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Plasmon heating mediated Friedel-Crafts alkylation of anisole using supported AuNP@Nb_2O_5 catalysts

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ABSTRACT

Two different hybrid materials composed of gold nanoparticles (AuNPs) supported on either commercial niobium oxide HY 340 or mesoporous niobium oxide catalyzed the Friedel-Crafts alkylation of anisole by benzyl chloride. Excitation of the surface plasmon of the supported AuNPs allowed the reaction to occur at lower temperatures by acting as an alternative heat source. The localized heating produced *via* plasmon excitation permitted the acid catalyzed reaction to occur - at the Lewis acid sites on the Nb_2O_5 support - at 80 °C while thermal-dark reactions using a conventional heat source, required temperatures of 120 °C or higher. The catalytic activity of the tested hybrid materials decreased with storage time. However, the deactivation showed to be reversible upon lyophilisation indicating that the nature of the deactivation could be due to water adsorption.

Introduction

Many organic compounds produced by catalytic reactions, such as the Friedel-Crafts reaction, require elevated temperatures and harsh acidic conditions in order to achieve high efficiencies.[1] The Friedel-Crafts reaction has become one of the most important tools in organic synthesis representing one of the oldest Lewis acid-assisted reactions for aromatic compounds. It was first reported in 1877[2] and numerous versions of this transformation have been reported in the last 140 years.[3–5] The conventional Friedel-Crafts alkylation mechanism occurs *via* electrophilic substitution using stoichiometric and/or sub-stoichiometric amounts of either Brønsted acids or strong mineral Lewis acids such as, $AlCl_3$, $FeCl_3$, BF_3, $ZnCl_2$, HF or H_2SO_4.[3,6,7] Recently, Nb_2O_5[8] and niobium phosphate[9] have been proposed as heterogeneous catalysts for the liquid phase Friedel-Crafts alkylation of anisole by benzyl chloride. Niobium-based acid catalysts have shown to be very promising as its Lewis acid sites present a certain degree of water tolerance, unlike other solid Lewis acid catalysts such as $AlCl_3$ making Nb_2O_5 a more robust catalyst compared to the conventional ones.[10] However, the main drawback continues to be the elevated temperatures required to perform the catalysis.[7–9] The harsh conditions required to achieve these transformations have stimulated the synthesis and design of new catalysts capable of performing under milder conditions.

Moreover, it is important to develop new photocatalytic materials that can be controlled and activated by light promoting environmentally friendly processes. Adapting traditional thermal processes to light activation generally allows milder experimental conditions and provides spatio-temporal control making them suitable for imaging and on-demand triggering.

Heterogeneous metal-nanoparticle photocatalysts have been recognized as suitable materials for green chemistry due to their efficient light harvesting properties.[11] Surface plasmon resonance (SPR) excitation of noble metal nanoparticles can induce antenna-like interactions leading to enhanced absorption, electron/hole transfer and localized plasmon heating. These effects can contribute to catalysis by activating molecules on the vicinity of the nanoparticles facilitating chemical transformations.[12] It has been reported that the excitation of the SPR of AuNPs can lead to local temperatures of approximately 500 °C.[13] Localized plasmon heating has been reported to be able to modify cargo diffusion kinetics within mesoporous silica matrices, to facilitate the generation and release of singlet oxygen from anthracene endoperoxide functionalized AuNPs and to promote the de-hybridization of double stranded DNA.[14,15]

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Two aspects related to plasmon excitation used in heterogeneous catalysis are charge-transfer and heating. Many examples are available in the literature regarding the active participation of charge-transfer -resulting from plasmon excitation- in the local chemistry; hydrocarbon reforming, oxidation and hydrogenation reactions, as well as the decomposition of phenol via assisted Fenton decomposition of hydrogen peroxide are some of the examples found in the literature.[16,17]

Besides the active participation of AuNP in the localized chemistry of catalytic processes it has also been reported that plasmonic nanostructures can be used to drive chemical reactions by behaving as a heat source alternative to conventional bulk heating providing the necessary energy for the catalytic reactions to occur at a lower temperature.[16] Moreover, it has been demonstrated that the plasmon excitation of AuNP deposited on metal oxide solids can enhance the performance of a catalyst through the SPR effects by assisting photocatalytic redox reactions or energy conversion processes giving rise to superior light-to-heat conversion efficiencies.[16,18,19]

While there are a few reports related to photocatalytic Friedel-Crafts chemistry, they refer to the photoexcitation of organic substrates rather than the photoactivation of the catalytic reaction. Our work examines the possibility of combining the Lewis acidic properties of two niobium oxide-based materials with the localized plasmon heating effect of AuNPs in order to perform a Friedel-Crafts reaction at low temperatures eliminating the need of an external heat source.

Results

Two different niobium oxide catalysts were synthesized in order to assess the feasibility of plasmon-mediated catalysis of the Friedel-Crafts alkylation of anisole. AuNPs were supported either on commercial niobium oxide (HY 340) or on mesoporous niobium oxide by adsorbing the gold salt in the materials followed by reduction - with sodium borohydride - to its metallic form. Fig. 1 shows the TEM images of the AuNP/Nb_2O_5 nanocomposites. The average diameter of the supported gold nanoparticles was found to be 6.2 nm and 4.4 nm for AuNP@Nb_2O_5 (HY340) and AuNP@mesoNb_2O_5, respectively. The corresponding size histograms can be found on Figs. S3 and S4 of the supporting information.

The number of Lewis and Brønsted acid sites for the different AuNP/Nb_2O_5 nanocomposites and bare niobium oxide materials was determined by the pyridine vapor adsorption method and reported on Table 1. These amounts were estimated by analyzing the characteristic FT-IR peaks at 1450 and 1540 cm^{-1}; the former corresponds to Pyridine-Lewis acid coordination adducts while the latter represents the number of pyridinium ions formed upon reduction of pyridine by Brønsted acid sites (see Fig. S5).

The decrease in Brønsted acidity of the catalyst upon AuNP incorporation can be attributed to the use of sodium borohydride as a reducing agent during their synthesis where an exchange between the sodium ions of $NaBH_4$ and the protons of the Brønsted acid sites is most likely to occur. This is clearly seen in the case of AuNP@Nb_2O_5 and is corroborated by the comparison between the Brønsted acidity of Nb_2O_5 and Na^+/ Nb_2O_5 in which the acidity decreases when sodium ions are added.

The Lewis acidity of the catalyst stays relatively constant when AuNPs are incorporated either on Nb_2O_5 (HY340) or on mesoporous Nb_2O_5.

Niobium phosphate has been reported as a potential catalyst for alkylation reactions of aromatic compounds with benzyl alcohol and benzyl chloride.[6,9,20,21] However, the use of AuNPs supported on niobium oxide to catalyze the benzylation of aromatic compounds using benzyl chloride had not been reported.

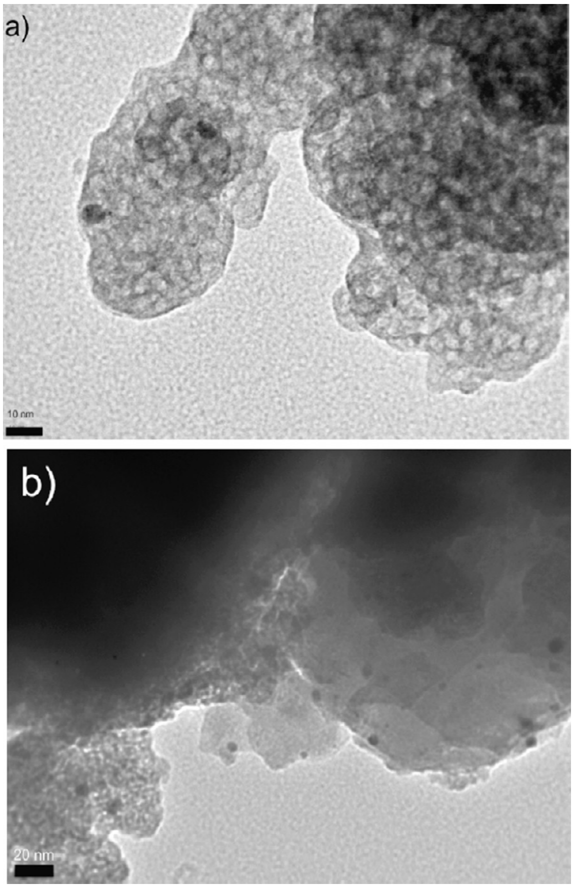

Fig. 1. TEM images of niobium based gold nanocomposites. (a) AuNP@Nb2O5 (HY-340; scale bar: 10 nm) and (b) AuNPmeso@Nb_2O_5 (scale bar: 20 nm).

Table 1
Number of Brønsted and Lewis acid sites for different Nb_2O_5 nanocomposites determined by Pyridine adsorption.

Material	Brønsted (μmol g^{-1})	Lewis (μmol g^{-1})
Nb_2O_5 (HY 340)	0.29	0.0091
Na^+/ Nb_2O_5	0.0	0.014
Au@Nb_2O_5 (HY 340)	0.17	0.021
Nb_2O_5 (mesoporous)	0.031	0.039
AuNP@mesoNb_2O_5	0.015	0.032

With the aim of exploring the extent of the contribution of AuNPs to the catalytic activity of the niobium-based materials, the Friedel-Crafts alkylation reactions were performed at different temperatures and followed over time in the presence and absence of LED irradiation. The reactions between anisole and benzyl chloride in the presence of the synthesized Nb_2O_5 hybrid materials were performed using a 1:50 benzyl chloride: anisole ratio in order to obtain quantitative amounts of alkylated - ortho and para - isomer products avoiding, at the same time, the formation of secondary dialkylated products.

Since the reactions were performed in small amounts of alkylating agent, the results shown in Figs. 2 and 3 are expressed in terms of the percentage conversion of benzyl chloride. As can be seen, in order for the reactions to proceed in the absence of LED irradiation, temperatures above 100 °C were required when using either bare Nb_2O_5 materials or supported-AuNP nanocomposites as catalysts. Nonetheless, the conversions increased significantly at higher

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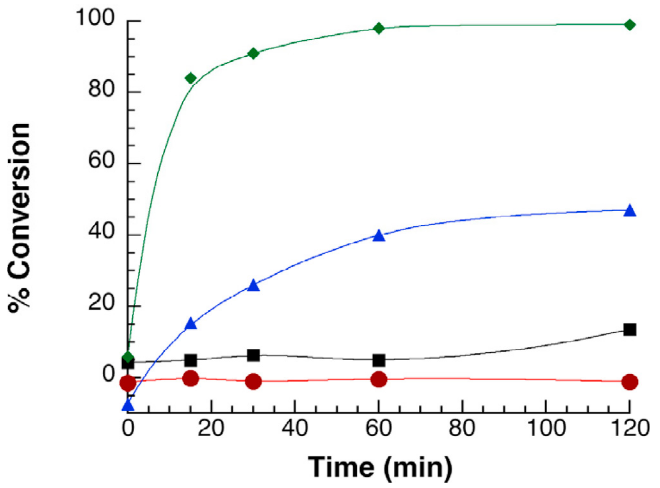

Fig. 2. % Conversion of benzyl chloride with time at (●) 80 °C, (■) 100 °C, (▲) 120 °C and (◆) 150 °C using AuNP@Nb_2O_5 as catalyst, under dark conditions.

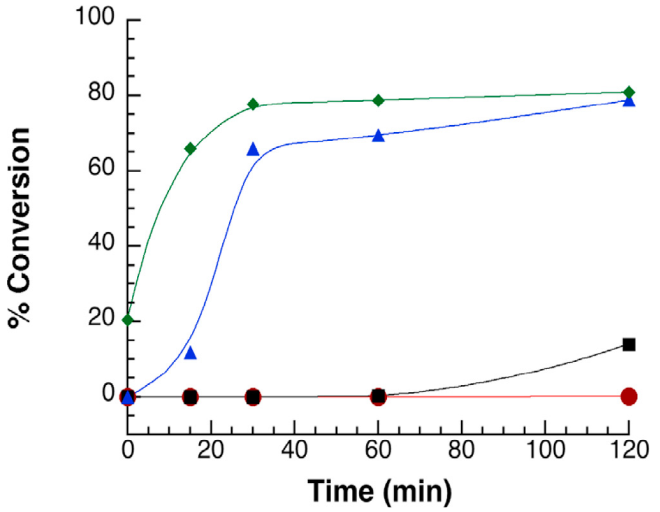

Fig. 3. % Conversion of benzyl chloride with time at (●) 80 °C, (■) 100 °C, (▲) 120 °C and (◆)150 °C using AuNP@mesoNb_2O_5 catalyst under dark conditions.

temperatures reaching 80% and 100% for AuNP@mesoNb_2O_5 and AuNP@Nb_2O_5, respectively.

When comparing the AuNP-supported catalysts with the analogous bare supports, the latter were more active in the absence of light yet, the opposite was observed under LED irradiation. The corresponding percent conversion curves for reactions performed in the presence of bare HY340 and mesoporous Nb_2O_5 are shown on Figs. S6 and S7 of the supporting information.

Fig. 4 shows the percent conversion of benzyl chloride with time for the reactions catalyzed by AuNP@Nb_2O_5 and AuNP@mesoNb_2O_5 under LED irradiation.

During irradiation, the sample temperature reached 80 °C; such bulk heating can be attributed to intense light absorption by the sample. However, in spite of the fact that the temperature reached was much lower than the temperature required for the reaction to proceed thermally (120 °C), 100% conversion was obtained within 2 h. Therefore, product formation under irradiation conditions can be attributed to the local plasmon heating effect generated by plasmon excitation.

The conversion of benzyl chloride proceeded faster when using AuNPmeso@Nb_2O_5 compared to AuNP@Nb_2O_5 (HY 340). These results are consistent with the fact that the former has a much higher surface area than the latter, reflecting its mesoporous structure. Since catalysis is a surface phenomenon this often results in faster reactions. In addition, these results agree with the fact that AuNPmeso@Nb_2O_5 contains more Lewis acid sites, which are suggested as responsible for the catalysis.

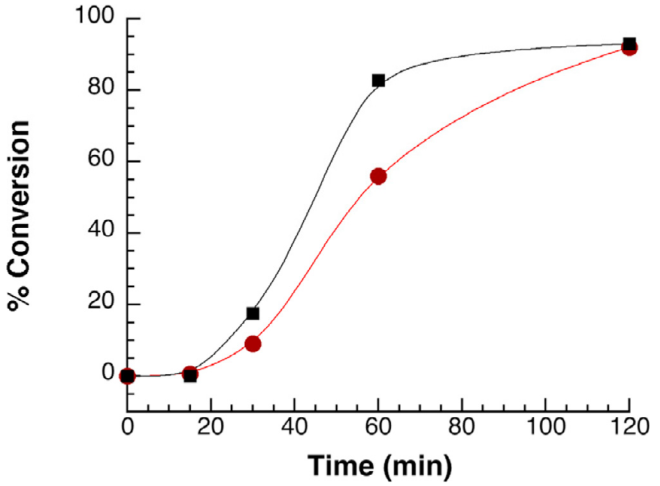

Fig. 4. % Conversion of benzyl chloride with time under green light LED irradiation. (●) AuNP@Nb_2O_5 and (■) AuNPmeso@ Nb_2O_5. During LED irradiation the temperature gradually rises to about 80 °C (see text).

So far, the use of supported AuNP in catalysis has been reported in the literature to elucidate the nature of active sites and reaction mechanisms.[22–25] Only a few publications have included information on the thermal stability and stabilization of gold nanoparticles on solid supports.[19,24] In this study, the stability of AuNP@Nb_2O_5 solid materials was assessed by monitoring the surface plasmon band of AuNPs by UV–vis diffuse reflectance (DR) spectroscopy.

The corresponding DR spectra of AuNP@Nb_2O_5 before and after reaction under LED irradiation at 80 °C can be seen in Fig. 5. A blue shift and change on the shape of the SPR band was recorded which is consistent with either a decrease in size and/or degree of aggregation of the AuNP, as previously reported in the literature.[26–29] SEM studies were not conclusive when proving decrease in size and/or degree of aggregation due to the polydisperse nature of the AuNPs on the catalyst. The possibility that the blue shift reflected Au cations leaching into solution,[30] was ruled out as the

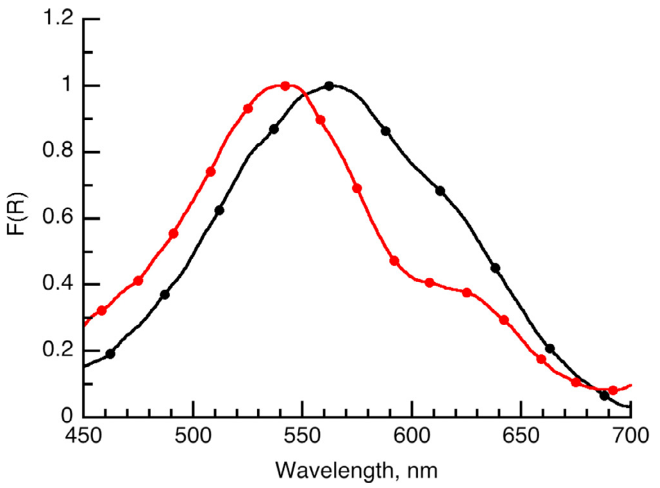

Fig. 5. Diffuse reflectance of AuNP@Nb_2O_5 (HY340) (●) freshly made catalyst and (●) after LED irradiation, 80 °C.

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supernatant tested negative for gold in solution. The recyclability of the AuNP@Nb_2O_5 catalysts was tested obtaining a maximum conversion of approximately 11% upon a second use. A blue shift in the diffuse reflectance spectrum was also observed when performing the reaction using a conventional heat source (see Fig. S9), which can also be interpreted as a possible decrease in AuNP size and/or degree of aggregation, which may cause deactivation of the catalytic sites.

Storage time dependence of the catalytic activity for plasmon-mediated reactions was also evaluated. In the case of AuNP@Nb_2O_5 HY340, the percent conversion of benzyl chloride decreased from 100% for a freshly prepared catalyst to approximately 60% and 13% for reactions performed utilizing the same catalyst batch upon 1 week and 2 weeks aging, respectively (see Fig. 6). A slower decay in activity was observed for AuNP@mesoNb_2O_5 for which 38% benzyl chloride conversion was still retained after five weeks storage time (Fig. S8). The DR spectra of freshly prepared AuNP@Nb_2O_5 catalyst and the same catalyst 2 weeks after preparation remained virtually unchanged. However, for a fully deactivated catalyst (5 week old) the DR spectrum showed significant differences compared to its active counterpart.

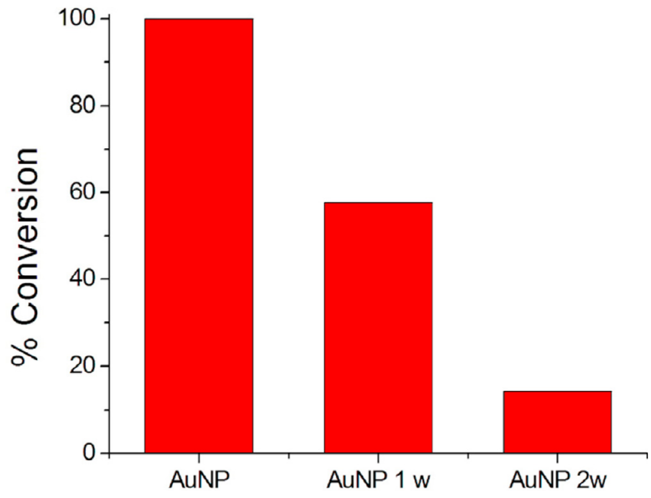

Fig. 6. % Conversion of benzyl chloride with AuNP@Nb_2O_5 HY 340 catalyst with storage time and reaction under green LED irradiation: freshly made catalyst (AuNP) after 1 week (AuNP 1w) and 2 weeks (AuNP 2w).

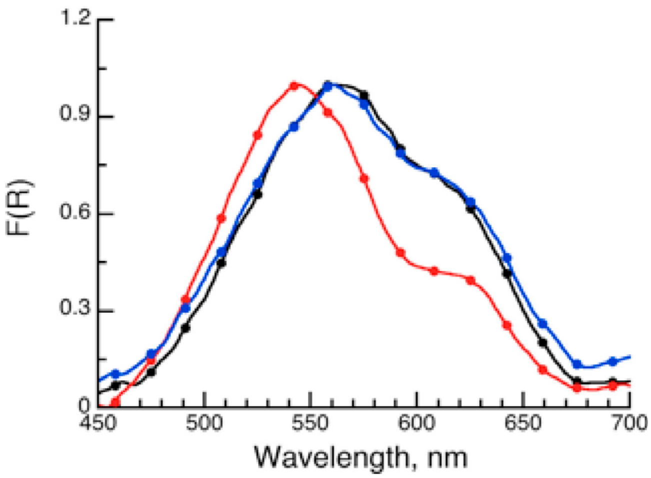

Fig. 7. Diffuse reflectance spectra of AuNP@Nb_2O_5 (HY340). (●) Freshly prepared, (●) 5 weeks old storage time previous lyophilization and (●) 5 weeks storage time after lyophilization.

Lyophilization of a fully deactivated catalyst for 8 h was performed to establish if Lewis acid deactivation was due to water adsorption, and the possibility to recover the lost catalytic activity by removing adsorbed water. Further analysis of the DR spectra (Fig. 7) showed that the blue shift in the absorption maxima upon complete catalyst deactivation (by 5 week storage) was reversed by lyophilization; the DR spectra of the lyophilized sample matches the one corresponding to the freshly prepared catalyst. Additionally, the catalytic activity of the lyophilized sample was tested resulting in 18% conversion compared to the null percentage before lyophilization indicating partial recovery of the catalytic activity. Heating of the catalyst under vacuum was also considered for water removal; however, complete catalyst deactivation was maintained making lyophilization the best method for reactivation.

Discussion

Significant differences were observed between reactions performed under irradiation, compared to those performed thermally in the dark. In order for the reaction to overcome the activation barrier and proceed thermally in the absence of irradiation the temperature must reach 120 °C or higher. Nonetheless, high conversions were obtained under irradiation in spite that the bulk temperature of the reaction mixture reached only 80 °C. Fasciani and co-workers[13] reported that the local temperature near the surface of AuNPs reaches 500 °C when the surface plasmon band is excited. These findings suggest that upon irradiation the localized plasmon heating effect near the active sites of the AuNP@Nb_2O_5 materials reach temperatures high enough to overcome the activation barrier. The use of light activated AuNP supported on Nb_2O_5 materials constitutes a major advantage due to its ability to perform transformations at lower temperatures and without the need of an external heat source.

The proposed mechanism for these transformations is an aromatic electrophilic substitution were the Lewis acid sites would facilitate the formation of a carbocation by reacting with benzyl chloride. Then, the aromatic system of anisole –present in excess– would attack the carbocation forming the final products.

Different strategies have been proposed to synthesize metal nanoparticles supported on metal oxide materials and how stabilizing the nanoparticles can control their corresponding catalytic activities. Most of the literature is focused on size stabilization and better thermal stability, which has been achieved by modifying the environment of gold AuNPs, *i.e.*, by strengthening metal–support interactions and/or designing stabilizers that encapsulate them.[19,31–33] Nevertheless, in the case of AuNPs supported on Nb_2O_5 materials, the efficiency of the plasmon heating effect was achieved by deposition of unprotected AuNPs to avoid possible secondary reactions.

In 2011, Nakashima et al., proposed the use of hydrated niobic acid ($Nb_2O_5{\cdot}nH_2O$) as heterogeneous Lewis acid catalyst proving that in spite the presence of water molecules the NbO_4-H_2O adducts formed could still behave as active Lewis sites.[10] However, the changes observed in the DR spectra on Fig. 7 accompanied by the decrease in catalytic activity with storage time, and the Lewis acid affinity for water molecules proposed by Nakashima, suggest that the deactivation of the catalysts with storage time could be due to the adsorption of water molecules, making the catalyst less active when used after long storage periods. This hypothesis would also explain the fact that the AuNP@mesoNb_2O_5 catalyst remained active for longer storage times (>5 weeks) – compared to its amorphous analogue shown in Fig. S8 – since the acid sites located inside the channels of the mesoporous materials are less accessible to water.

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Finally, the partial reactivation of the plasmon-mediated catalytic activity of a 5-week-old lyophilized sample of amorphous AuNP@Nb_2O_5 (HY340) was tested giving 18% benzyl chloride conversion in 2 h compared to the 100% and 0% observed for the freshly made and deactivated catalyst, respectively. The fact that the reactivation of the catalyst is incomplete indicates that either extended lyophilization times are needed or that the deactivation is partially reversible. Future efforts will be made in order to study in depth the deactivation/reactivation process of these catalysts and the optimization of the storage conditions.

Conclusions

The Friedel-Crafts alkylation of anisole by benzyl chloride was catalyzed by AuNPs supported Nb_2O_5 composites. The localized plasmon heating effect by means of green light irradiation acts as an alternative heat source and allows for this reaction to occur at lower temperatures. On the other hand, the deactivation of the studied catalysts with storage time would likely be due to water adsorption and it is partially reversible upon water removal by lyophilisation.

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A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2016.12.048.

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