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On the mixed oxides-supported niobium catalyst towards benzylamine oxidation

Álisson Silva Granato [a,b], Gustavo S. Gonçalves de Carvalho [a], Carla G. Fonseca [a], Javier Adrio [b], Alexandre A. Leitão [a,*], Giovanni Wilson Amarante [a,*]

[a] *Chemistry Department, Federal University of Juiz de Fora, São Pedro, Juiz de Fora, 36036-900, Brazil*

[b] *Departamento de Química Orgánica and Institute for Advanced Research in Chemical Sciences (IAdChem), Facultad de Ciencias, Universidad Autónoma de Madrid, Cantoblanco, 28049, Madrid, Spain*

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ABSTRACT

A series of mixed oxides-supported niobium-based catalysts has been synthesized and applied towards oxidation reactions of benzylamine derivatives. Under the optimized reaction conditions, the selectivity to oxime enhanced, leading to the main product with up to 72 %. Moreover, even α-substituted benzylamines were well tolerated and led to oximes in good isolated yields. It is important to mention; four equivalents of the harmless and inexpensive hydrogen peroxide were employed as oxidizing agent. Mechanism hypothesis suggested that the reaction proceed to selective benzylamine oxidation into nitroso intermediate, following by formation of the corresponding oxime tautomer mediated by an unstable water produced by NbO_x supported catalyst. This consists the first mixed oxides-supported niobium-based catalyst for selective oxidation of benzylamines to oximes.

1. Introduction

Niobium-containing catalysts have been attracting attention within heterogeneous catalysis due to their unique properties and to the several described applications attributed to a wide range of reactions such as acid-base, oxidation-reduction and photocatalyzed [1,2]. Due to the characteristic of enhancement of surface properties when coordinated with metal oxides, these supported niobium catalysts have expanded their applications in redox reactions [3–5].

The niobium is normally incorporated by the wetness impregnation method and good dispersion of the particles is observed on mixed oxides obtained from thermal decomposition of Layered Double hydroxides (LDHs). These mixed metal oxides exhibit porous structure and high thermal stability besides versatile chemical composition [6].

The characterization of niobium supported compounds is very important to the discussion of their catalytic activity and selectivity. A representative theoretical-experimental investigation on mixed oxides supported niobium oxide was performed in our previous work and shed some light on this complex situation. At low loading niobium can form monomers and dimmers species on support [6].

An important application associated with Niobium catalysts relies on the oxidation of organic compounds achieved under mild conditions [7–9]. More recently, Bolotin and colleagues presented a review describing several metal- involving pathways to render oximes, but the direct oxidation of primary amines into its corresponding oximes is still object of study [10].

Considering this scaffold, some endeavors have been reported in the literature (Fig. 1a–d). For instance, the conversion of benzylamine into its corresponding oxime using an expensive Ti based catalyst required high loadings (Fig. 1a), while the use of unsupported Nb_2O_5 resulted only in modest con- version rates (Fig. 1b) [11]. Additionally, this last work indicated that using only hydrogen peroxide, in absence of any catalyst, led to very low conversions. In order to achieve higher yields, the employment of a more hazardous and expensive oxidizing agent such as m-CPBA was required (Fig. 1c) [12]. On the other hand, the use a homogeneous catalyst such as methyltrioxorhenium, despite the good yields observed, did not allow further use due to the nature of the catalytic system (Fig. 1d) [13].

Recently, our research group reported the development of a series of mixed oxides supported niobium photocatalysts, successfully employed in the conversion of aromatic amines to azoxy compounds [6]. Inspired by these findings, we envisioned these catalysts were then applied

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* Corresponding authors.
E-mail addresses: alexandre.leitao@ufjf.edu.br (A.A. Leitão), giovanni.amarante@ufjf.edu.br (G.W. Amarante).

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towards reactions with a primary amine such as benzylamine, in the presence of hydrogen peroxide as oxidizing agent, aiming the selective formation of benzaldehyde oxime (Fig. 1e).

Quantum chemistry calculations are an excellent investigation tool to provide information hardly obtained experimentally. Hence, in this work were used to assist the characterization of the catalysts, to understand part of the oxime formation mechanism and to obtain the correlated reaction barriers.

2. Experimental details

2.1. General information

All reagents were obtained commercially and used without further purification. General synthetic procedures were performed by addition of 5 mmol of benzylamine into a round bottom flask containing 5 ml of methanol followed by addition of 20 mmol of H_2O_2 (30 % v/v) and 10 % m/m of catalyst under continuous stirring up to 72 h. Analytical thin-layer chromatography (TLC) was performed on precoated aluminum TLC plates (silica gel 60 F254) and visualized by a UV lamp (254 nm). Conversion rates and selectivity were determined by area normalization in a Shimadzu GC–MS 2010 Plus single quadrupole equipped with electroimpact ionization source and a Restek Rtx-5MS fused silica capilary column (30 m, 0.25 mm × 0.25 μm). Yields refer to chromatographically purified and spectroscopically pure compounds, unless stated otherwise. ^{1}H spectra were recorded on 300 and 500 MHz spectrometer and spectra are referenced to CDCl3 (7.26 ppm). Chemical shifts are reported in ppm. Peak multiplicities are designated by the following abbreviations: s, singlet; d, doublet; m, multiplet and J, coupling constants in hertz. Infrared spectra were obtained in Bruker Alpha and Agilent Cary 630 FT-IR spectrometers, using the Attenuated Total Reflectance (ATR) method, recorded from 4000−600 cm^{-1} and resolution of 4 cm^{-1}. The 27Al solid-state NMR (SSNMR) spectra were recorded in a Bruker 300 MHz spectrometer, operating at a Larmor frequency of 78 MHz and using an AlCl3.6H2O sample as standard (0 ppm). Difractograms were recorded in Bruker AXS D8 Da Vinci diffractometer, equipped with Ni-filtered CuKα radiation (λ = 1.5418), a Lynxeye liner Position Sensitive Detector and the following optics: primary beam Soller slits (2.94◦), fixed divergence slit (0.3◦) and receiving slit 7.68 mm. The generator was set at 40 kV and 40 mA.

2.2. Catalysts preparation

Each Layered Double Hydroxide (LDH), precursors of mixed metal oxides, was prepared by a co-precipitation of a mixture of metallic nitrates solution into an aqueous solution of NaOH (254 mmol, 6.35 equiv.) and Na2CO3 (25.4 mmol, 0.65 equiv.) at constant pH (10). For the LDH-01 system it was considered an aqueous solution of Zn(NO3)

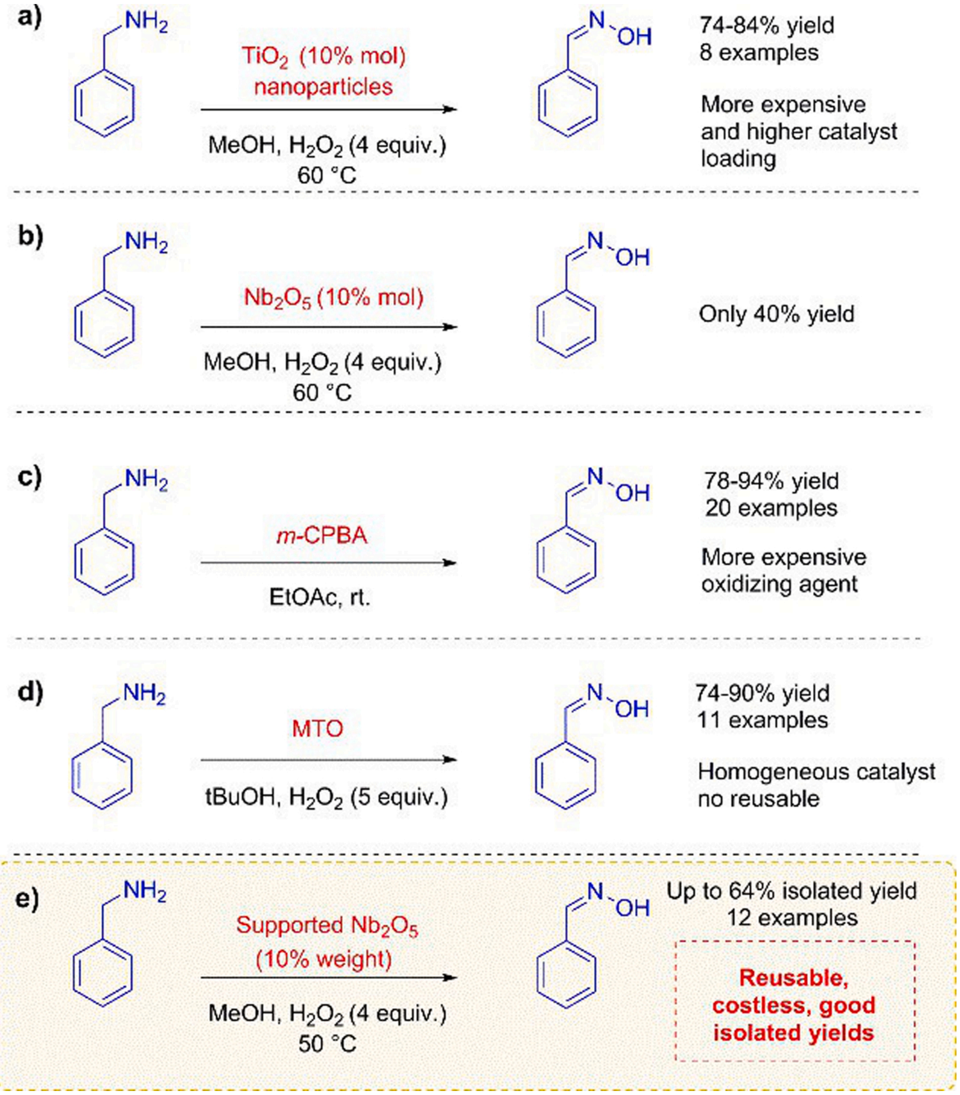


Fig. 1. Several oxidation procedures described for the conversion of amines into the corresponding oximes (a-d) and our proposal (e).

2.6H2O (80 mmol, 2 equiv.) and Al(NO3)3.9H2O (40 mmol, 1 equiv.). For LDH-02 system it was considered an aqueous solution of Mg(NO3) 2.6H2O (80 mmol, 2 equiv.) and Al(NO3)3.9H2O (40 mmol, 1 equiv.). Finally, for the LDH-03 system it was considered an aqueous solution containing Zn(NO3)2.6H2O (40 mmol, 1 equiv.), Mg(NO3)2.6H2O (40 mmol, 1 equiv.) and Al(NO3)3.9H2O (40 mmol, 1 equiv.).

For each LDH system, both metallic and basic solutions were mixed in a dropwise manner under continuous stirring, kept for 24 h. The white precipitate observed was filtered in paper filter and washed with distilled water until pH 7. The filtrates were dried in oven at 50 ◦C for 24 h. The dried materials were macerated and calcinated at 500 ◦C in a ceramic muffle furnace for 5 h, leading to the mixed metal oxides MMO-01 (Zn^{+2} 0.67 M/Al^{+3} 0.33 M) MMO-02 (Mg^{+2} 0.67 M/Al^{+3} 0.33 M) and MMO-03 (Zn^{+2} 0.33 M/ Mg^{+2} 0.33 M/Al^{+3} 0.33 M).

Finally, a solution of ammonium niobium oxalate (6.3 mmol), was prepared in 5 ml of distilled water and added in a dropwise manner to 5 g of each MMO support under maceration. The resulting materials were calcinated at 500 ◦C for another 3 h aiming a final supported amount of 10 % m/m of Nb_2O_5, leading to the mixed oxide-supported niobium-based catalysts NbCAT-01, NbCAT-02 and NbCAT-03.

3. Theoretical methodology

Ab Initio calculations were performed using the Quantum-Espresso package [14]. The electronic structure calculations were based on density functional theory (DFT) implemented with periodic boundary conditions [15,16]. The effect of the exchange-correlation (XC) potential was explored by generalized gradient approximation with PW91 functional. Kohn-Sham orbitals were expanded in a plane wave basis set to a kinetic energy cut-off of 50 Ry for all structures [17]. For MgO:Al,Zn terrace calculations, the unit cell of the MgO(001) surface was replicated four times on the x axis (a = 8.52) and three times on the y axis (b = 6.39). A vacuum layer of 25 was used in the slab models to avoid interactions between the periodic images perpendicular to the surface.

The minimum energy path (MEP) was constructed in order to obtain the transition state, the reaction barrier and the main structural modifications involved in the process of the tautomerism. The calculation of the MEP connecting different minimum geometries is based on the climbing image nudged elastic band (CI-NEB) method [18,19] which accurately describes the MEP between the initial and the final states of a reaction, and evaluates the transition state and the resulting activation energy barriers. A total of 11 configurations were used to compute the MEP.

4. Results and discussion

4.1. Catalysts characterization

The materials from LDH, MMO and NbCAT series were analyzed through I.R., Powder X-Ray diffraction and ^{27}Al Solid State NMR (data available in supporting information). The Infrared analysis for each LDH system indicated O—H stretching signals at 3500 cm^{-1} from water molecules and hydroxyls and C—O stretching at 1400 cm^{-1} from carbonate present in LDH interlayers. Those signals were abrogated after calcination step leading to the obtention of the mixed metal oxides as result from the obliteration of LDH lamellar structures. Similar patterns were maintained after impregnation of ammonium niobium oxalate solution to each MMO with wide signals verified at 500–600 cm^{-1} which may relate to a symmetric stretching metal-oxygen bonding. The XRD diffractograms showed broad patterns for MMO series when compared to its LDH precursors indicating the obtention of a low crystallinity powder. The presence of peaks 2θ (CuK_α) around 33° (100), 34° (002), 36.5° (101), 48° (102), 57° (110), 63° (103) and 69° (112) for MMO-01 and MMO-03, which consists in Zn^{+2}/Al^{+3} (0.67/0.33 M) and $Zn^{+2}/Mg^{+2}/Al^{+3}$ (0.33/0.33/0.33 M) mixed oxides, respectively, suggests Zn—O bonding formation after calcination of LDH systems. These findings also support I.R. data indicating the breakage of LDH lamellar structures resulting in a thin powder composed by a mixture of metal oxides. After impregnation of ammonium niobium oxalate solution to each MMO little to no difference were observed in XRD patterns, suggesting a good dispersion of niobium species over the surface of MMO systems. Additionally, the Solid State ^{27}Al NMR reveals signals close to 50 and 70 ppm for MMO and NbCAT, absent in LDH series, suggesting the formation of a distorted tetrahedral sites and AlO_4 respectively, after calcination of LDH to obtain the MMO. Further details and analyses related to NbCAT catalysts development and characterization can be found in our recent manuscript [6].

4.2. Reactions towards benzylamine

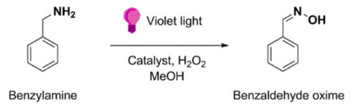
Our research investigation initiated by taking the NbCAT-01 catalyst in the presence of benzylamine, using 30 % aqueous H_2O_2 as oxidizing agent and MeOH as solvent and at room temperature. Additionally, based on previous results from our group, indicating higher catalytic activities when in presence of low visible spectrum light, the reactions were carried out under irradiation of violet light (380 nm) in a reaction chamber equipped with a 50 W LED (Table 1).

The first series of results indicated a good conversion of starting material using 4 equivalents of H_2O_2 within 72 h of reaction under continuous irradiation of violet light (Table 1, entries #1 and #2). However, only modest selectivity for oxime production was achieved, being identified the formation of benzylidene benzylamine as side product. These results may relate to the dehydrogenation of amine mediated by transition metal oxides. The hydrolysis of the corresponding imine, followed by a condensation with the primary amine may lead to the dimer, as suggested in the literature [20].

Interestingly, when the reactions were performed in absence of light (entry #3) or even under room light (entry #4), led to slightly inferior conversion rates. These data appear to differ from previous findings in the literature, indicating the oxidation of benzylamine into the corresponding imine when Nb_2O_5 was used as photocatalyst. This conversion was achieved even wavelengths up to 460 nm, but poorly 10 registered in the absence of light. In addition, previous results in our research group, indicated the light dependence of these reactions [6].

On the other hand, as mentioned before, a background reaction by

Table 1
Reactions under violet light.



Entry	Parameters	Amine conversion (%) *	Selectivity for Oxime (%) *
Influence of H_2O_2			
#1	4 eq. H_2O_2	89	51
#2	6 eq. H_2O_2	82	45
Influence of light and time			
#3	Dark	70	44
#4	Room Light	73	53
#5	48 h	71	47
Influence of catalyst			
#6	No catalyst	42	37
#7	Pure Nb_2O_5	46	30
#8	MMO-01	76	37
#9	MMO-02	71	45
#10	ZnO	97	55

a) Standard reaction conditions: 10 % weight catalyst (NbCAT-01), violet light, 4 equivalents of H_2O_2 and MeOH as solvent, unless otherwise mentioned. Reactions kept for 72 h unless otherwise mentioned. *Calculated over GC–MS; b) NbCAT-01 consisted in 10 % m/m of Nb_2O_5 impregnated over MMO-01. MMO-01 consisted in Zn^{+2}/Al^{+3} (0.67/0.33 M) based mixed metal oxide while MMO-02 consisted in Mg^{+2}/Al^{+3} (0.67/0.33 M) based mixed metal oxide.

using the oxidizing agent H_2O_2, in absence of any catalyst, was verified (entry #6). As result, a major conversion rate and selectivity drop was observed for oxime as product.

Using pure Nb_2O_5 as catalyst in presence of H_2O_2 resulted in lower conversion rates, in accordance with previous data from literature (entry #7) [11]. Moreover, the result indicated an increase of the dimer benzylidene benzylamine as main reaction product.

To our surprise, using the Zn/Al support (MMO-01) instead of our supported Nb-based catalyst (NbCAT-01) resulted in good conversion of starting material, but with much lower selectivity for oxime (entries #8 and #9). To the same extent, using ZnO as catalyst resulted in almost complete consumption of starting material, but once again, only modest selectivity for oxime production was achieved (entry #10).

These last observations may relate to the fact that the interaction between H_2O_2 and the surface of a catalyst may dictate the cleavage of oxygen atom bonds, leading to formation of different reactive oxygen species. An interesting series of work demonstrated that the interactions between hydrogen peroxide with different metallic species might have diverge, with similar findings for Nb oxides, leading to distinct profile in oxidation reactions [21,22]. These results may suggest that the supported niobium oxide species can interact in a different manner with hydrogen peroxide in the media, resulting in a different behavior towards conversion of benzylamine. An enhancement of acidic or basic properties of ZnO when mixed with other oxides is also an interesting property of zinc-based catalysts, and the use of ZnO in photodegradation of aniline and benzylamine in aqueous solution has been already demonstrated under visible light [23]. Despite Nb based catalysts have been recognized by their acidic character, previous work from our group using NbCAT series towards isopropanol conversion showed dehydrogenation route leading to acetone rather than a dehydration, suggesting that the zinc content within NbCAT may be associated with a higher surface basicity for those catalysts [6].

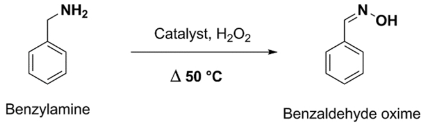
Considering these first series of results, the incidence of light does not seem to alter significantly the course of reactions (entries #3 and #4). The occurrence of an interesting background reaction upon contact between benzylamine and H_2O_2 in the media (entry #6), along the influence of supports on redox properties over the H_2O_2 degradation, otherwise, may suggest the occurrence of a distinct route for the oxidation of benzylamine than the classical electron transfer mechanism attributed to semiconductor photocatalysts. Based on these without the use of light irradiation, but exploring the effect of temperature over the course of reactions (Table 2).

When the reactions were carried out at 50 ◦C, the complete consumption of starting material and an increase in terms of selectivity for oxime as pro- duct were observed. Reaction using 4 equiv. of H_2O_2 and for 72 h gave the corresponding product in 72 % yield (entry #13). An increase in the temperature up to 80 ◦C did not seem to produce major changes in terms of selectivity. Otherwise, switching the amount of oxidizing agent seemed to reduce conversion rate and selectivity. Using ethyl acetate or ethanol as solvent also did not led to significant changes in results, but apolar solvents either toluene or chloroform resulted in loss of conversion rates.

Despite resulting in same conversion rates, NbCAT-01 catalyst led to greater selectivity for oxime production when compared to the use of support MMO-01 as catalyst (entry #25). Interestingly, the use of catalysts NbCAT-02 (entry #23) and NbCAT-03 (entry #24) preserved conversion rates, but gave lower selectivity. On the other hand, the use of their supports resulted in lower con- version rates and selectivity (entries #26 and #27).

Considering higher amount of Zn species contained within NbCAT-01 system, reactions were performed in presence of ZnO and Zn powder as catalysts, leading to complete consumption of starting material, but with lower selectivity for oxime as when compared to NbCAT-01 system. When the unsupported pure Nb_2O_5 was applied as a catalyst, a major loss in terms of selectivity was registered (entry #30). In this particularly case, an increase in formation of the dimer benzylidene benzylamine as byproduct was detected.

Table 2
Reactions under heating.



Entry	Parameters	Amine conversion (%) *	Selectivity for Oxime (%) *
Time			
#11	24 h	82	53
#12	48 h	98	59
#13	72 h	97	72
Influence of H_2O_2			
#14	6 eq. H_2O_2	99	45
#15	2 eq. H_2O_2	56	68
Temperature			
#16	40 °C	99	55
#17	80 °C	99	72
Solvent comparison			
#18	AcOEt	99	68
#19	EtOH	96	66
#20	Toluene	68	68
#21	Chloroform	85	67
Catalysts evaluation			
#22	No catalyst	53	43
#23	NbCAT-02	97	58
#24	NbCAT-03	95	49
#25	MMO-01	99	58
#26	MMO-02	78	54
#27	MMO-03	89	49
#28	ZnO	99	59
#29	Zn powder	99	59
#30	Nb_2O_5	90	27

a) Standard reaction conditions 10 % weight catalyst (NbCAT-01), 50 °C, 4 equivalents of H_2O_2 and MeOH as solvent, otherwise mentioned. Reactions kept up for 72 h unless otherwise mentioned. * Calculated over GC–MS; b) The catalysts NbCAT-01, NbCAT-02 and NbCAT-03 consisted in 10 % m/m of Nb_2O_5 impregnated over the corresponding mixed metal oxides MMO-01 (Zn^{+2} 0.67 M/Al^{+3} 0.33 M) MMO-02 (Mg^{+2} 0.67 M/Al^{+3} 0.33 M) and MMO-03 (Zn^{+2} 0.33 M/ Mg^{+2} 0.33 M/Al^{+3} 0.33 M).

While in absence of any catalyst system a clearly unselective background reaction occurs (entry #22), the abovementioned data suggests a compelling synergic effect between Nb oxide and the support MMO-01, showing higher content of Zn species, resulting in pronounced gain towards conversion and selectivity. The NbCAT-01 system clearly proved to be the most effective in the series tested (Fig. 2a) and showed reproductive results after three reusable consecutive cycles towards reactions with benzylamine without any additional thermal treatment (Fig. 2b). Interestingly, similar reuse results were observed by our group when applying the same catalyst towards aniline conversion suggesting loss of catalytic activity after fourth reuse cycle [6]. This may be associated to the leaching of Nb species from the mixed oxide surfaces.

Considering the previous experiments and the best conditions established with the use of NbCAT-01 (entry #13), a series of reactions with different substituted benzylamines was then conducted (Scheme in Fig. 3).

The benzylamines were submitted to the optimized reaction conditions and the corresponding oximes were isolated in good yields, ranging from 51 to 64 %. The reactions were carried out in the presence of substituted benzylamine derivatives containing groups bearing -o, -m and -p positions on the aromatic ring and all compounds were well tolerated. Remarkably, α-substituted benzylamine derivatives could be used as substrates and gave the corresponding oximes in 54 and 56 % isolated yield.

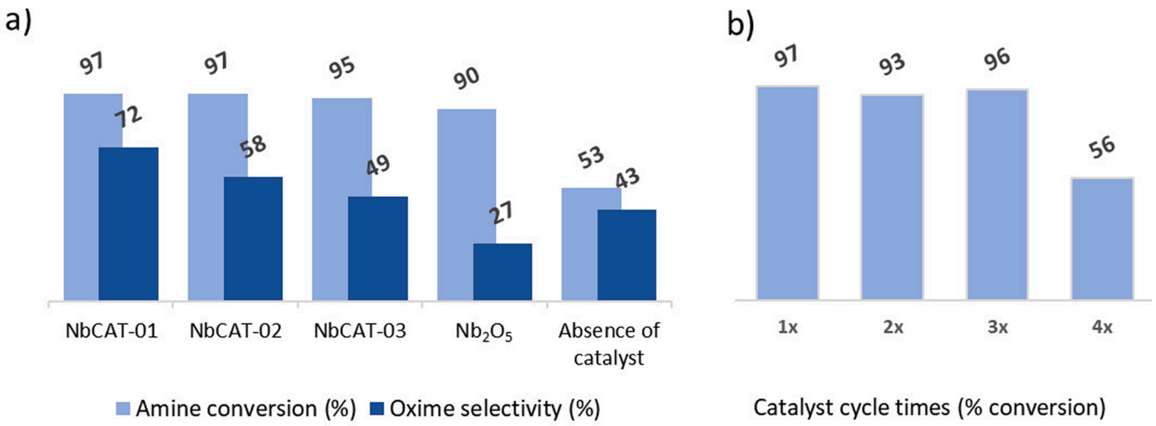


Fig. 2. a) Comparison between different catalysts systems towards oxidation of benzylamine using H_2O_2 as oxidizing agent; b) Lifecycle of catalyst NbCAT-01 after 4 consecutive cycles, washed in MeOH and dried in low pressure for 1 h prior to each new cycle, without any further calcination step. The catalysts NbCAT-01, NbCAT-02 and NbCAT-03 consisted in 10 % m/m of Nb_2O_5 impregnated over the corresponding mixed metal oxides MMO-01 (Zn^{+2} 0.67 M/Al^{+3} 0.33 M) MMO-02 (Mg^{+2} 0.67 M/Al^{+3} 0.33 M) and MMO-03 (Zn^{+2} 0.33 M/Mg^{+2} 0.33 M/Al^{+3} 0.33 M).

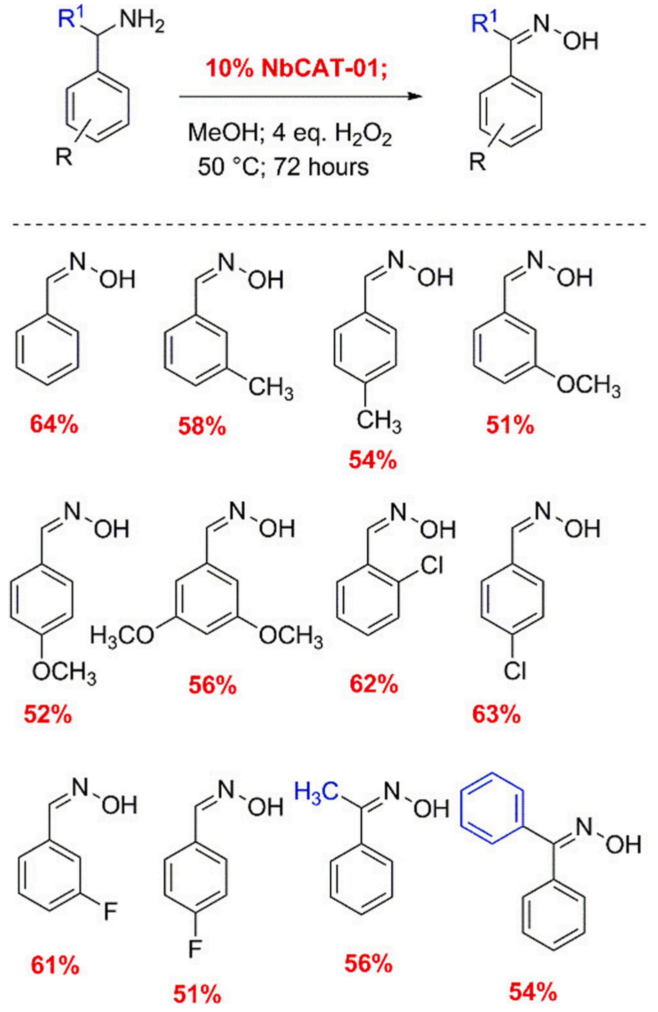


Fig. 3. Substrate reaction scope.

4.3. Mechanistic investigation

The proposed reaction mechanism towards oxidation of benzylamine with H_2O_2 suggests that the reaction proceeds to selective benzylamine oxidation into nitroso intermediate, following to oxime tautomer. In this sense, *ab initio* calculations were performed to evaluate the energy barriers of the oxime tautomer formation from nitroso intermediate. The adsorption of both compounds was initially done on NbO_x supported on the mixed oxide catalyst model. This model was obtained through a detailed study of Nb oxide grafting on support performed previously [6]. The adsorption energies (ΔE_{ads}) were -17.50 kcal mol^{-1} and -17.09 kcal mol^{-1} for oxime tautomer and nitroso intermediate, respectively. The oxime is slightly more stabilized for the catalyst surface than the nitroso intermediate. Fig. 4 shows the adsorbent-adsorbate scheme.

The results show a weak interaction between nitroso intermediate and oxime with catalyst surface, as indicated by the distances N-Nb, 2.47 and 2.34, respectively. The distances N═O (1.21), N—C (1.50) and C—C (1.49) in the adsorbed nitroso intermediate are equal to the free molecule values, and the distances Nb—O (1.87) and Nb−OH (2.00 and 2.07) remain practically the same as the isolated catalyst. Many sites of the catalyst were evaluated for adsorption reaction and the configurations presented in Fig. 4, for both molecules, were the most stable. These structures were used in the calculation of the minimum energy paths (MEPs) to obtain the reaction barriers and the main structural modifications.

The structure of the adsorbed nitroso intermediate through the niobium atom of the catalyst corresponds to the reactant to the tautomerism process. The molecule adopts a preferential conformation in such a way than its H atom from H2C-N group interacts with the −OH group of the catalyst. The first transition state (TS) consists of the proton transference from the nitroso intermediate to catalyst resulting in an unstable water molecule formation. The MEP reported in Fig. 5 implies a first activation energy barrier of 19.5 kcal mol^{-1}, which was calculated using the energy difference between the saddle point structure and the reactant structure. As the reaction proceeds through the first transition state, there is a progressive approximation between the hydroxyl group from the catalyst and the nitrogen-bound oxygen from the molecule which finally results in the transfer of the proton from this hydroxyl group to the oxygen atom of the molecule and consequently the formation of the oxime compound. The reaction proceeds along the MEP with the catalyst restructuring by the loss of a proton from the water molecule and two hydroxyl group formation. The second reaction barrier is 1.93 kcal mol^{-1} and it is related to oxime rotation. It can also be noted that the product represents the most stable configuration along the whole reaction path with −29.0 kcal mol^{-1}. The simulated MEP of the corresponding reaction is reported in Fig. 5 with the illustration of the initial reactant, the transition states (TS), and the resulting product.

The activation barrier for the rate-limiting step, among the calculated ones, is 19.5 kcal mol^{-1}, which corresponds to the formation of a

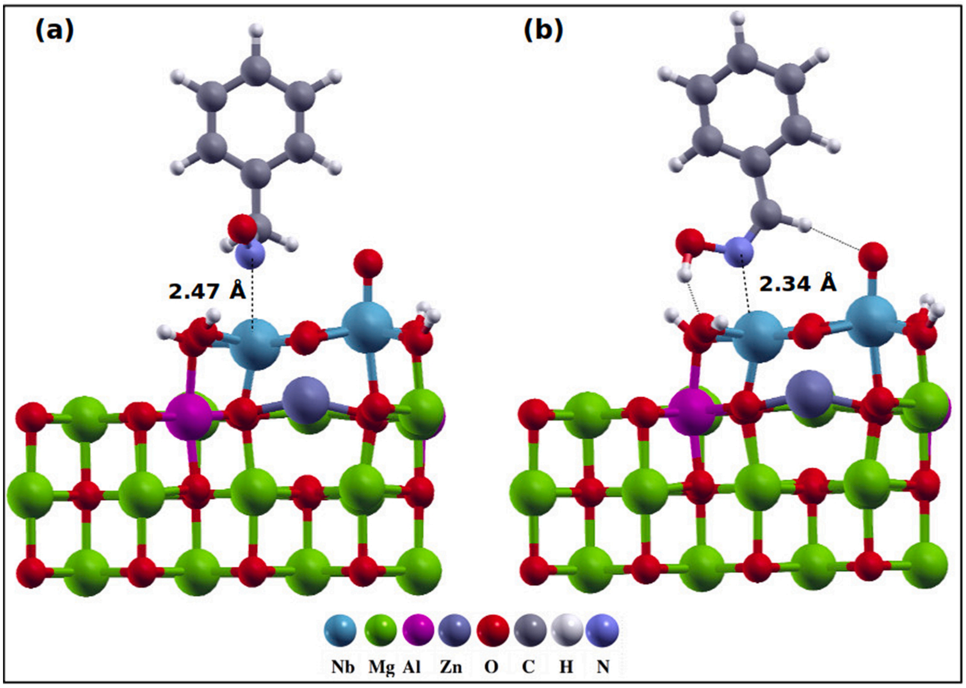


Fig. 4. Optimized models for a) nitroso intermediate and b) oxime adsorbed on NbO*x* supported on mixed oxide catalyst.

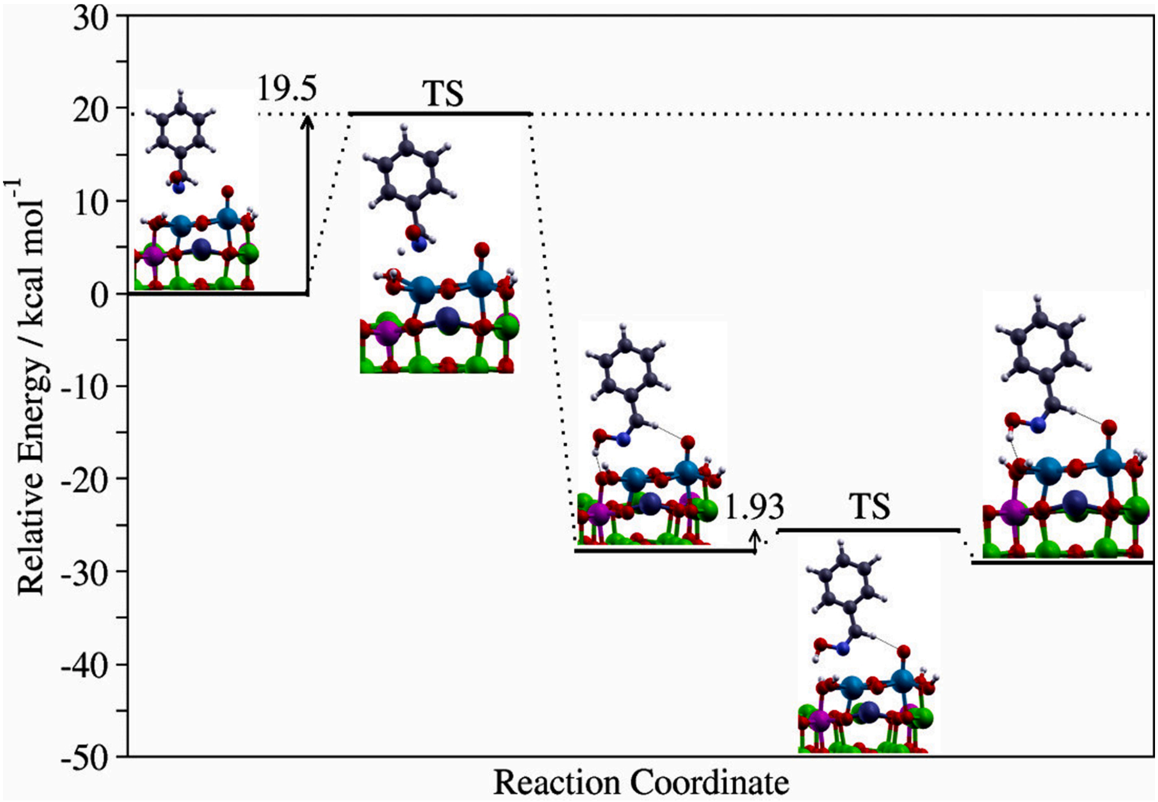


Fig. 5. Calculated minimum-energy path for the tautomerism between nitroso intermediate and oxime compound catalyzed by NbO*x* supported on mixed oxide.

water molecule by the nitroso intermediate hydrogen donation to the catalyst. As can be noticed, the oxime formation is kinetically and thermodynamically favored, since, the reverse barriers are much larger than the direct and the product is more stable than the reactant.

To confirm the catalytic activity of the mixed oxides supported niobium, the tautomerism process was evaluated without the catalyst presence, as a unimolecular reaction. The reaction barrier and the reactant, transition state and product structures can be seen in Fig. 6.

The comparison between the calculated minimum-energy path in Figs. 5 and 6 shows clearly the potential of the mixed oxides-supported Niobium-based catalysts to the conversion of the nitroso intermediate in the oxime compound. The calculated activation energies are 19.5 and

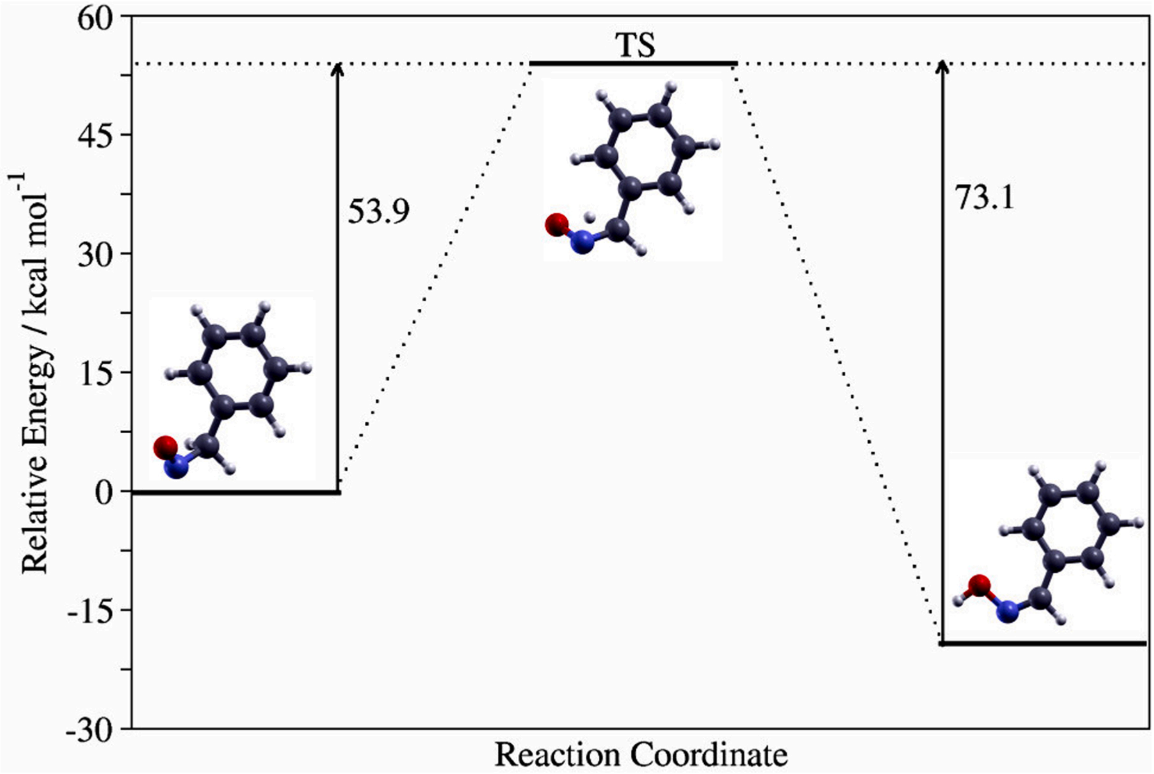


Fig. 6. Calculated minimum-energy path for the tautomerism between nitroso intermediate and oxime compound without catalyst.

53.9 kcal mol^{-1} for the reaction with and without the catalyst, respectively. The presence of the Niobium-containing catalyst cuts the activation energy to almost a third.

5. Conclusions

The application of mixed oxides-supported niobium-based catalyst for selective conversion of benzylamines to oximes is presented. Reaction carried out at 50 ◦C led to good results in terms of conversion rates and selectivity for oxime as main reaction product. Several substituted benzaldehyde oximes were obtained under the optimized reaction conditions, employing the promptly available, inexpensive and harmless hydrogen peroxide as oxidizing agent, leading to good isolated yields. Besides the advantage of employing a reduced amount of niobium species over the supports surface, the mixed oxides-supported niobium-based catalyst NbCAT-01 led to the best conversion rates and selectivity for oxime production (up to 72 %). Interestingly, α-substituted benzylamines were well tolerated and gave the corresponding oximes in good isolated yields. DFT calculations suggested that the reaction proceed to selective benzylamine oxidation into nitroso intermediate, following by formation of the corresponding oxime tautomer mediated by unstable water produced by NbO_x supported catalyst. To the best of our knowledge, this consists in the first mixed oxides-supported niobium-based catalyst for selective oxidation of benzylamines to oximes.

CRediT authorship contribution statement

Álisson Silva Granato: Investigation, Writing - original draft. **Gustavo S. Gonçalves de Carvalho:** Investigation. **Carla G. Fonseca:** Investigation, Writing - original draft. **Javier Adrio:** Conceptualization. **Alexandre A. Leitão:** Conceptualization, Supervision. **Giovanni Wilson Amarante:** Conceptualization, Supervision, Writing - original draft, Project administration.

Declaration of Competing Interest

The authors report no declarations of interest.

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Appendix A. Supplementary data

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