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Efficient and selective oxidation of aromatic amines into nitrosoarenes catalyzed by supported polyoxometalates

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ABSTRACT

In this article we studied the selective oxidation of various aryl amines into the corresponding nitrosoarenes, over polyoxometalates anions supported on mesoporous TiO_2 nanoparticles assemblies (POM-MTA) using H_2O_2 as "*green*" oxidant. The use of supported catalyst for heterogeneous catalysis offers several advantages on the catalyst reusability and the regio- and chemo-selectivity of the reaction process. Our catalytic experiments showed an exceptionally high activity of these catalysts towards aryl amines oxidation in the presence of H_2O_2, with high yields and selectivity at ambient conditions and short reaction times.

Keywords: *polyoxometalates, decatungstate, amine oxidation, nitrosoarenes, heterogeneous catalysis, mesoporous assemblies.*

1. INTRODUCTION

Synthesis of nitrosoarenes from the corresponding aryl amines is an important process, in laboratory and chemical industry due to their versatility as key intermediates in several biologically active natural products synthesis [1]. Despite their potentially wide applications, many of the reported methods[2] utilize a single or limited subset of several functionalized nitrosoarenes. Among the most common synthetic procedure, nitrosation of simple arenes and arylmetallics [2,3], the oxidation of anilines to the corresponding nitrosoarene is the most widely utilized [4]. Although many protocols for this conversion have been reported in the literature [2], yet formation of undesired side products such as azo- and azoxy-compounds or over-oxidized nitro compounds were observed in significant amounts. So far, various synthetic routes have been explored for the fabrication of C-nitroso arenes [2-8], such as nitrosation of arenes [3], organometallics and organoborates [3,6], addition reactions to C-C double bond, oxidation of primary amines or hydroxyl amines [4,7], and reduction of nitro compounds [2]. Perhaps, the most popular methodology to synthesize C-nitroso compounds is the transition metal-catalyzed oxidation of primary amines in the presence of hydrogen peroxide [2,8], although this process suffers from low chemoselectivity due to the formation of the corresponding dimeric products or over-oxidation to the nitro compounds. Herein, we studied the general applicability of various decatungstate catalysts supported on mesoporous titania [9] for the selective oxidation of several aryl amines into the corresponding nitrosoarenes, using H_2O_2 as a "*green*" oxidant. For comparison, the corresponding homogeneous reactions were recorded under the same reaction conditions. The use of supported catalyst for heterogeneous catalysis offers several advantages on the catalyst reusability and the chemo-selectivity of the reaction process. Under our catalytic conditions, an exceptionally high activity of these composite materials towards aryl amines oxidation in the presence of H_2O_2 was observed, with high yields at ambient conditions and short reaction times.

2. EXPERIMENTAL SECTION

2.1. Synthesis of DT-MTA catalyst.

Mesoporous TiO_2 nanoparticle assemblies (MTA) were synthesized using previously reported procedure [10]. The mesoporous structure of MTA was investigated by small-angle X-ray scattering (SAXS) and transmission electron microscopy (TEM). Analysis of the TEM images gives an average particle size of about ~7.8 nm for TiO_2 nanocrystals. In addition, N_2 adsorption-desorption measurements showed the MTA catalyst contains narrow-sized mesopores between nanoparticles. The specific Brunauer-Emmett-Teller (BET) surface area and the average pore diameter of MTA were calculated to be 157 m^2g^{-1} and 7.7 nm, respectively [10]. Tetrabutylammonium decatungstate ($[Bu_4N]_4W_{10}O_{32}$) was synthesized and purified by literature procedures [11]. The $[W_{10}O_{32}]^{4-}$ anions supported on mesoporous titania (DT-MTA) were prepared as follows: 1 g of Brij-58($HO(CH_2CH_2O)_{20}C_{16}H_{33}$) surfactant was dissolved in 10 mL of anhydrous ethanol with stirring at room temperature. Then, an appropriate amount of $[Bu_4N]_4W_{10}O_{32}$, 1.56 mmol of titanium tetrachloride ($TiCl_4$) and 5.55 mmol of titanium(IV) propoxide were slowly added to the surfactant solution with continuous stirring. The mixture was kept at room temperature for 2 h and then was transferred to a Petri dish and stored in an oven at 40 °C for 7 days. Mesoporous solid was prepared by heating the gel product at 100 °C under vacuum for 12 h, and then gently calcining in air to 260 °C for 4 h and, subsequently, to 350 °C for 6 h with a heating rate of 0.5 °C min^{-1}. A series of mesoporous

$W_{10}O_{32}^{4-}/TiO_2$ composite structures (denoted as DT-MTA) with different loading amount of decatungstateclusters was prepared by varying the amount of $W_{10}O_{32}^{4-}$ from 1 to 4, and then to 9 wt.% with respect to TiO_2.

2.2. Physical Characterization.

Small-angle X-ray scattering (SAXS) measurements were performed on a Rigaku S-MAX 300 high-brilliance system using Cu K*α* radiation (80 kV and 40 mA). The sample-to-detector distance and center of the beam were precisely measured using a Ag-behenate standard (d_{001} = 58.38 Å). The two-dimensional diffraction images were integrated into a one-dimensional diffraction pattern, as a function of q, with the Fit2D program. Scattering data were corrected for dark current and empty tube scattering. Transmission electron microscopy (TEM) images were taken with a JEOL JEM-2100 electron microscope (LaB_6 filament) operating at an accelerated voltage of 200 kV. Elemental compositions were obtained using a JEOL JSM-6390LV scanning electron microscope (SEM) operated at 20 kV. Data acquisition was performed using an 100 s accumulation time. Nitrogen adsorption and desorption isotherms were measured at -196°C with a Quantachrome Nova 3200*e* sorption analyzer. Before analysis, the samples were degassed at 150 °C under vacuum ($<10^{-4}$ mbar) for 12 h. The surface areas were calculated using the Brunauer-Emmett-Teller (BET) model on the adsorption data for 0.05 – 0.25 relative pressure (P/P_o) region, the total pore volumes were calculated from the adsorbed amount at the P/P_o of 0.95, and the distributions of pore sizes were derived from the adsorption branch of isotherms, using the non-local density functional theory (NLDFT) method for slit pore geometry.

2.3. Catalytic reactions.

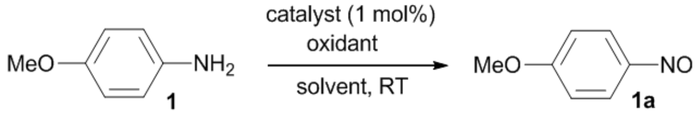
In a typical procedure, 0.6 mmol of H_2O_2 and DT-MTA catalyst (45 mg, 1 mol%) were added into a sealed tube containing *p*-anisidine (**1**, 37 mg, 0.3 mmol) and acetonitrile (1 mL). The reaction was stirred at room temperature for appropriate time. After completion as evidenced by TLC, the slurry was filtered under pressure through a short pad of celite-silica to withhold the catalyst and the excess of H_2O_2 with the aid of acetonitrile (~5 mL). The filtrate was evaporated under vacuum to afford pure 1-methoxy-4-nitrosobenzene (**1a**, 34 mg, 91% yield) which in solution gives a green-blue characteristic color.

3. RESULTS AND DISCUSSION SECTION

So far, we have reported the catalytic behavior of the decatungstate anion supported into TiO_2 mesoporous assemblies (DT-MTA) and $[Bu_4N]_4W_{10}O_{32}$ (TBADT) compound with respect to the selective photooxidation of *para*-substituted benzyl alcohols into the corresponding ketones [9h,12]. To study the general applicability of these catalytic systems, herein we oxidized a series of *p*-substituted anilinesinto the corresponding nitroarenes under mild conditions.To evaluate the reaction conditions, the oxidation of *p*-anisidine (**1**) by different oxidants, solvents and catalysts was initially investigated (Table 1). For this reason various decatungstate catalysts supported on mesoporous TiO_2 (MTA) with different wt% loading amount of $W_{10}O_{32}^{4-}$(DT-MTA(wt%)) have been prepared, i.e. DT-MTA(1), DT-MTA(4) and DT-MTA(9). Under the evaluated conditions, DT-MTA (1), 3.0 equiv of H_2O_2 and acetonitrile as the solvent of choice, provide almost quantitative (91%) and selective oxidation of **1** into the corresponding nitrosoarene **1a** within 30 min (Table 1, entry 11). The same reaction is also feasible with homogeneous $[Bu_4N]_4W_{10}O_{32}$ (TBDA) and $Na_3PW_{12}O_{40}$ (SPDA) catalysts (Table 1, entries 5 and 6), although with lower conversion yield and with a significant amount of the corresponding nitroarene at longer reaction time. No reaction product was observed when *tert*-butyl hydroperoxide and molecular oxygen were used as oxidants under the same reaction conditions (Table 1, entries 8 and 9). In the presence of Degussa TiO_2 (P25) nanoparticles and MTA mesoporous a mixture of the corresponding azoxy-, nitroso- and nitro compounds was observed based on ^1H NMR spectroscopy (Table 1, entries 10 and 14), while in the absence of catalyst, *p*-anisidine was completely unreactive (Table 1, entry 7).

For comparison, the corresponding heterogeneous catalytic reactions, using the supported DT-MTA catalysts, lead to the high conversion of the **1** into the nitroso compound at 0.5 h (Table 1, entries 11 - 13). It is worthnoting that in these reactions a remarkable amount of the corresponding azoxy-arene was observed ranged from 10% to 19% and from 19% to 26% relative yield, respectively (results not shown). In consistent with this observation, under homogeneous conditions TBDA catalyze the oxidation of anisidine (**1**) forming the corresponding nitrosoarene as the major product accompyining with a small amount of the corresponding azoxyarene in 11% relative yield (Table 1, entry 5).

Table 1. Evaluation of POM catalysts, oxidants and solvents, in the catalytic oxidation of *p*-anisidine (**1**) into 1-methoxy-4-nitrosobenzene (**1a**).



Entry	Catalyst[a]	Solvent	Oxidant[b]	Time/Yield[c]
1	TBDA	DCM	H_2O_2	0.5 h/44%
2	TBDA	EA	H_2O_2	0.5 h/no reaction
3	TBDA	acetone	H_2O_2	0.5 h/15%
4	TBDA	MeOH	H_2O_2	0.5 h/69%
5	**TBDA**	**CH_3CN**	**H_2O_2**	**0.5 h/89%**
6	SPDA	CH_3CN	H_2O_2	0.3 h/90%[d]
7	no catalyst	CH_3CN	H_2O_2	1 h/no reaction
8	TBDA	CH_3CN	O_2	1 h/no reaction
9	TBDA	CH_3CN	tBuOOH	1 h/no reaction
10	Degussa (P25)	CH_3CN	H_2O_2	0.3 h/ 87%[e]
11	**DT-MTA(1)**	**CH_3CN**	**H_2O_2**	**0.5 h/91%**
12	DT-MTA(4)	CH_3CN	H_2O_2	0.5 h/81%
13	DT-MTA(9)	CH_3CN	H_2O_2	0.5 h/74%
14	MTA	CH_3CN	H_2O_2	0.5 h/82%[e]

[a]45mg of the catalyst were used in each oxidation.[b] 3.0 equiv. [c] Relative yield of **1a** as determined by ^1H NMR. [d]The corresponding nitro compound was observed by ^1H NMR, in 15% relative yeld. [e]The corresponding azoxy- and azo compounds were observed by ^1H NMR spectroscopy.

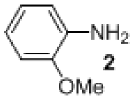
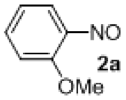
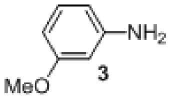
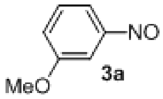
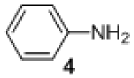
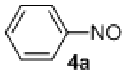
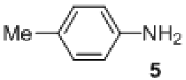
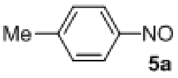
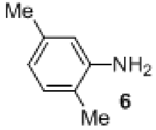
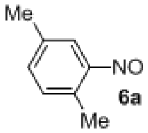
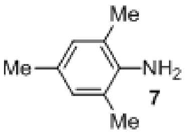
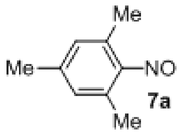
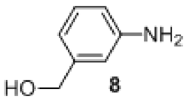
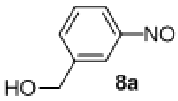
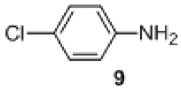
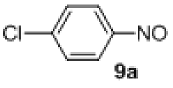
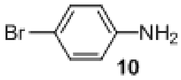
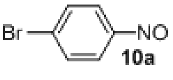
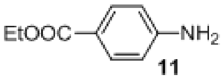
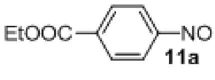
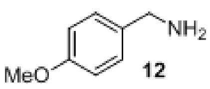
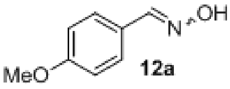
The use of supported catalysts on a well ordered metal oxide surface for heterogeneous catalysis offers several advantages on the catalyst reusability and the chemo-selectivity of the reaction process. To study the general applicability of this catalytic system DT-MTA(1), a series of substituted anilines (**2**-**11**) were oxidized under similar conditions using H_2O_2 as *green* oxidant. The results from these oxidations were summarized in Table 2. In all cases the corresponding nitrosoarenes (**2a**-**11a**) were formed, with high yields (up to 99%) and selectivity (>90%). It is remarkable that in all cases the nitrosoarenes *versus* the corresponding azoxy-compounds were formed in a ratio up to 12/1. This ratio was determined by ^{1}H NMR spectroscopy. It is intereting to note here that the electron reach aromatic amines (**2**-**8**) are oxidized faster, with excellent isolated yields, compared to the electron poor amines (**9**-**11**), in which 5 equivalent of H_2O_2 were necessary to form the nitrosoarenes **9a**-**11a** as major product. In the oxidations of **9** and **11** significant amounts (~10 %) of the corresponding nitroarene were observed by ^{1}H NMR (results not shown). Benzyl amine (**12**) were also oxidized under the above described conditions to the corresponding oxime(**12a**) in good yield (45%), yet, excess of hydrogen peroxide (6 equiv) and prolonged reaction time is required (Table2). After simple filtration of the reaction mixture, the corresponding oximes were isolated by column chromatography in a ratio of E/Z = 9/1.

In all cases, the nitrosoarene was isolated by a simple filtration of the reaction mixture through a short pad of silica in order to withhold the catalyst and the amount of the unreactive hydrogen peroxide with the aid of acetonitrile (∼5 mL). The filtrate was evaporated under vacuum to afford the corresponding products in pure form. Product analysis was conducted by ^{1}H NMR and ^{13}C NMR spectroscopy (Bruker AM 300 and Agilent AM 500). The high isolated yields and the simple and mild oxidation conditions make this heterogeneous catalytic reaction a synthetically useful organic transformation of aryl amines into nitrosoarenes.

Because of the extended network of interconnected decatungstate anion andTiO$_2$ nanoparticles, the DT–MTA(x) catalyst can be easily separatedfrom the reaction mixture by filtration and could be reused forthe next catalytic reaction. The reusability of the DT–MTA(1) was examined using anisidine(**1**) as a model substrate. Under the above described catalytic conditions, **1** was oxidized into the corresponding nitrosoarene (**1a**) with high yields(in a range of 89 to 91%) even after three successivecatalytic runs, reflecting very good reusability (results not shown).

Table 2. Chemoselective oxidation of aryl amines into nitroso arenes with H_2O_2 catalyzed by DT-MTA(1).

$$\text{R-NH}_2 \xrightarrow[\text{H}_2\text{O}_2\text{, CH}_3\text{CN, RT}]{\text{DT-MTA(1) (1\% mol)}} \text{R-NO}$$

Reactant	Product	Time/Yield[a]
 **2**	 **2a**	1 h / 96%
 **3**	 **3a**	0.5 h / 93%
 **4**	 **4a**	1 h / 95%
 **5**	 **5a**	1 h / 96%
 **6**	 **6a**	1 h / 99%
 **7**	 **7a**	1 h / 98%
 **8**	 **8a**	2 h /94%
 **9**	 **9a**	24 h /65%
 **10**	 **10a**	3 h /94%
 **11**	 **11a**	24 h /61%
 **12**	 **12a**	24 h /45%[b]

[a]Isolated yields. [b] A mixture of oximes, nitro compound and unreactive amine was isolated and the corresponding oximes (*E* and *Z* isomers) were isolated by column chromatography.

4. CONCLUSIONS

In conclusion, we report that titania-supported decatungstate catalysts can oxidize a series of aryl and benzyl amines into nitrosoarenes and oximes using hydrogen peroxide as *green* oxidant. The reaction is fast and highly chemoselective under ambient conditions, which is proven to be a synthetically useful organic process. Further studies on the effect of the inorganic support nature, as well as on using different polyoxometalates clusters for the mechanistic pathway elucidation are in progress.

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