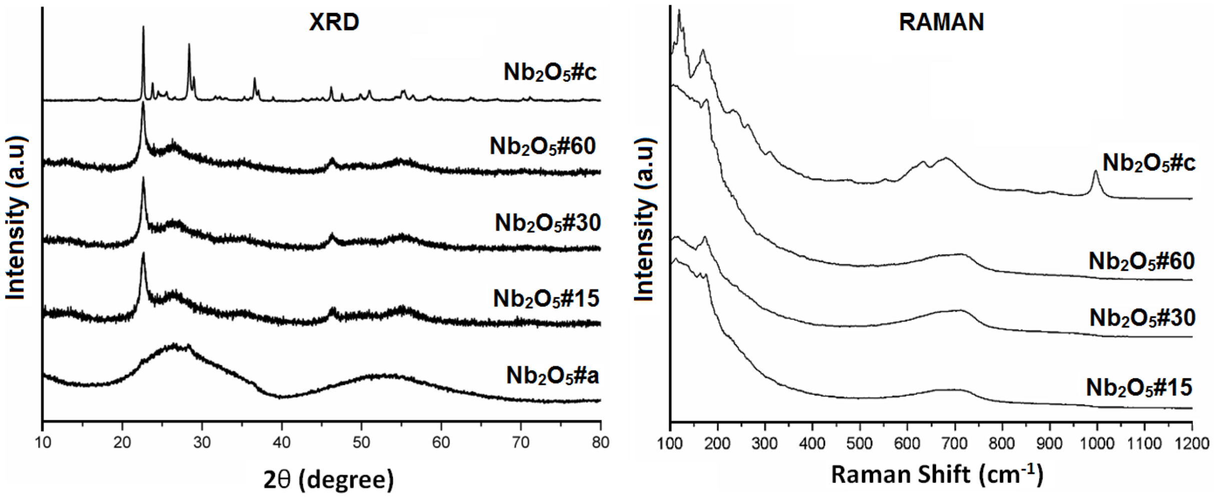


Figure 1. XRD patterns and Raman spectra of Nb_2O_5 catalysts.

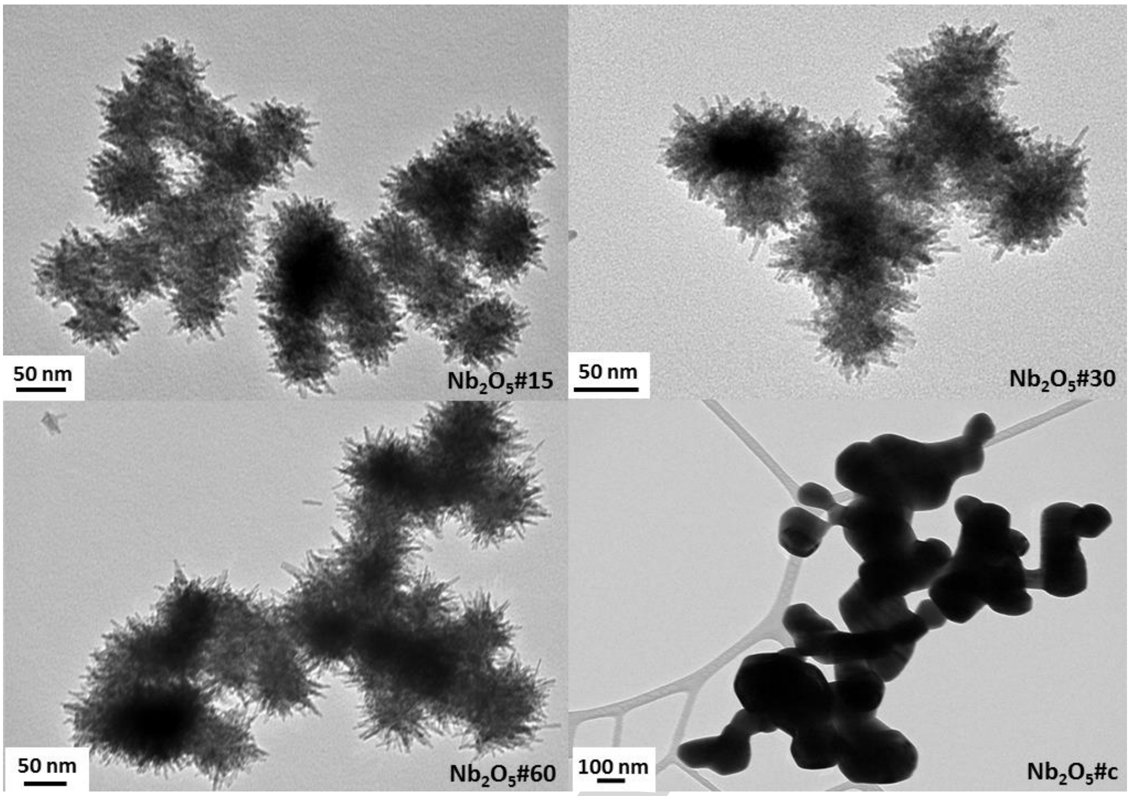


Figure 2. TEM images of Nb_2O_5 catalysts.

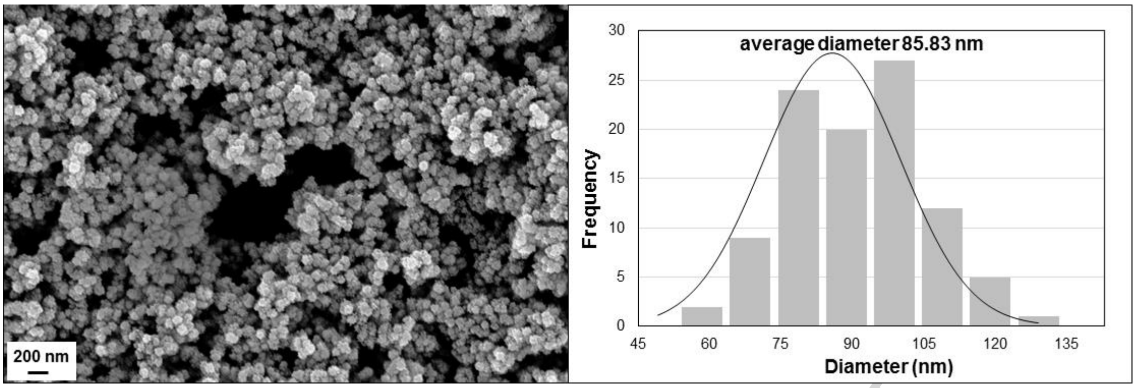


Figure 3. FE-SEM image and histogram of size distribution of Nb_2O_5#30 catalyst.

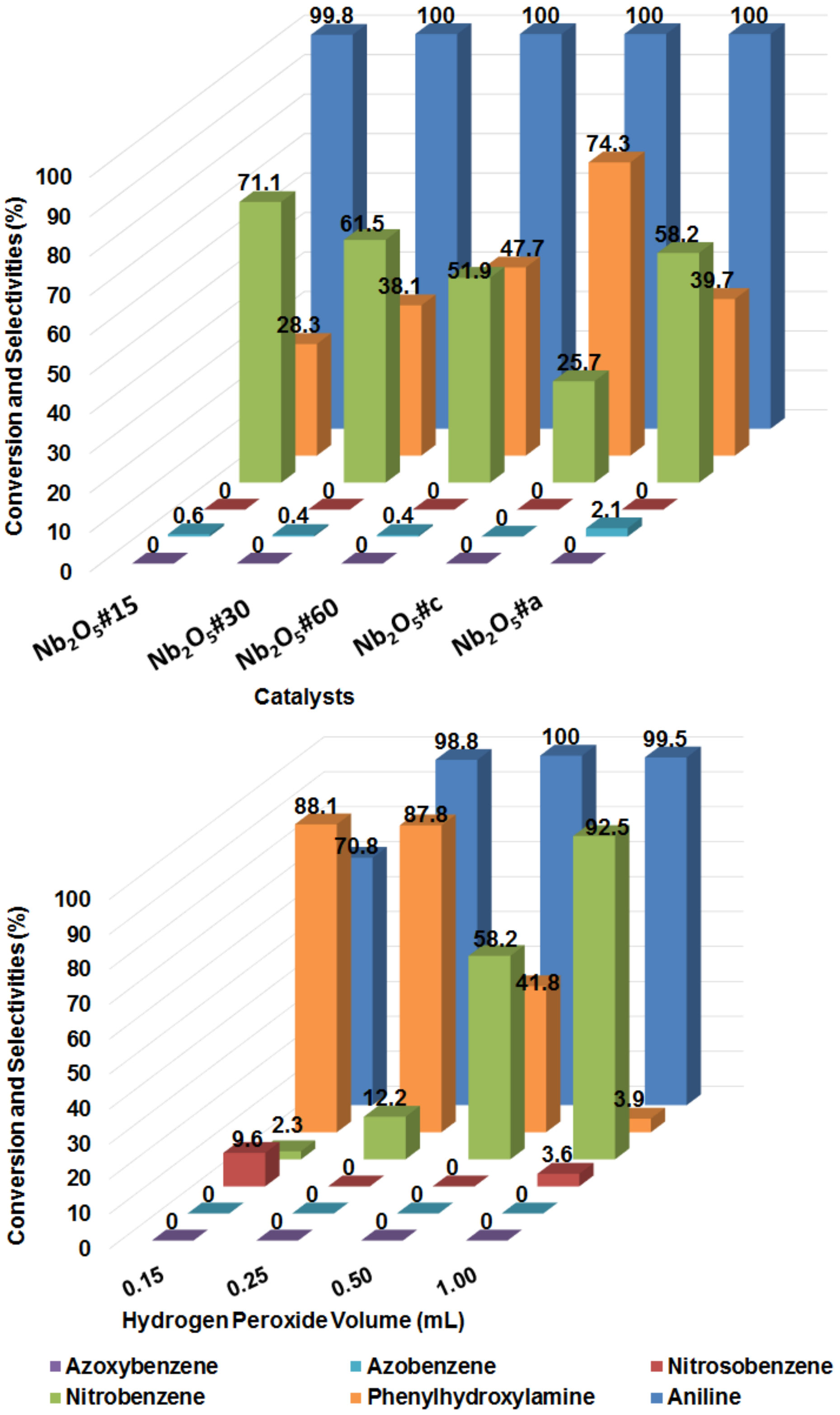


Figure 4. Aniline oxidation catalyzed by different Nb_2O_5 catalysts (with 0.5 mL of H_2O_2 and water as solvent) and effect of H_2O_2 volume on oxidation of aniline over Nb_2O_5#60 catalyst (with acetonitrile as solvent).

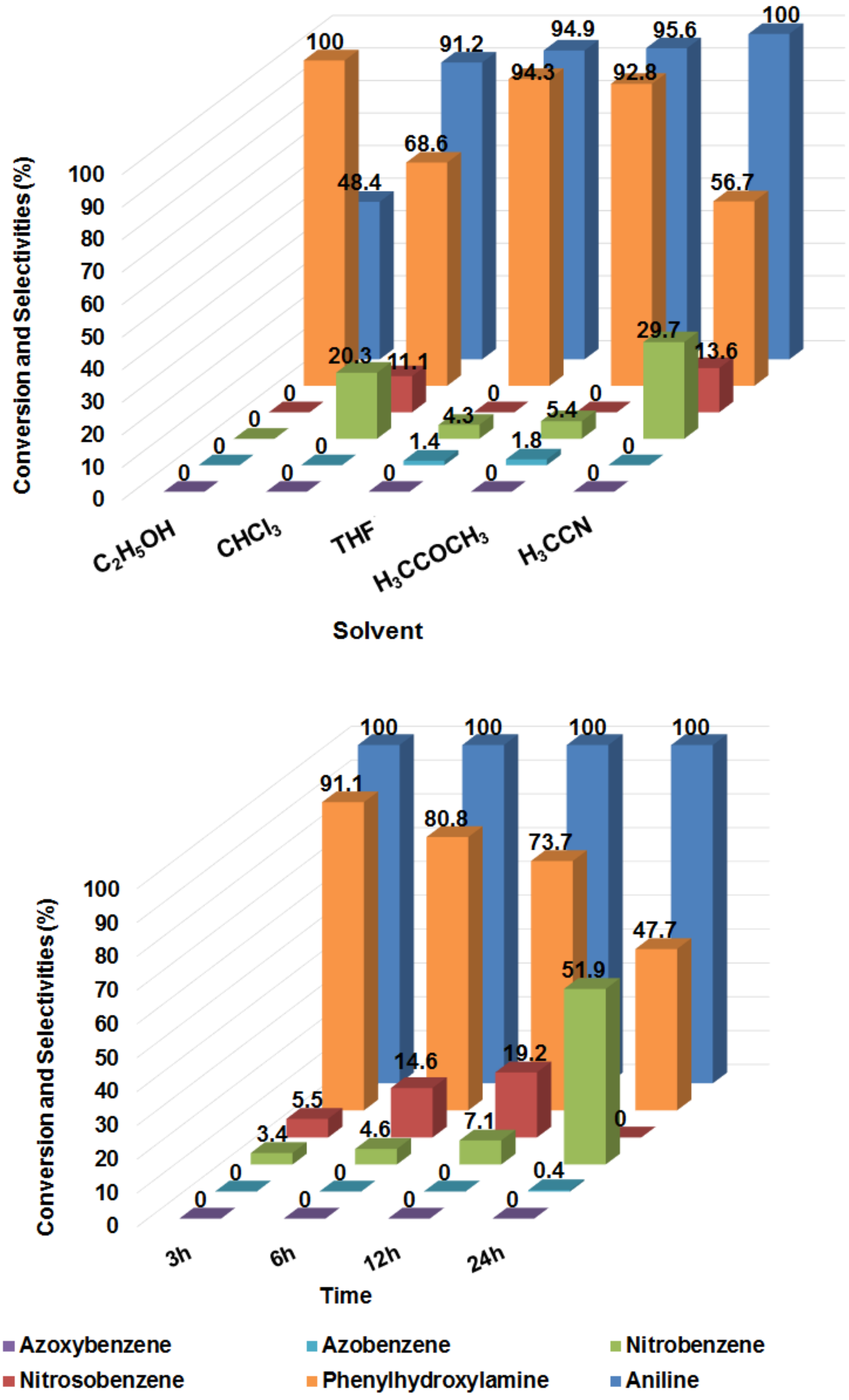


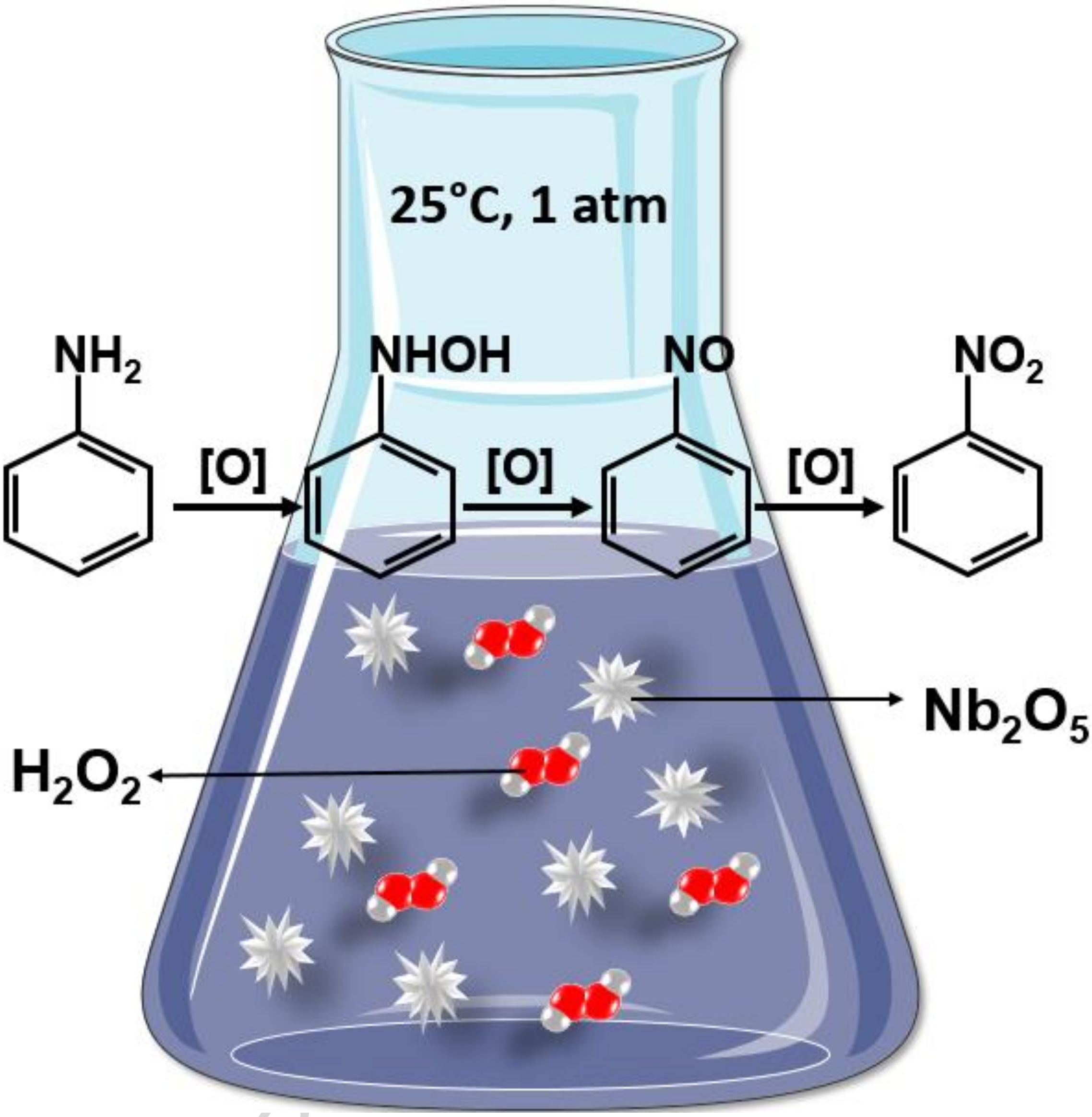
Figure 5. Effect of solvent on oxidation of aniline over Nb_2O_5#30 catalyst (with 0.5 mL of H_2O_2) and effect of reaction time on oxidation of aniline over Nb_2O_5#60 catalyst (with 0.5 mL of H_2O_2 and acetonitrile as solvent).

Table

Table 1. Textural properties measured by N_2-physisorption 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 (Å)	Acid sites (H^+ sites/g)
Nb_2O_5#c	6.3	0.003	20.84	$30.1x10^{20}$
Nb_2O_5#60	151.6	0.074	19.43	$91.3x10^{20}$
Nb_2O_5#30	109.4	0.053	19.43	$74.3x10^{20}$
Nb_2O_5#15	97.3	0.047	19.28	$90.3x10^{20}$
Nb_2O_5#a	-	-	-	$75.2x10^{20}$

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



Graphical abstract

Highlights

- Low temperature liquid phase catalytic oxidation of aniline
- Hydrogen peroxide is a milder oxidant
- Selective oxidation of aniline
- Niobium mineral