



Article Selective Catalytic Oxidation of Benzyl Alcohol by MoO₂ Nanoparticles

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Abstract: Selective oxidation of benzyl alcohol to benzaldehyde was carried out with MoO₂ nanoparticles (MoO₂ NPs). MoO₂ NPs were synthesized by two different approaches and characterized by several techniques. The synthesis was done by a hydrothermal procedure using ethylenediamine and either Fe₂O₃ or hydroquinone. In the latter case, an additional calcination step under N₂ was performed to eliminate passivating agents at the surface of the nanoparticles. The synthesized nanocatalysts showed similar catalytic properties, being efficient catalysts in the oxidation of benzyl alcohol. High substrate conversion and product selectivity were achieved under all tested conditions. Studies were conducted using two different oxidants: *tert*-butyl hydroperoxide and hydrogen peroxide, in our continuous effort to obtain more efficient catalysts for more sustainable catalytic processes. When H₂O₂ was used as the oxidant, 94% yield was achieved with 100% selectivity for benzaldehyde, which was a very promising result to undergo other studies with this system. Moreover, to elucidate some aspects of the reaction mechanism, a study was conducted, and it was possible to conclude that the reaction undergoes, to some extent, through a radical mechanism with both oxidants.

Keywords: MoO₂ nanoparticles; green catalysis; oxidation; hydrogen peroxide; benzyl alcohol

1. Introduction

Molybdenum complexes are largely known for their good catalytic activity and have been widely used, especially in oxidation reactions, as homogeneous catalysts. However, heterogeneous catalysts present a much easier way of separation and can be easily recyclable. Nanotechnology has been a major breakthrough in recent times, allowing the possibility of producing materials with a higher surface area. Hybrid and non-hybrid metal-oxide nanoparticles have proven to be very active heterogeneous catalysts [1,2], while some can be highly selective in oxidation reactions [3]. Metal and metal oxide-containing nanostructures with different morphologies (nanowires, nanobelts, nanofibers, etc.) are known to exhibit better adjustable properties in fields such as gas sensors, electrodes, and optoelectronics than their conventional counterparts [4].

Partial oxidation of primary alcohols to aldehydes is of great interest worldwide because of its wide application in the perfume and food industries. However, it remains difficult to avoid over oxidation and specially to make them without using harmful solvents in the process. The oxidation of benzyl alcohol (BzOH) to benzaldehyde (BzCHO) is an important reaction because of the wide applications of the latter in industry [5]. Numerous methods have been developed to achieve the desired transformation with the use of a stoichiometric amount of oxidant. The oxidation of benzyl alcohol to benzaldehyde continues to be studied, since this reaction has a high reactivity, but presents selectivity issues yielding some by-products, which are well-known [6]. In this context, both homogeneous and heterogeneous transition metal-based catalysts have been developed for aerobic alcohol oxidations [7].

The liquid phase catalytic oxidation method is more common for this process than the gas phase oxidation, whereas the control in selectivity is generally a problem for the latter. In traditional oxidation processes, large amounts of toxic and volatile organic solvents and inorganic oxidants (CrO₃, KMnO₄, NaClO, MnO₂, etc.) are extensively used [8,9]. Therefore, these oxidants are toxic, difficult to handle, and expensive. They are also less selective to the desired product and generate a larger amount of waste. From an environmental point of view, such conditions are mandatorily unwanted, while searching for more sustainable alternatives is highly desirable.

In recent years, nanocatalysts have received great attention in nanoscale heterogeneous catalysis with the advantage of practical recovery by separation of the solid catalyst from the medium. They also offer higher surface areas, low-coordinating sites, and surface vacancies compared to bulk heterogeneous systems.

In continuation of our efforts to investigate more sustainable processes for the catalytic oxidation of several organic substrates, we report in this work the oxidation of benzyl alcohol catalyzed with two different types of synthetized MoO_2 nanoparticles (Scheme 1).



Scheme 1. Schematic representation of the reactions occurring with the different catalysts reported in this work.

In this work, we synthesized different MoO₂ nanoparticles and explored their catalytic activity in the oxidation of benzyl alcohol to benzaldehyde in a solventless process, preferably. For MoO₂ synthesis, we used a hydrothermal method using ethylenediamine (*EDA*) as the reducing agent and Fe₂O₃ [10] or hydroquinone [11] as assisting agents. In the final product, the assisting agent remains in residual amounts at the surface of the material [11]. Fe₂O₃ nanoparticles have also been produced by a co-precipitation method [12,13] to understand the influence of iron oxide in catalytic studies.

The catalytic experiments were conducted by testing the temperature of the reaction, amount of oxidant, and the different types of nanoparticles, in accordance with the synthesis method. Several reaction conditions were screened. Two different oxidants were used, *tert*-butyl hydroperoxide (TBHP) and hydrogen peroxide (H₂O₂), and different amounts of them were added to the reactions to study the influence of the oxidant on the catalytic oxidation of benzyl alcohol. Different reaction temperatures and solvents were tested to assess the optimized reaction conditions for this system.

2. Results and Discussion

2.1. Characterization of the Catalyst

MoO₂ NPs were synthesized by two different methods as reported previously [10,11,14,15]. This involved merging the solvothermal synthesis with thermal reduction using commercial MoO₃ in the presence of a mixture of ethylenediamine (*EDA*) as the reducing agent and Fe₂O₃ (first method) or hydroquinone (second method) as assisting agents, respectively [10]. In the former case, synthesis with Fe₂O₃ working as an assisting agent has two roles: the first is to act as a nucleation seed for the growth of the MoO₂ NPs; the second is a role as a regenerator of the oxidized *EDA* during the process. These MoO₂ NPs will be denoted hereafter as MoO₂–Fe₂O₃ NPs.

In the second method, the synthesis of MoO_2 NPs was done by replacing Fe_2O_3 by hydroquinone, using a reported procedure [11]. However, since it was described that hydroquinone was retained at the surface of the NPs [14], the final product was calcined under nitrogen to prevent the oxidation of MoO_2 back to MoO_3 , in order to obtain MoO_2 NPs without any trace of (in)organic agents. These will be denoted afterward as MoO_2 . A synthesis procedure test without *EDA* and Fe_2O_3 (or hydroquinone) was also performed without any success [14].

These MoO₂ NPs synthesized by the different protocols were characterized by powder X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), and Fourier-Transform Infrared Spectroscopy (FTIR). The XRD powder pattern profile of the MoO₂–Fe₂O₃ NPs (Figure 1) displayed Bragg diffraction peaks corresponding to a typical pseudo-tetragonal rutile MoO₂ phase in agreement with other literature reports [10] (P63/mmc, JCPDS card, 50-0739, a = 2.838 Å, c = 4.720 Å). Analysis of the XRD powder pattern also showed that there was the presence of both Mo- and Fe-containing oxide phases. However, specifically concerning the Mo oxide, the pattern also showed that this was a pseudo-tetragonal rutile MoO₂ sample (i.e., without any other detectable Mo-containing phase) [14]. The average crystallite size of the NPs was 16.7 nm in the case of MoO₂–Fe₂O₃, which agreed with the published data [11,14].



Figure 1. Powder X-ray diffraction (XRD) for the calcined MoO₂ and MoO₂–Fe₂O₃ nanoparticles (NPs) (* denotes silica diffraction peak from the support glass slide).

For the (calcined) MoO₂ NPs, the XRD powder pattern profile depicted in Figure 1 shows the Bragg diffraction peaks corresponding only to the pseudo-tetragonal rutile MoO₂ phase [10] (P63/mmc, JCPDS card, 50-0739, a = 2.838 Å, c = 4.720 Å). The obtained X-ray diffraction pattern shows three reflections at 2θ = 36.73°, 53.49°, and 66.16° indexed to 100, 102, and 110 planes, respectively. The XRD powder diffraction pattern also showed a wide peak at 2θ = 23.5° that could be attributed to the silica from the support glass slide. The average crystallite size of the nanoparticles, estimated using the Scherrer equation, was 9.7 nm, approximately.

SEM microscopy was used to assess the morphology of both types of MoO_2 nanoparticles. Figure 2 shows the SEM images from both MoO_2 nanoparticles confirming that the structures were formed by aggregated ultrathin nanosheets, as reported in previous studies. The aggregated ultrathin nanosheets formed hierarchical uniform-sized tremella-like structures, displaying an almost spherical morphology.

Fourier-transform infrared spectroscopy (FTIR) was used to characterize the calcined MoO₂ NPs, as shown in Figure 3. Given that ethylenediamine and hydroquinone were removed by a calcination step, this spectrum was simpler than when the calcination step was not carried out [11]. In this way, the FTIR spectrum of the MoO₂ NPs was typical of a Mo oxide, showing a broad band at 3417 cm⁻¹ ascribed to the stretching modes of the hydroxyl groups at the surface of the MoO₂ nanoparticles.

The absorption band at 1626 cm⁻¹ was due to the O–H bending modes [16,17]. Other bands observed at 894 and 711 cm⁻¹ could be ascribed to the vibration of the Mo–O–Mo bonds [18].



Figure 2. Scanning Electron Microscopy (SEM) images of the MoO₂–Fe₂O₃ and MoO₂ calcined nanoparticles (NPs).



Figure 3. Vibrational Fourier-Transform Infrared (FTIR) spectrum of the calcined MoO₂ NPs.

2.2. Catalytic Tests and Optimization of Alcohol Oxidation Conditions

Liquid phase oxidation of benzyl alcohol (BzOH) to benzaldehyde (BzCHO) was selected as the model reaction to assess the performance of the catalysts herein reported and to find the optimized reaction conditions using the MoO_2 –Fe₂O₃ and MoO_2 calcined nanoparticles (MoO_2 NPs) as catalysts. First, the optimization of the reaction conditions was achieved by testing the conversion of BzOH into BzCHO under solvent-free conditions. Following that, a series of experiments was conducted to investigate crucial factors such as different types of solvents and the influence of the temperature on the reaction, namely the solvent acetonitrile at different temperatures, 353 or 383 K, and decane at 383 K. The catalysts were tested with different oxidants. *Tert*-butyl hydroperoxide (TBHP) and hydrogen peroxide (H_2O_2) were used as oxygen donors and to evaluate the oxidant effects on the catalytic system's performance, the TBHP:substrate ratio was varied using 100, 150, and 200 mol%.

Blank runs (without the catalyst and in the presence of an oxidizing agent) gave virtually no conversion (<3%) of the starting material.

In all tested conditions using the studied catalysts, conversions were high and benzaldehyde was obtained as a major product, achieving excellent yields. As seen in Table 1, and as a general rule, in all cases, benzyl alcohol was converted to benzaldehyde with high selectivity. The only exception was when γ -Fe₂O₃ was used as the catalyst for control purposes to understand the influence of Fe₂O₃ in the MoO₂-Fe₂O₃ catalyst.

Entry	Catalyst	Oxidant (mol%)	Yield (%) [a]	Selectivity (%) [b]		
5	y_			BzCHO	BzCOOH	
1		TBHP (200%)	74	91	9	
2	MoOr ForOr	TBHP (150%)	95	92	7	
3	M0O ₂ -re ₂ O ₃	TBHP (100%)	61	92	7	
4		Leaching 2 h/24 h 22/27		100/100	0	
5		TBHP (200%)	74	100	0	
6	MoO ₂ calcined (MoO ₂ NPs)	TBHP (150%)(1 st /2 nd run)	89/65	100/100	0/0	
7		TBHP (100%)	82	100	0	
8		TBHP (200%) solventless	69	100	0	
9	γ -Fe ₂ O ₃	TBHP (200%)	97	1	99	

Table 1. Results from benzyl alcohol oxidation with tert-butyl hydroperoxide (TBHP) as oxidant.

All reactions were carried out at 383 K in the presence of different mol% oxidant (TBHP), 4.32 mmol of alcohol, 0.56 mmol of the Mo nanocatalyst, and 1 mL decane; [a] Calculated after 24 h; [b] calculated as "Yield of product"/"Conversion" × 100.

The MoO_2 -Fe₂O₃ and MoO_2 calcined catalysts were investigated for the oxidation of benzyl alcohol at 383 K with TBHP as the oxidant in the presence or absence of a solvent (Table 1).

The MoO₂–Fe₂O₃ catalyst was very active for this reaction, achieving 61–95% conversion with 100, 150, and 200% of TBHP (Table 1, entries 1–3). These results showed that 150% of TBHP was the optimum amount of oxidant, reaching 95% conversion after 24 h of reaction time. The selectivity for benzaldehyde when the MoO₂–Fe₂O₃ catalyst was used with different ratios of oxidant/catalyst, did not suffer almost any change, reaching ca. 90%, and benzoic acid was the only by-product detected, although with very low selectivity. On the other hand, when the MoO₂ calcined catalyst was used, the achieved results were also very high, reaching 89–74% conversion (Table 1, entries 5–7). The selectivity for the desired product, benzaldehyde, was also excellent, being 100% under the tested conditions.

Aside from the study of different oxidant:substrate ratios, recyclability is also a crucial parameter to evaluate a heterogeneous catalyst. The recycling experiments were conducted using MoO_2 calcined nanoparticles as the catalyst, 150% of TBHP as the oxidant, and benzyl alcohol as the substrate in

two successive runs (Table 1, entry 6). The catalyst was filtered after the first run, washed with dichloromethane, and dried prior to the recycling experiment. This recycling experiment was done with the MoO_2 calcined catalyst and 150% of TBHP, since it was the condition that presented higher selectivity. This reached 89% conversion and 100% selectivity for benzaldehyde, which was a very promising result. After the second cycle, 65% conversion was obtained and once again, the selectivity remained very high, achieving 100%. This result showed that this catalyst was very active for the oxidation of benzyl alcohol.

When assessing the catalytic performance of heterogeneous systems, it was important to evaluate the stability of the catalyst in terms of active center leaching and to ensure that the catalyst was robust and heterogeneous in nature.

To test active site leaching, the oxidation of benzyl alcohol was performed using the MoO_2 –Fe₂O₃ nanoparticles as the catalyst and 200 mol% TBHP. During a normal reaction, the catalyst was removed by hot filtration after 2 h, and the reaction was followed until the end of the 24 h period. After filtering upon 2 h (at 22% conversion), the reaction was continued only with the homogeneous part. At the end of the 24 h period, the reaction reached only 27% conversion (Table 1, entry 5). Under regular conditions (with the catalyst), it reached 74% when the catalyst was not removed (Table 1, entry 1) with 91% selectivity toward benzaldehyde, showing that the catalyst was robust and there was almost no leaching detected after the first 2 h reaction (Table 1, entry 4).

This clearly showed that the reaction almost stopped when the heterogeneous catalyst was filtered off from the reaction slurry, and therefore there was little or no leaching to the homogeneous phase. Thus, it was possible to conclude that the catalysts were truly heterogeneous in nature.

Analyzing Figure 4, which shows the curves for the use of different amounts of TBHP oxidant, it was possible to observe that the kinetics at the beginning of the reaction was not affected by the different amounts of added TBHP from 100–200 mol%. However, they presented large differences after a 4 h reaction time, particularly for the catalytic reaction done with 150% of TBHP, where it clearly detached from the remaining reactions with different oxidant:substrate ratios.



Figure 4. Kinetics with MoO₂-Fe₂O₃ with different added amounts of TBHP.

The reason why the 200 mol% ratio was not the highest performing has to do with the fact that such a high amount of TBHP yielded larger amounts of *t*-butanol, which competes with TBHP for the active sites [19]. Therefore, using a lower ratio of TBHP at 150 mol% (relative to the substrate) was found to be an optimal balance for the catalyst performance, while the results reported here matched those in the literature for related systems [20].

3. Mechanistic Study

To determine whether the reaction proceeded through radical intermediates, their presence in the reaction mixture was analyzed. To a typical reaction mixture, a substrate equimolar amount (4.32 mmol) of the radical scavenger 2,6-di-*tert*-butyl-4-methylphenol was added and the reaction was followed for 24 h. This was tested for both the MoO_2 -Fe₂O₃ and MoO_2 calcined catalysts.

Analyzing the obtained results, it was possible to confirm that only 33% and 39% conversion after the 24 h reaction was obtained, respectively (Table 2, entries 2 and 4). The results from these tests were compared with those obtained previously and found to be lower in comparison with the first experiments with 74% (Table 2, entries 1 and 3) for the MoO_2 –Fe₂O₃ and MoO_2 calcined catalysts.

Entry	Catalyst	Oxidant (mol%)	Conversion	Selectivity (%) [b]	
j	<u> </u>		(%) [a]	BzCHO	BzCOOH
1	MaQ- Ea-Q-	TBHP (200%)	74	91	9
2	1002-10203	radical scavenger (200%)	33	88	11
3	MoO ₂ calcined	TBHP (200%)	74	100	0
4	(MoO ₂ NPs)	radical scavenger (200%)	39	100	0

Table 2. Results from the benzyl alcohol oxidation with TBHP as the oxidant and a radical scavenger.

All reactions were carried out at 383 K in the presence of 200 mol% oxidant (TBHP), 4.32 mmol of alcohol, 0.56 mmol of the Mo nanocatalyst, and 1 mL decane; [a] Calculated after 24 h; [b] calculated as "Yield of product"/"Conversion" \times 100.

it could be rationalized that the radical scavenger From the above results, (2,6-di-*tert*-butyl-4-methylphenol) would compete for active sites at the surface of the catalysts, although this was hard to conceptualize. Given its structure with the bulky *t*-butyl groups *ortho* to the phenol group, it would be extremely difficult for this molecule to approach the surface and bind strongly. In this way, the results showed that there was good evidence that the mechanism involves a radical path. However, since a considerable level activity was also detected, it also demonstrated that there was an alternative path that was not radical. It was also possible to observe that the kinetics of the reactions presented differences from the previous ones (Figures 4 and 5), showing that the reaction did not proceed at the same rate, as expected. When the MoO_2 calcined catalyst was used with the radical scavenger, the reaction kinetics showed analogous trends, as observed for MoO₂–Fe₂O₃. It is known from the literature that oxidation reactions catalyzed by metal oxides involve metal reduction/re-oxidation steps involving TBHP, while the migration of lattice oxygen also occurs [21,22]. These steps at some point may occur through radical species, which can be scavenged by the radical scavenger, leading to the observed rate decrease.

These results concerning the existence of a radical mechanism were the first to the best of our knowledge as we could not find evidence in the literature for similar findings in related systems [23–25]. However, proof of evidence for ruling in or ruling out radical mechanisms was also not found. In this way, these results are worth further investigation.

The shape of the kinetic curves should also be discussed. As observed in Figures 4 and 5, these followed stepwise profiles, which indicate a complex reaction system with different mechanisms involved. These observations may be related to the fact that these catalysts have different active sites where the reaction takes place and display different reactivities, as recently reported by us using neutron scattering [15]. The profiles also demonstrated that as proof of a complex reaction with different mechanisms occurring, radical pathway(s) could not be ruled out, giving credit to the results from the experiment with the radical scavenger.

Given that the MoO_2 – Fe_2O_3 catalyst was synthesized using Fe_2O_3 as the assisting agent and was incorporated as a dopant [14], we assessed if this contaminant had any influence on the catalytic reaction. In this way, a reaction with Fe_2O_3 nanoparticles was run to infer its influence on the catalytic oxidation reaction of benzyl alcohol for control purposes.



Figure 5. Use of a radical scavenger, with 200% TBHP and MoO₂–Fe₂O₃ (**top**) and MoO₂ calcined (**bottom**) as catalysts.

Figure 6 shows the kinetics of the catalytic reaction with Fe₂O₃, and it was possible to observe that γ -Fe₂O₃ had an apparent influence in the obtained result of conversion and in the obtained product selectivity. At the beginning of the reaction, benzaldehyde was formed. However, after 1 h reaction time, the benzaldehyde concentration decreased, being converted into benzoic acid. After 24 h of reaction, benzoic acid was the sole product (Table 1, entry 9). After obtaining these results, it was possible to conclude that the γ -Fe₂O₃ had an influence on the selectivity of benzaldehyde when MoO₂–Fe₂O₃ was the catalyst. In this catalyst, there was only a small amount of γ -Fe₂O₃, most likely at the surface of the catalyst, which led to the formation of small amounts of benzoic acid (Table 1, entries 1–4), thus supporting the observed selectivity. This was not observed for the MoO₂ calcined catalyst (Table 1, entries 5–8) lacking Fe₂O₃ and corroborated these findings.

In a continuous effort to obtain more efficient catalysts and green processes, we tested the MoO_2 calcined catalyst in a reaction without solvent. Analyzing Table 1, entry 8, it is possible to observe that the reaction reached 69% substrate conversion and achieved 100% selectivity for benzaldehyde. This was a remarkable result, which matched almost the same conversion levels observed with the use of a solvent (Table 1, entries 5–7).



Figure 6. Catalytic oxidation of BnOH with γ -Fe₂O₃ NPs with TBHP 200%.

After these promising results, we tried to replace the oxidant TBHP by hydrogen peroxide with the MoO_2 –Fe₂O₃ catalyst. The first tests were carried out with some solvents and solventless condition (Table 3), since promising results were obtained without a solvent with TBHP.

Entry	Catalyst	Oxidant	Solvent	Yield (%)	Selectivity (%)	
5			oorrent		BzCHO	BzCOOH
1			Acetonitrile 353 K	25	100	0
2	MoO ₂ -Fe ₂ O ₃	H_2O_2	Acetonitrile 383 K	23	97	1
3			Decane 383 K	16	96	2
4			Solventless 383 K	12	78	11
5			New H ₂ O ₂ addition at 4 h Acetonitrile 353 K	48	100	0
6			New H ₂ O ₂ addition at 4 h and at 8 h Acetonitrile 353 K	94	100	0

Table 3. Results from benzyl alcohol oxidation with H_2O_2 as the oxidant.

All reactions were carried out at 383 or 353 K in the presence of 200 mol% of oxidant (H_2O_2), 4.32 mmol of alcohol, 0.56 mmol of the Mo nanocatalyst, and 1 mL solvent or without. [a] Calculated after 24 h; [b] calculated as "Yield of product"/"Conversion" × 100.

Regarding the use of H_2O_2 , the results were not so promising at first sight. Conversions were found to range from medium to fair, between 12–48%. The effect of the temperature was also tested in the reaction performance. It was possible to say, after analyzing Table 3, that temperature had a slightly negative effect in the final conversion with H_2O_2 as the oxidant (Table 3, entries 1–3). This demonstrated that in the reactions at 353 K and 383 K with acetonitrile as the solvent when the temperature was raised, although marginally, both the substrate conversion and benzaldehyde selectivity dropped. Changing the solvent to decane or using solventless conditions (Table 3, entries 3 and 4) had an even more dramatic negative impact on the reaction by lowering the substrate conversion, and by significantly affecting product selectivity as well.

It is known that H_2O_2 decomposes inefficiently in parallel processes. To try to circumvent this, we then took the best conditions (Table 3, entry 1) and explored the effect of new additions of the oxidant during the catalytic reaction (Table 3, entries 5 and 6). The obtained results allowed us to investigate the effect of adding a similar amount of H_2O_2 at the beginning of the reaction and after 4 h. We found that the obtained substrate conversion was twice the original one after 24 h (Table 3, entries 1)

and 5). Taking this result into consideration and in the same trend, we conducted a new reaction and the oxidant was added in similar amounts at the beginning of the reaction, and then after 4 h and 8 h (Table 3, entry 6). In this experiment, 94% substrate conversion was obtained with 100% selectivity for the desired product, benzaldehyde, at a relatively low temperature (353 K), which was remarkable. These results showed that it was possible to use hydrogen peroxide as an oxidant, adding it at known times and overcome the inefficient decomposition of H_2O_2 . It also confirmed that degradation of H_2O_2 occurred in parallel processes, making the reaction less efficient. Despite this, it also demonstrated that the process was feasible and, more importantly, highly selective toward benzaldehyde.

In Figure 7, it is possible to observe that the kinetics of the reaction had a higher rate when more oxidant was added after 4 h reaction time. At 4 h reaction time, 24% conversion was obtained and at 6 h (2 h after the addition of a new amount of oxidant), almost 60% conversion was reached. From 6 h to 8 h reaction, the kinetics was slower again and only 72% conversion was obtained. At 8 h, more H_2O_2 was added again and the reaction proceeded from 72% to 94% after 24 h. A faster kinetics was not observed. However, the final conversion was improved, reaching 94% with 100% selectivity for benzaldehyde.



Figure 7. Catalytic oxidation of BnOH with MoO_2 –Fe₂O₃ and H₂O₂, with two extra additions of H₂O₂ at 4 h and 8 h. Arrows denote the new additions of H₂O₂.

Catalyst stability was also evaluated for the MoO₂ calcined nanomaterial by FTIR analysis of the recovered catalyst at the end of the reaction. According to Figure 8, the FTIR spectrum seems to globally match that of the fresh MoO₂ calcined NP catalyst (Figure 3). It is possible to see that there was the presence now of low intensity vC–H modes at ca. 2900–3000 cm⁻¹, which are mostly due to surface-adsorbed species from the reaction. More importantly, the most striking feature is the presence of a pair of bands at 935 and 914 cm⁻¹ due to the vMo=O modes, which is indicative that there are Mo^{VI}=O species at the surface of the catalyst, as expected. This observation agrees with the mechanistic proposals and is also evidence that the MoO₂ NPs are preserved after catalysis [11,14].

On the other hand, the XRD powder pattern from the recovered catalyst (Figure 8) shows that, overall, there was a similar pattern to that in Figure 1 concerning the existence of the MoO_2 phase. However, diffraction peaks arising from the MoO_3 phase were found at the surface along with some other sharp diffraction peaks that were due to surface-adsorbed organics. These data corroborated the FTIR results discussed above, being supported by recent findings using neutron scattering [15], and explaining the considerable activity decrease in recycling experiments.



Figure 8. Infrared spectrum (**top**) and X-ray diffraction (XRD) powder pattern (**bottom**) of the MoO₂ NPs after catalysis.

The catalytic performance demonstrated by the two different catalysts was relevant and their performances in the oxidation of BzOH to BzCHO using TBHP or H_2O_2 with or without solvent are compared in Table 4. As shown in entries 14–16, the overall catalytic performance of the MoO_2 –Fe₂O₃ and MoO_2 calcined nanomaterials was comparable or better than other catalytic nanomaterials reported in the literature [6,23–34]. The catalysts shown in Table 4 cover a wide selection of homogeneous and heterogeneous catalysts and in terms of the BzCHO yield, it was higher than those of other catalysts. In some cases, the obtained results with other catalysts were better, however, the amount of the catalysts, oxidant, temperature, and pressure were higher.

Entry	Catalyst	Oxidant	Temp (°C)	Time (h)	Yield or Conv./%	Ref.
1	Fe ₃ O ₄ -MoO ₃	TBHP	80	6	89	[26]
2	Ag–ZnO	TBHP	80	0.5	77	[25]
3	Mo(VI) peroxo	H_2O_2	80	8	79	[24]
4	Mo(VI)O ₂ -Schif	TBHP	r.t.	2	90	[23]
5	Pt/BiOCl	O ₂ press	r.t.	5	100	[27]
6	Au–Pd–TiO ₂	$O_2 4 bar$	120	1	10-50	[28]
7	Cu–Ni–Carbon	H_2O_2	80	2	14–47	[29]
8	Au-M (Cu, Ni, Co, Zn)	K ₂ CO ₃ /O ₂	80	16	23-81 (Conv)	[30]
9	Fe ₃ O ₄ –ECH	H_2O_2	100	1.5	8–34	[31]
10	Au-Supported (SiO ₂ , Al ₂ O ₃ , HAP, MgAl ₂ O ₄ , MgO)	O_2/K_2CO_3 O_2 5 bar	60 150	3 5	60 (Conv) 47–94 (Conv)	[32]
11	MR-MS-Mo	H_2O_2	65	1–5	0–99	[33]
12	MgO-CoFe ₂ O ₄ -Au	O_2 2 bar	100	2.5	18-42	[34]
13	Pd–Zn–TiO ₂	O ₂ 1 bar	120	1	3–55 (Conv)	[6]
14	MoO ₂ –Fe ₂ O ₃	TBHP	110	24	61–95	This work
15	MoO ₂ -Fe ₂ O ₃	H_2O_2	110	24	12–94	This work
16	MoO ₂ calcined	TBHP	110	24	74–89	This work

Table 4. Comparison of the catalytic performance of the MoO₂ NP catalysts described in this work with other systems reported in the literature.

4. Materials and Methods

4.1. General

All reagents were of analytical grade, obtained from Aldrich and used as received. Fourier-Transform Infrared (FTIR) spectra were obtained using a Diffuse-Reflectance DRIFT Smart-accessory on a Nicolet 6700 (Waltham, MA, USA) in the 400–4000 cm⁻¹ range using 4 cm⁻¹ resolution. Powder X-ray Diffraction (XRD) measurements were taken on a Philips Analytical PW 3050/60 X'Pert PRO (theta/2 theta) equipped with an X'Celerator detector (Almelo, The Netherlands) and automatic data acquisition (X'Pert Data Collector (v2.0b) software) using monochromatized CuK α radiation as the incident beam. The Scanning Electron Microscopy (SEM) images were acquired on a FEG-SEM (Field Emission Gun Scanning Electron Microscope) from JEOL, model JSM-7001F (Akishima, Tokyo, Japan), operating at 15 kV, in Microlab at Instituto Superior Técnico, Lisboa, Portugal. Synthesis of the MoO₂ nanomaterials has been reported elsewhere [11,14,15]. From the two protocols adopted for the synthesis of the MoO₂ nanoparticles, the one using hydroquinone was slightly adapted by adding a calcination step under a N₂ atmosphere at the end of the synthesis to eliminate the organic shell adsorbed at the surface of the nanoparticles, which was found to passivate the reactivity of the catalyst as recently described in the literature [15].

4.2. Catalytic Tests

MoO₂ nanomaterials (MoO₂–Fe₂O₃ and calcined MoO₂) were tested as catalysts for the oxidation of benzyl alcohol. To a 25 mL two-necked round bottom flask fitted with a reflux condenser and a magnetic stirrer was added: MoO₂, benzyl alcohol, and *tert*-butylhydroperoxide (TBHP 5.5 M in decane) or hydrogen peroxide (H₂O₂, 30% aqueous) as oxidants. In the case of H₂O₂, 2 mL of solvent (decane or acetonitrile) was also added. The mixture was heated to 353 or 383 K under a normal air atmosphere and stirring at 300 rpm for 24 h. In a typical experiment, the vessel was loaded with benzyl alcohol (4.32 mmol, 100 mol%), the internal standard (dibutyl ether, 3.60 mmol), catalyst (1 mol%), and in the end, the oxidant (100, 150, or 200 mol% relative to the substrate amount). The addition of the oxidant determines the initial time of the reaction. The course of the reactions was monitored by quantitative Gas-Chromatography-Mass Spectrometry (GC-MS) analysis by collecting samples at 10,

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30 min, 1, and 1.5 h, then at 2, 4, 6, 8, and 24 h of reaction. These samples were treated as described previously prior to injection in the GC column [35] using a Shimadzu QP2100-Plus GC/MS system with a capillary column Tecknokroma TRB-5MS (Barcelona, Spain) operating in the linear velocity mode.

The presented results (conversion, yield, etc.) were the average of three replicates, each obtained by two different people to ensure their repeatability and reproducibility.

5. Conclusions

Normally, the most widely used catalysts for the reaction of the oxidation of benzyl alcohol to benzaldehyde described in the literature are nanoparticles of noble metals such as Pt, Au, Pt, or Ru. In this work, we developed heterogeneous based catalysts of MoO_2 NPs and demonstrated that they were efficient for the selective oxidation of benzyl alcohol to benzaldehyde using 30% aqueous H_2O_2 or TBHP as the oxidant, which are considered as green oxidants, under solvent or solventless conditions. The results were very promising, exhibiting excellent catalytic efficiency, reaching 95% yield and almost 100% selectivity for benzaldehyde under the optimized tested conditions with TBHP. The existence of a radical pathway was supported by the experimental results and will be further addressed in the future.

Of even higher relevance were the studies with H_2O_2 , which allowed us to achieve 94% substrate conversion with 100% selectivity, although it has the drawback of the cost of feeding additional oxidant to the reaction after 4 h and 8 h reaction time. This result showed that hydrogen peroxide was also consumed during the reaction in parallel inefficient processes. We are endeavoring further efforts to fine-tune the efficiency of the reaction by adjusting the initial H_2O_2 amounts and the periodicity of additions to optimize the process. Additionally, a comparison with results found in a survey from the published literature for related catalytic systems showed that although the system reported here was not the best performing, it reached a similar performance under somewhat milder conditions, which is also advantageous.

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