Arylalkane photo-oxidation under visible light and O_2 catalyzed by molybdenum(VI)dioxo-dibromo (4,4′-dicarboxylato-2,2′-bipyridine) anchored on TiO_2

Carlos A. Páez [a,1], Oscar Lozada [a], Nelson J. Castellanos [a,d], Fernando O. Martínez [a], Fabio Ziarelli [b], Giuseppe Agrifoglio [c], Edgar A. Páez-Mozo [a,*], Henri Arzoumanian [d,**]

[a] Escuela de Química, Centro de Investigación en Catálisis-CICAT, Universidad Industrial de Santander, Km 2 vía El Refugio, Piedecuesta, Santander, Colombia
[b] FR1739 CNRS, Université Paul Cézanne, Faculté des sciences, St Jérôme, Marseille, France
[c] Centro de Química, Instituto Venezolano de Investigaciones Científicas (IVIC), Apartado 21827, Caracas 1020-A, Venezuela
[d] Chirosciences UMR 6263 CNRS ISM2, Université Paul Cézanne, Faculté des Sciences, St Jérôme, Marseille, France

ABSTRACT

The molybdenum(VI)dioxo-dibromo compound bearing a carboxylate substituted bipyridyl ligand was anchored covalently onto a TiO_2 matrix (DG-25). It was fully characterized by IR(KBr), UV-diffuse reflectance, IR-photoacoustic (FT-IR/PAS) and solid state ^{13}C NMR spectroscopies. Its reactivity as an O-atom transfer agent was tested under visible light irradiation on ethylbenzene and tetraline, stoichiometrically under N_2 and catalytically under O_2 and then compared with the analogous homogeneous complex bearing a carbomethoxy substituted bipyridine. An important synergic effect was observed, attributed to the photogenerated electron flux, via TiO_2, onto the coordination sphere of molybdenum. The anchored system, furthermore, prevented any deactivation of the reactive center, as it is observed in the homogeneous medium, through the formation of a μ-oxo species.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

The chemistry of transition metal-oxo compounds is an area of particular interest with potential relevance to oxygen atom transfer processes in a wide range of catalytic reactions [1–3]. This function is found in many systems ranging from metallo enzymes to solid state reactions on metal oxide surfaces [1–4]. When modeling enzymatic systems for the alkane or alkene oxidation, the metals of choice have been chromium [5], manganese and iron [2], whereas rhenium [6] and ruthenium-oxo [7–9] have been studied widely as catalysts for alkane or alcohol oxidation. In this context, molybdenum-oxo compounds hold an important place, specially as models for the active site of oxo-transfer molybdenum-enzymes [10,2–4].

In order to oxidize phosphines, arylalkanes or olefins, we have reported several molybdenum-oxo, -dioxo and -μ-oxo complexes

bearing various ligands among which some exhibited exceptional oxo-transfer capability under stoichiometric and catalytic conditions using various oxygen atom donors [11–14]. In the majority of these complexes the ligands present in the coordination sphere were bipyridyl ligands and exhibited a significant acceleration under UV irradiation [15]. However, in the oxo-transfer process, one major problem lies in the irreversible formation of Mo(V)-μ-oxo dimer species which are often totally inert in the reoxidation process [16]. In order to isolate the metallic center and avoid any μ-oxo dimer formation, much effort has been done by heterogenizing various molybdenum catalyst such as $MoO_2(acac)_2$, MoO_2Cl_2L, on different inorganic supports such a silicates, zeolites and other molecular sieves [17–22]. The resultant materials catalyzed the epoxidation of olefins, but proved to be unstable towards molybdenum leaching and were active only with hydroperoxides (t-ButOOH) as their oxygen donor agents.

The use of O_2 as the oxidant in any catalytic oxidation process is a difficult task, specially under mild conditions (pressure and temperature) and constitutes a major endeavour both for the academic and industrial world. In this context, we have covalently immobilized the $Mo(VI)(O)_2(Br)_2(4,4′-dicarboxylato-2,2′-bipyridine)$ complex on a TiO_2 solid matrix (Degussa-P25) by a carboxylate linkage, This system was evaluated as an oxo-transfer agent, toward triphenylphosphine, under visible light irradiation

* Corresponding author.
** Corresponding author. Tel.: +33 491288256; fax: +33 491289146.
E-mail addresses: epaez@uis.edu.co (C.A. Páez), henri.arzoumanian@univ.u-3mrs.fr (H. Arzoumanian).
[1] On leave at Univ. P.C. Marseille. Present address: Univ Liege Dept chimie appliquée, Belgium.

and using O_2 as oxo-donor agent [23]. It was compared with the complex molybdenum(VI)dioxo-dibromo-(4,4′-dicarbomethoxy-2,2′-bipyridine) under homogeneous conditions. The anchoring on the TiO_2 matrix brought important improvements to the oxygen atom transfer catalytic system. On one hand, it increased significantly the O-transfer capability, via the photo generated flux onto the Mo(VI) coordination sphere, and on the other, by isolating the metallic centers, it prevented the formation of the inactive Mo(V)-μ-oxo dimer and thus lengthened significantly the catalyst life span.

In the present work, we have prepared the catalytic entity MoO_2/TiO_2 according to reported synthetic route with some slight modifications [23] Their capability as oxygen atom transfer agent was evaluated toward arylalkanes (ethylbenzene and tetraline) under stoichiometric (N_2 atmosphere) and catalytic (O_2) conditions, with visible light irradiation, $\lambda \geq 380$ nm.

2. Experimental

2.1. General

All materials were commercial and were used without further purification unless otherwise noted. All solvents were thoroughly degassed prior to use. Acetonitrile was distilled and kept under argon, thionyl chloride was doubly distilled. Titanium oxide (Degussa-P25) with $50 \, m^2/g$ specific area and crystalline structure of 80% anastase and 20% rutile was dehydrated at $100\,^{\circ}$C and 5×10^{-4} mbar for 48 h prior to use. IR (KBr) and IR-PAS (photoacoustic) spectra were recorded on PerkinElmer 1720XFT and Schimatzu 8400S spectrometers, respectively. UV–vis spectra were obtained on a HP 8423 spectrophotometer and UV–vis-DR (diffuse reflectance) spectra were recorded on a PerkinElmer 2034RD Lambda 35 UV (integrating sphere P/NC 6951014). ^{1}H and ^{13}C NMR were performed on Bruker Avance 200 and 400 spectrometers. All solid state CPMAS NMR spectra were obtained on a Bruker Avance-400 MHz NMR spectrometer operating at a ^{13}C resonance frequency of 101.6 MHz. The ^{13}C experiments were performed with a commercial Bruker double-bearing probe with zirconium dioxide rotors of 4-mm outer diameter. The CP technique [24] was applied during Magic Angle Spinning (MAS) of the rotor at 10 kHz. A ramped ^{1}H-pulse starting at 100% power and decreasing until 50% was used during contact time in order to circumvent Hartmann–Hahn mismatches [25,26]. The contact time were 2 ms. To obtain a good signal-to-noise ratio in ^{13}C CPMAS experiment 2048 scans were accumulated using a delay of 2 s. The ^{13}C chemical shifts were referenced to tetramethylsilane and calibrated with glycine carbonyl signal, set at 176.5 ppm [27]. Gas chromatography (CG) analysis of the photo-oxidation products were performed with a HP-6890 equipped with a flame ionization detector and HP5 column (30 m × 0.32 mm × 0.25 μm). Toluene was used as internal standard.

2.2. Synthesis of complexes

2.2.1. 2,2′-Bipyridine-4,4′-dicarboxylic acid [28] (1)

It was prepared according to a reported procedure from 4,4′-dimethyl-2,2′-bipyridine [29,30]. IR(KBr): ν (cm^{-1}) 3441 (s), 2446 (s), 1729 (s), 1604 (s), 1461 (s), 1366 (s), 1290 (s), 1268 (s). ^{13}C NMR/CPMAS (400 MHz): δ (ppm) 123.2; 140.0; 150.3; 164.7.

2.2.2. $Mo(O)_2Br_2[OP(C_6H_5)_3]_2$ (3)

To an HBr (45%) solution (6 mL) containing 1.0 g of $Na_2MoO_4 \cdot 2H_2O$ (4.15 mmol) was added 15 mL of diethyl ether and the mixture vigorously stirred for five minutes, before the ether layer was separated and dried over anhydrous sodium sulfate.

To the dried diethyl ether solution was added an acetone solution (60 mL) containing 1.9 g (7.4 mmol) of triphenylphosphine oxide. Stirring at room temperature for a few minutes resulted in the precipitation of a green solid which was filtered and recrystallized from CH_2Cl_2/Et_2O (1/1). IR(KBr): ν (cm^{-1}) 3099 (w), 1702 (w), 1437 (s), 1174 (s), 1146 (s), 1121 (s), 1089 (s), 946 (s), 903 (s), 724 (s), 692 (s). ^{1}H NMR ($CDCl_3$): δ (ppm) 7.38 (m, 2H), 7.53 (t, H), 7.76 (m, 2H). Anal. Calc. For $C_{36}H_{30}Br_2MoO_4P_2$: C, 51.21, H, 3.62. Found: C, 51.24 and H, 3.58.

2.2.3. $Mo(O)_2Br_2(4,4′-dicarbomethoxy-2,2′-bipyridine)$ (5)

The acid chloride (2) obtained from the $SOCl_2$ treatment of 2,2′-bipyridine-4,4′-dicarboxylic acid (0.13 g, 0.53 mmol) was dissolved in CH_2Cl_2 and added to a CH_2Cl_2 (30 mL) solution containing 0.22 g (0.24 mmol) of $Mo(O)_2Br_2[OP(C_6H_5)_3]_2$ (3). The mixture stirred at $40\,^{\circ}$C for 12 h resulted in the precipitation of a yellow solid and filtered under inert atmosphere. This solid (4) was re-dissolved in 30 mL of CH_2Cl_2 and MeOH (0.5 mL), and kept under reflux for 12 h. Evaporation of the solvent and recrystallization (ether/CH_2Cl_2) gave the desired diester in 70% yield. IR(KBr): ν (cm^{-1}) 3082 (w), 2085 (w), 1733 (s), 1565 (m), 1437 (s), 1401 (s), 1333 (s), 1274 (s), 1233 (m), 946 (s), 913 (s). ^{1}H NMR ($CDCl_3$): δ (ppm) 4.12 (s, 3H), 8.29 (d, 1H), 8.92 (s, 1H), 9.78 (t, 1H). ^{13}C NMR/CPMAS: δ (ppm) 52.8, 54.6, 124.5, 140.8, 142.0, 148.9, 152.9, 161.2.

2.2.4. $Mo(O)_2Br_2(4,4′-dicarboxylato-2,2′-bipyridine)/TiO_2$ (6)

To 20 mL of $SOCl_2$ was added 0.25 g (1 mmol) of 2,2′-bipyridine-4,4′-dicarboxylic acid (1) and the mixture was heated to reflux for 3 h. The excess $SOCl_2$ was evaporated under vacuum, the residue dissolved in dry CH_2Cl_2 and added to a CH_2Cl_2 (50 mL) solution containing 0.5 g (0.6 mmol) of $Mo(O)_2Br_2[OP(C_6H_5)_3]_2$ (3). The mixture stirred at $40\,^{\circ}$C for 12 h resulted in the precipitation of a yellow solid and filtered under inert atmosphere. This solid (4) was dissolved in 80 mL of CH_3CN and added to a CH_3CN (50 mL) suspension containing 0.5 g of anhydrous TiO_2. The mixture was vigorously stirred at reflux for 14 h and filtered under N_2 atmosphere to give a light violet solid. The amount of linked dioxo-complex on the TiO_2 was determined by desorption with 0.1 M NaOH and the supernatant solution was analysed by UV–vis spectroscopy (0.105 mmol/g of TiO_2). IR(KBr) ν (cm^{-1}) 1731 (s), 1603 (w), 1561 (w), 1395 (w), 1366 (s), 1291 (s), 1262 (s), 940 (s), 915 (s) and 766 (m). IR-PAS (900-1800 region): ν (cm^{-1}) = 1731, 1600, 1562, 1450, 1427, 1396, 1365, 1215, 941 and 906. ^{13}C NMR/CPMAS: δ (ppm) = 124.3, 127.8, 141.3, 151.6 and 165.9.

2.3. Arylalkane photo-oxidation

The photocatalytic oxidation of the arylalkanes was carried out using a 10 mL batch micro-reactor (Ace-Glass model T-121m) with immersion lamp (Phenix, 220 V). The photon flux (Io) per unit volume and unit time, was determined by chemical actinometry using potassium ferrioxalate [30,31]. Measured Io = 5.3×10^{-5} moles of photons/L s ($\lambda \geq 380$ nm).

In a typical experiment, a 0.076 M solution of arylalkane in CH_3CN was thoroughly deoxygenated by bubbling N_2 gas for several hours at $5\,^{\circ}$C before the addition of 0.011 g of either MoO_2/TiO_2 (6), a "mechanical" mixture of (5) and TiO_2 in the same proportion as (6) or pure TiO_2. In the case of the homogeneous system, 2 mg (5.5×10^{-6} mol) of (5) was added to the oxygen free solution. In all cases the mixture was kept in the dark and under nitrogen for 1 h, to assure adsorption/desorption equilibrium, before visible light was turned on and kept for 4 h. Nitrogen was then replaced by O_2 in the dark. After a period of 2 h the mixture was rendered, again, O_2-free by bubbling N_2 before the light was turned back on. The sequence was repeated at will.

3. Results and discussion

The synthetic route for the preparation of MoO_2/TiO_2 (**6**) is depicted below. The 2,2′-bipyridine 4,4′-dicarboxylic acid (**1**) was obtained by permanganate oxidation in basic medium of the 4,4′-dimethyl-2,2′-bipyridine. The 2,2′-bipyridine-4,4′-di-carboxylic acid chloride complex (**4**) has been prepared *in situ* by complexation of the acid chloride **2**, onto the molybdenum(VI)dioxo-dibromo complex **3**, and fully characterized by derivatization, via esterification in methanol. This dimethyl ester complex (**5**) was fully identified by IR and ^{1}H NMR spectroscopy [23].

The synthetic route chosen for complex **6** consisted of anchoring the complex **4** onto the solid TiO_2 matrix, via "esterification" reaction with the "titanol" group (Ti–OH) on the TiO_2 Degussa-P25 surface. The characterization of **6** was done by IR(KBr), UV-diffuse reflectance and more thoroughly by IR-photoacoustic (FT-IR/PAS) and solid state ^{13}C NMR spectroscopies. The complexes **5** and **6** exhibits, in IR(KBr) spectroscopy, two absorption bands in the 950–900 cm^{-1} region attributed, respectively, to ν_{sym}Mo=O and ν_{asym}Mo=O of *cis*-MoO_2 unit [32]. Furthermore, the system MoO_2/TiO_2 (**6**) showed a strong absorption in 1734 cm^{-1} assigned

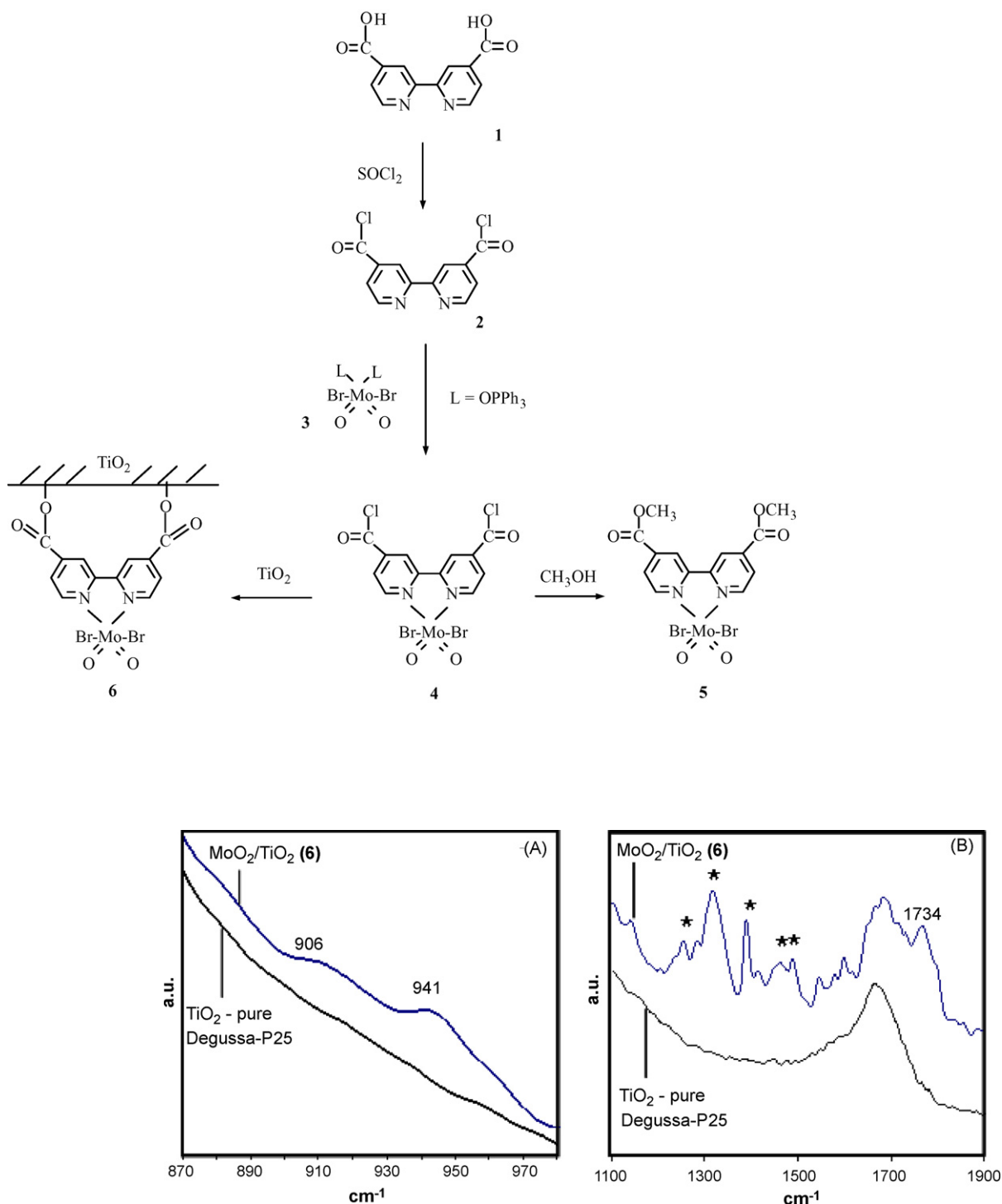**Fig. 1.** FT-IR/PAS spectra of MoO_2/TiO_2 (**6**) and TiO_2 (P-25) pure: (A) 870–980 cm^{-1} region and (B) 1100–1900 cm^{-1} region.
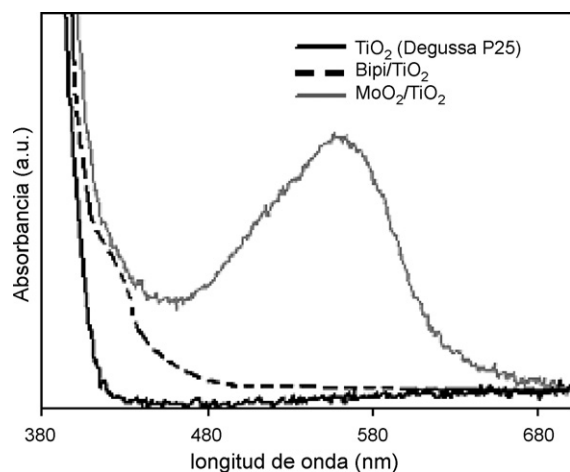
Fig. 2. Comparison of the UV–vis diffuse reflectance spectra of MoO_2/TiO_2 (**6**), Bipy/TiO$_2$ and TiO$_2$ (P-25).

to the carboxylate linkage (C(O)–O–Ti^{4+}) which is very close to that observed in the complex **5**, ν_{asym}COOCH$_3$ [33].

The anchored character of **6** was further made evident by IR-photoacoustic spectroscopic analysis as shown in Fig. 1. When comparing the TiO$_2$ matrix before and after modification with the Mo(VI)(O)$_2$ complex (**6**), the absorption bands corresponding to Mo=O are observed at 906 and 941 cm^{-1}. The carboxylate linkage is revealed by a band at 1734 cm^{-1} whereas the corresponding bands expected in the 1350–1450 cm^{-1} region [34] are included in the 1260–1450 cm^{-1} region attributed to the ν-bipyridyl framework. Diffuse reflectance spectra, likewise (Fig. 2) show the $n \rightarrow \pi^*$ transition band ($\lambda \approx 560$ nm) of the Mo=O group [2] in MoO$_2$/TiO$_2$ (**6**) as well as a slight shoulder around 400 nm, which could be attributed to the bipyridyl moiety. This is corroborated when compared with the bipyridine carboxylate, alone, bonded to TiO$_2$, whereas TiO$_2$ pure does not show any absorption in the visible range.

All these observations are corroborated by ^{13}C NMR (CP/MAS) spectroscopy (Fig. 3). Formation of the "inorganic ester" (C(O)–O–Ti^{4+}) is evidenced by the resonance at 167 ppm (Fig. 3A) which is close to, but significantly different from that observed in the diester complex **5** ($\delta = 163$ ppm, Fig. 3B). Likewise, the α, β and γ carbon atoms on the pyridyl ring are observed in the 153–125 ppm region but shifted in comparison with the free 4,4′-dicarbomethoxy-2,2′-bipyridine (Fig. 3C), indicating clearly that a molybdenum species is bonded to a bipyridyl moiety and anchored on the TiO$_2$ surface.

3.1. Arylalkane oxidation

The oxygen atom transfer process was examined for the oxidation of ethylbenzene and tetraline with the anchored complex **6** under both stoichiometric (N$_2$ atmosphere) and catalytic (in the presence of O$_2$ as the O-donor) conditions. It was compared with the analogous complex **5** under homogeneous conditions and the pure TiO$_2$ suspension. Each experiment was run under identical conditions at room temperature, in the presence and absence of visible light irradiation ($\lambda \geq 380$ nm).

3.1.1. Stoichiometric conditions

The stoichiometric reaction was run under nitrogen inert atmosphere and at room temperature, as a suspension in acetonitrile for complex **6** and in solution for complex **5**. The arylalkanes chosen for
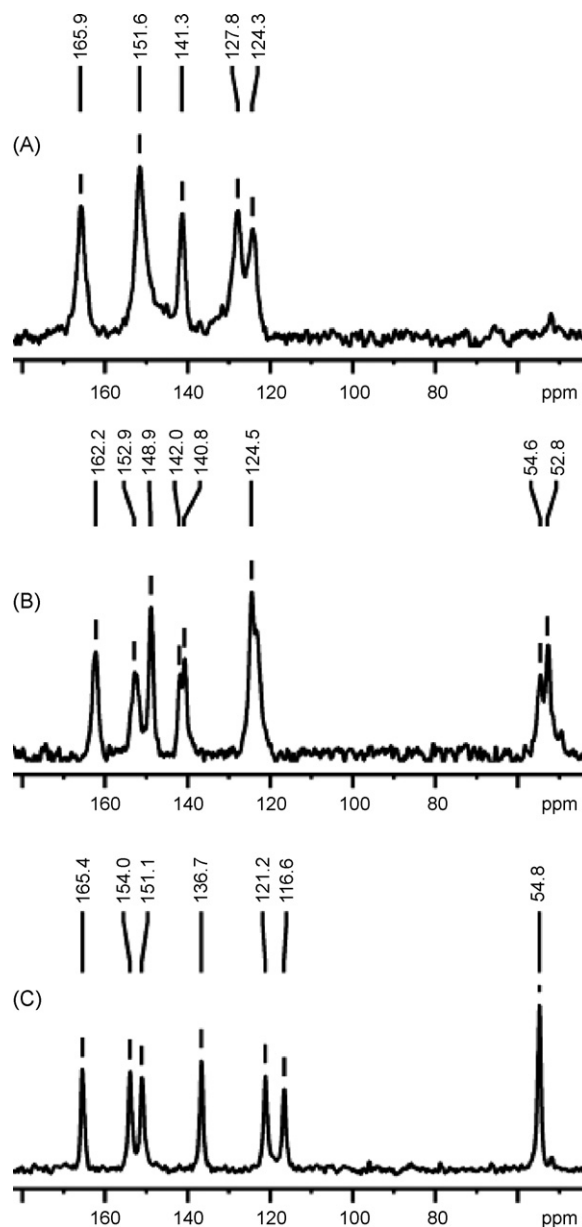

Fig. 3. ^{13}C CPMAS NMR Spectra recorded at 10 kHz for complex **6** (A), complex **5** (B) and 4,4′-dicarbomethoxy-2,2′-bipyridine (C).

this study were ethylbenzene and tetraline which have been shown [12] to be oxidized, under homogeneous conditions in the presence of analogous molybdenum-dioxo complexes to give respectively acetophenone and tetralone most probably via the initial formation of the corresponding alcohol.

As depicted in Fig. 4, all reactions were allowed to stand in the dark and under nitrogen for a period of 60 min, in order to establish an adsorption/desorption equilibrium (Section A), before light was turned on (Section B). The suspension of TiO$_2$ (DG 25), is totally inert indefinitely under these conditions, whereas complex **5**, as expected, undergoes an oxygen atom transfer similar to previously reported observations with analogous complexes [12], although to a slower rate due to the milder conditions (25% after 300 min). On the other hand, the anchored complex **6** displays a faster reaction rate yielding quantitatively (50%) through two successive O-transfer to give the ketonic product within 1 h. This is indicative of a significant synergic effect due to the photogenerated electronic flux, via
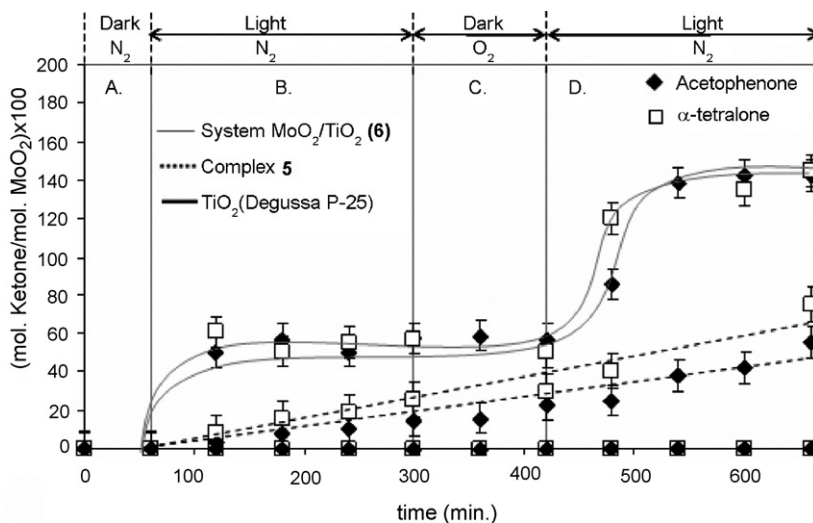
Fig. 4. Time evolution of the [mol. ketone]/[mol. MoO$_2$]) as a function of time in: (A) dark under N$_2$; (B) light ($\lambda \geq 380$ nm) under N$_2$; (C) dark under O$_2$; (D) light under N$_2$.
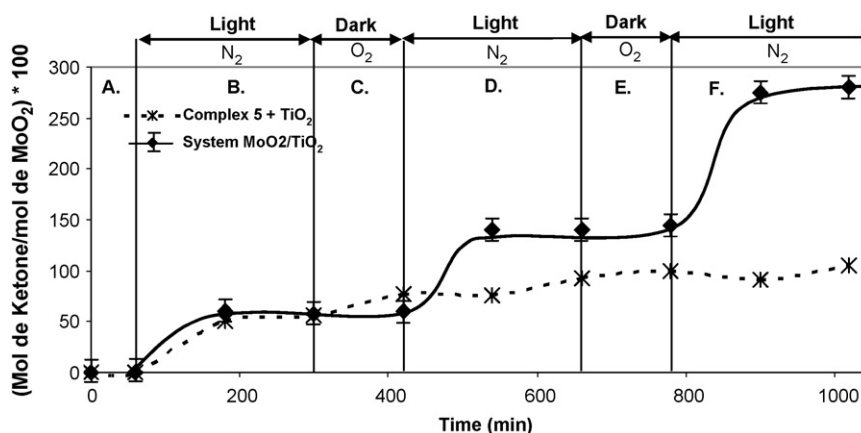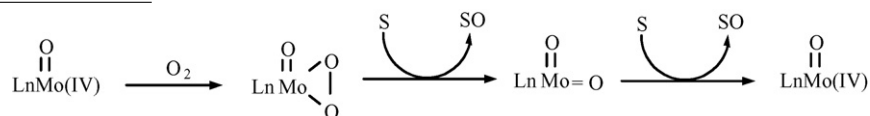

Fig. 5. Ethylbenzene oxidation. Time evolution of the [mol. acetophenone]/[mol. MoO$_2$] as a function of time in: (A) dark under N$_2$; (B) light ($\lambda \geq 380$ nm) under N$_2$; (C) dark under O$_2$; (D) light under N$_2$; (E) dark under O$_2$; (F) light under N$_2$.

the TiO$_2$ matrix onto the coordination sphere of the molybdenum complex.

When the light was turned off (Section C) and the dinitrogen evacuated and replaced by dioxygen in an attempt to reoxidize the reduced molybdenum species, no additional substrate oxidation was observed for 2 h with complex **6** whereas a very

slight increase of oxidized products was obtained with complex **5**. After this period of time (Section D), the dioxygen was evacuated, replaced by dinitrogen and the visible light turned back on. The homogeneous system with complex **5** continued the O-transfer process at the same rate most probably due to the presence of unreacted residual MoO$_2$(VI) complex, until it reached 50% of ketonic product after a total of 11 h. The anchored system, on the other hand, exhibited immediately an oxidation process analogous to the one observed in Section B, however, the O-atom transfer proceeded in this case to an extend twice as important (100%) indicating that two oxygen atoms per molybdenum center had been transferred.

Two very important precepts can be retained from these observations: first, that the anchored reduced Mo=O(IV) species is reoxidized *in the dark* under an O$_2$ atmosphere, and second that the reoxidation occurs to give, plausibly, an oxo-peroxo Mo(VI) species capable of transferring successively two oxygen atoms to a substrate as shown below.

Such peroxidation of a Mo=O(IV) entity [15,20] to give an oxo-peroxo molybdenum(VI) compound as well as its reduction to the corresponding molybdenum-dioxo(VI) [10,35,36] have indeed been reported. In addition the consumption of both oxygen atoms of O$_2$ in the complex **6** system can be compared to the Groves Ru-porphyrin system [37].

Results shown in Fig. 4 constitute, indeed, a novel, unprecedented and unambiguous observation of a stoichiometric O-transfer to an alkane. It was worth while to verify if this reoxidation/O-transfer sequence could be repeated more than once. The reaction with ethylbenzene was thus reiterated for a longer
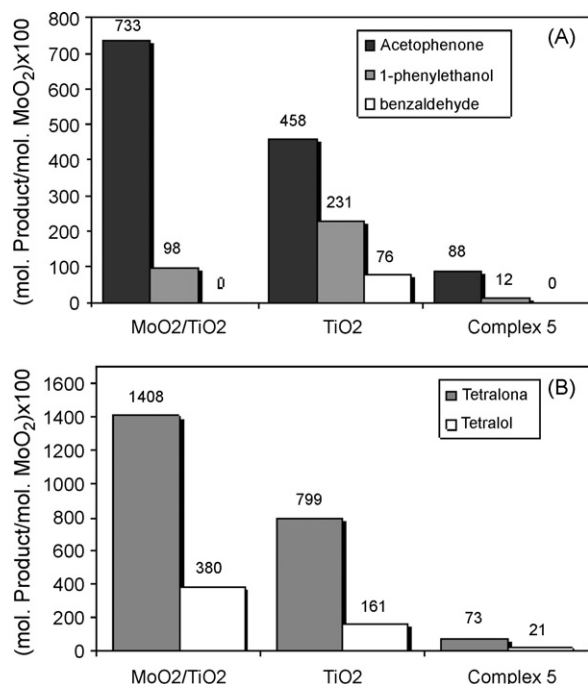
Fig. 6. Bar plot of oxidized products of ethyl-benzene (A) and tetraline (B), under catalytic conditions (O$_2$ and visible light irradiation) at room temperature and atmospheric pressure.

period. The results given in Fig. 5 confirm the recurrent character of the process and emphasize the stability of the MoO$_2$/TiO$_2$ system under the reaction conditions. This, furthermore, underlines the importance of anchoring the complex on the matrix, isolating thus the metallic centers, avoiding any deactivation by μ-oxo dimer formation [16,23]. This is unambiguously established by comparing the evolution of the reaction with complex **6** and with a "mechanical" mixture made of complex **5** and TiO$_2$ (Fig. 5).

3.1.2. Catalytic conditions

The oxidation reactions under catalytic conditions were run under dioxygen and with visible light irradiation at room temperature and atmospheric pressure.

The results illustrated in Fig. 6 show that contrary to the reaction run under inert atmosphere, TiO$_2$ alone, under O$_2$, generates products via a photogenerated charge transfer process [38–42]. The nature of the oxidized species, namely benzaldehyde from ethylbenzene, are wholly consistent with a typical TiO$_2$ induced oxidation. When the anchored MoO$_2$/TiO$_2$ complex **6** is used under identical reaction conditions, one observes an increase in the yield of oxidized products by a factor of two and above all the total absence of free radical generated benzaldehyde from ethyl benzene indicating in this case the presence of a different reaction pathway. Although one cannot totally exclude the existence of any TiO$_2$ induced oxidation via TiO$_2$(e$^-$) and TiO$_2$(h$^+$) generated upon irradiation, it seems plausible that such route is minimal and that complex **6** oxidation proceeds mainly via an O-transfer process identical to the one depicted under stoichiometric conditions under N$_2$. This is corroborated furthermore by the results obtained with complex **5** which exhibits the same selectivity as complex **6**. One must underline in addition the very important increase in reactivity when comparing complexes **5** and **6**. This significative synergic effect can be clearly attributed to the TiO$_2$ photogenerated flux onto the molybdenum coordination sphere.

4. Conclusions

The molybdenum(VI)dioxo-dibromo-(4,4′-dicarboxylato-2,2′-bipyridine) complex was anchored covalently on a TiO$_2$ solid matrix (**6**) and fully characterized by IR(KBr), UV-diffuse reflectance, IR-photoacoustic (FT-IR/PAS) and solid state ^{13}C NMR spectroscopies. When compared to the homogeneous molybdenum(VI)dioxo-dibromo-(4,4′-dicarbometoxy-2,2′-bipyridine), it brought two important improvements to the oxygen atom transfer system both under stoichiometric and catalytic conditions. On one hand, it increased significantly the O-transfer capability, via the photogenerated flux onto the molybdenum coordination sphere, and on the other, it showed that the reduced Mo(IV)O/TiO$_2$ unit obtained upon the O-transfer process could easily be reoxidized and reactivated under O$_2$ atmosphere, even in the dark, probably via the formation of the MoO(O)$_2$/TiO$_2$ species, capable in turn to transfer two oxygen atoms. In addition, the present study showed that anchoring the molybdenum-dioxo complex on the TiO$_2$ matrix isolated the metallic centers and avoided any undesired deactivation by μ-oxo dimer formation and lengthening, thus, significantly the lifetime of the catalyst.

Acknowledgments

References

[1] R.H. Holm, Chem. Rev. 87 (1987) 1401.
[2] R.H. Holm, Coord. Chem. Rev. 100 (1990) 183.
[3] F. Bottomley, L. Sutin, Adv. Organometal. Chem. 28 (1998) 339.
[4] I.A. Weinstock, Chem. Rev. 98 (1998) 113.
[5] A.M. Khenkin, L. Hill, J. Am. Chem. Soc. 115 (1993) 8178.
[6] W.A. Herrmann, Angew. Chem. Int. Ed. Engl. 88 (1988) 339.
[7] M.S. Thompson, J.T. Meyer, J. Am. Chem. Soc. 104 (1982) 4106.
[8] M.S. Thompson, J.T. Meyer, J. Am. Chem. Soc. 104 (1982) 5070.
[9] A.S. Goldstein, R.S. Drago, J. Chem. Soc. Chem. Commun. 21 (1991).
[10] H. Arzoumanian, Coord. Chem. Rev. 178 (1998) 191.
[11] H. Arzoumanian, G. Agrifoglio, H. Kreintzien, New J. Chem. 20 (1996) 699.
[12] H. Arzoumanian, L. Maurino, G. Agrifoglio, J. Mol. Catal. A: Chem. 20 (1997) 471.
[13] H. Arzoumanian, G. Agrifoglio, M. Capparelli, R. Atencio, A. Briceno, A. Alvarez-Larena, Inorg. Chim. Acta 359 (2006) 81.
[14] H. Arzoumanian, R. Bakhtchadjian, G. Agrifoglio, R. Atencio, A. Briceno, Trans. Metal. Chem. 31 (2006) 681.
[15] H. Arzoumanian, G. Agrifoglio, H. Kreintzien, M. Capparelli, J. Chem. Soc. Chem. Commun. (1995) 655.
[16] H. Arzoumanian, R. Bakhtchadjian, R. Atencio, A. Briceno, G. Verde, G. Agrifoglio, J. Mol. Catal. A: Chem. 260 (2006) 197.
[17] C.D. Nunes, M. Pillinger, A.A. Valente, A.D. Lopes, I.S. Goncalves, Inorg. Chem. Commun. 6 (2003) 1228.
[18] M. Jia, W.R. Thiel, Chem. Commun. (2002) 2392.
[19] M. Masteri-Farahani, F. Farzaneh, M. Ghandi, J. Mol. Catal. A: Chem. 248 (2006) 53.
[20] S.M. Bruno, J.A. Fernandes, L.S. Martins, I.S. Goncalves, M. Pillinger, P. Ribeiro-Claro, J. Rocha, A. Valente, Catal. Today 114 (2006) 263.
[21] P. Ferreira, I.S. Goncalves, F.E. Khun, A.D. Lopes, M.A. Martins, P. Pillinger, A. Pina, J. Rocha, C.C. Romao, A.M. Santos, T.M. Santos, A. Valente, Eur. J. Inorg. Chem. (2000) 2263.
[22] C.D. Nunes, A. Valente, M. Pillinger, A.C. Fernandes, C.C. Romao, J. Rocha, I.S. Goncalves, J. Mater. Chem. 12 (2002) 1735.
[23] C.A. Páez-Martínez, N. Castellanos, F. Martínez, F. Ziarelli, G. Agrifoglio, E.A. Páez-Mozo, H. Arzoumanian, Catal. Today 133–135 (2008) 619.
[24] J. Schaefer, E.O. Stejskal, J. Am. Chem. Soc. 98 (1976) 1031.
[25] O.B. Peersen, X. Wu, I. Kustanovich, S.O. Smith, J. Magn. Reson. 104 (1993) 33.
[26] R.L. Cook, C.H. Langford, R. Yamdagni, C.M. Preston, Anal. Chem. 68 (1996) 3979.
[27] G.J. Martin, M.L. Marin, J.P. Gouesnard, 15N NMR Spectroscopy, Springer-Verlag, Berlin, 1981, p. 18.
[28] A. Launkonis, D. Lay, A. Mav, A. Sarageser, W. Sasse, Aust. J. Chem. 39 (1986) 1053.

[29] T. Ben-Hadda, H. Le-Boezec, Polyhedron 7 (1988) 575.
[30] H.J. Kuhn, S.E. Braslavsek, R. Schmidt, Pure Appl. Chem. 76 (2004) 2105.
[31] G. Hatchard, C. Parker, Proc. R. Soc. Lond. A 235 (1956) 518.
[32] W.A. Nuget, J.M. Mayer, Metal–Ligand Multiple Bonds, Wiley, New York, 1988, pp. 113–119.
[33] R. Argazzi, C.A. Bignozzi, T.A. Heimer, F.N. Castellano, G.J. Meyer, Inorg. Chem. 33 (1994) 5741.
[34] B. Smith, Infrared Spectral Interpretation, CRC Press, Boca Raton, 1999, p. 103.
[35] H. Arzoumanian, J.-F. Petrignani, M. Pierrot, F. Ridouane, J. Sánchez, Inorg. Chem. 27 (1988) 3377.
[36] H. Mimoun, J. Mol. Catal. 7 (1980) 1.
[37] J.T. Groves, R. Quinn, J. Am. Chem. Soc. 107 (1985) 5790.
[38] Del T. Giacco, M. Ranchella, C. Rol, G.V. Sebastiani, J. Phys. Org. Chem. 13 (2000) 745.
[39] L. Amori, T. Del Giacco, C. Rol, G.V. Sebastiani, J. Chem. Res. (1998) 644.
[40] M. Bettoni, T. Del Giacco, C. Rol, G.V. Sebastiani, J. Photochem. Photobiol. A: Chem. 163 (2004) 481.
[41] M. Bettoni, T. Del Giacco, C. Rol, G.V. Sebastiani, J. Phys. Org. Chem. 19 (2006) 18.
[42] S. Evas, J.R. Lindsay, J. Chem. Soc., Perkin Trans. 2 (2002) 1541.