



Catalytic desulfurization of dibenzothiophene using nickel supported on cross-linked polystyrene-PPh₃ catalysts

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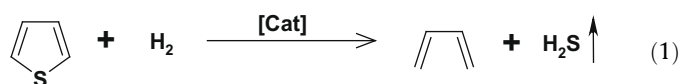
ABSTRACT

Nickel catalysts supported on a cross-linked polystyrene-PPh₃ resin were easily prepared in different oxidation states (0 and II) and used (0.1 mol% Ni) in conjunction with MeMgBr to achieve the desulfurization of dibenzothiophene (DBT), resulting in the formation of 2,2'-dimethylbiphenyl as the sulfur-free product (100%). The recycling of these catalysts was addressed in consecutive runs, from which a decrease in catalytic activity was observed within the recycling cycles. Comparison of SEM micrographs of the catalysts before and after the desulfurization process confirmed a decrease in the size of the polymeric resin particles as a result of their progressive dissolution into the organic phase, the latter being the major cause of the decrease in the catalytic activity, associated with gradual loss of the nickel catalysts by leaching.

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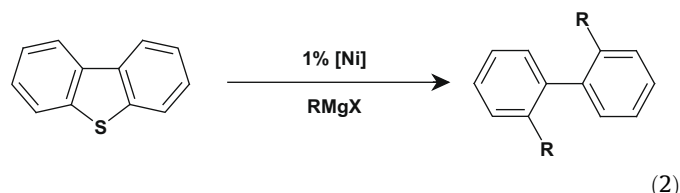
1. Introduction

The removal of sulfur from petroleum and other fossil feedstocks is a very important global issue in order to decrease atmospheric pollution caused by sulfur oxides, which are released during the combustion processes [1]. As a result of this, a large number of countries have restricted the amount of acceptable sulfur content present in fuels to very low limits [2]. The process that is used to remove sulfur-compounds is known as catalytic *hydrodesulfurization* (HDS) which typically uses cobalt or nickel doped molybdenum sulfide catalysts supported over alumina and requires both large amounts of hydrogen and high temperatures to operate at industrial scale (Eq. (1)) [3]. Additionally, commercial HDS processes often encounter difficulties in succeeding with the complete removal of dibenzothiophene (DBT) and its more hindered analogues, 4-methyldibenzothiophene (4-MeDBT) and 4,6-dimethyldibenzothiophene (4,6-Me₂DBT); the latter compound exhibit a very low reactivity being in fact the major residual organosulfur component after HDS present in fuels such as diesel [4]



Recently, our group reported the use of homogeneous nickel and platinum catalysts that in the presence of alkyl Grignards drive the desulfurization reaction of DBT, 4-MeDBT and 4,6-Me₂DBT in

good yields, which leads to the formation of substituted biphenyls via C–C cross-coupling reactions [5] (Eq. (2))



It is well known that two important disadvantages that homogeneous catalysts have with respect to their heterogeneous counterparts are related with the separation and recovery procedures that are required for these at the end of each process. For these reasons, several supporting materials have been systematically tested in the intent of allowing the preparation of *heterogenized* systems that could be used in the same processes for which the homogeneous systems were developed [6]. As particular cases, several cross-coupling reactions have been reported to be successful when using palladium catalysts supported on polymeric materials [7] and also, different types of heterogenized metal complexes have been employed in a variety of reactions such as olefin metathesis using ruthenium [8], oxidations using osmium [9] and hydroformylation and isomerization of olefins using rhodium catalysts [10]. In all these examples, the recovery of the metal compounds was achieved readily, also finding a sustained catalytic performance upon consecutive recycling. In the case of the HDS reactions, only one example using a polymer supported rhodium catalyst has been reported to the best of our knowledge. The catalyst was able to drive the hydrogenolysis of benzothiophene

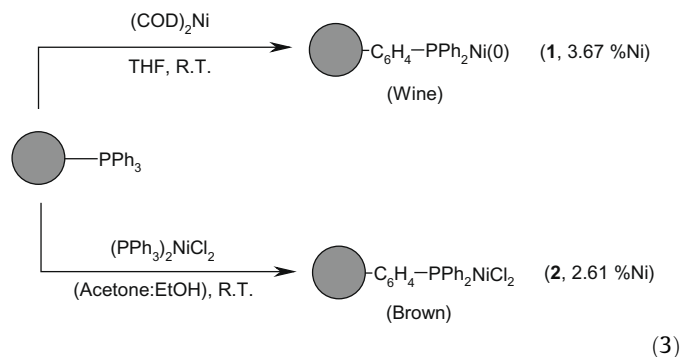
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producing 2-ethyl-thiophenol in moderate yields. The sulfur-free product (ethylbenzene) was obtained only in poor yields (3%) during the same process [11].

In the current report we disclose our findings on the catalytic desulfurization of DBT using nickel catalytic precursors in different oxidation states (0 and II) which were supported on a cross-linked polystyrene-PPh₃ resin. This *heterogenized* systems showed recycling ability to produce 2,2'-dimethylbiphenyl (2,2'-DMBP) as the sole sulfur-free product.

2. Results and discussion

The nickel catalysts were easily synthesized by stirring a solution of 1 equiv. of the nickel precursor, [(COD)₂Ni] for the Ni(0) (**1**) or [(PPh₃)₂NiCl₂] for the Ni(II) (**2**) catalyst, additionally adding 4 equiv. of the cross-linked polystyrene-PPh₃ resin which yielded a colored solid (red-wine and brown, respectively) that contained the supported nickel center (Eq. (3)). The nickel content was determined by atomic absorption spectroscopy (AAS)



2.1. Catalytic desulfurization of DBT with nickel supported catalysts

The catalytic desulfurization reactions using the supported nickel catalysts **1** and **2** were performed in a variety of conditions, the representative results of which are presented in Table 1.

As indicated in Table 1, the results obtained with both nickel catalysts (**1** and **2**) were very similar regardless the difference in the oxidation state of the nickel center in each of these (0 and II, *vide infra*). The complete desulfurization of DBT was observed when the reaction was carried out in toluene using 0.1 mol% Ni

of the supported catalyst **1** or **2**, selectively producing 2,2'-dimethylbiphenyl as the sole sulfur-free product (entries 1 and 5). These results are very similar to those obtained with the homogeneous systems that were reported before by our group [5], therefore suggesting that the catalytic activity of the *heterogenized* systems used herein is maintained when compared with those exhibited by the homogeneous ones. To note, no desulfurization activity was observed when using THF as the solvent regardless of the use of greater catalyst loadings (entries 2 and 6), the latter results being similar to the one depicted by the homogenous systems when used in the presence of polar solvents that result in significant diminishment or even halting of, the catalytic activity. In both cases, the inhibition of the catalytic process may be due as a result of THF coordination to the metal centers, that in the case of the heterogenized systems is rationalized as a passivation of the catalyst active sites within the polymer matrix. Consistent with this conclusion, the activity of the supported systems was not decreased when using non-polar higher boiling point solvents such as *o*-xylene (entries 3 and 7) or mesitylene (entries 4 and 8), indicating that it is indeed the greater coordinating capability of THF that ultimately inhibits the process.

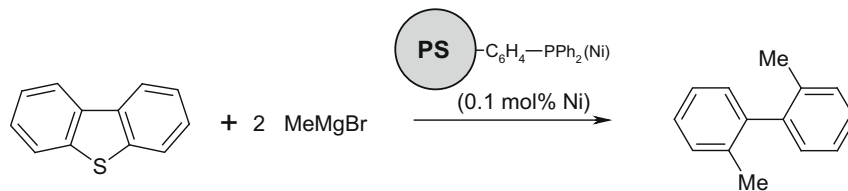
2.2. Catalyst recycling experiments for continuous desulfurization of DBT

The recycling capability of the nickel supported catalysts was also addressed for all the such conditions in which DBT desulfurization was found to be successful. The experiments were conducted using 1 equiv. of catalyst, 1000 equiv. of DBT and 2000 equiv. of MeMgBr, heating the reaction mixture during 5 days in refluxing toluene. After such time, the heating was stopped and the solution filtered *via* cannula to analyze conversions by means of GC-MS, leaving the insoluble catalyst and other solid residues which are mainly composed by MgBr₂ and MgS [5], the latter compound being the final fate of the sulfur. Fresh loadings of 1000 equiv. of DBT and 2000 equiv. of MeMgBr were then added to them and the resulting mixtures heated again for 5 days. This process was consecutively repeated until the complete loss of catalytic activity was encountered. The results for the recycling capability of both catalysts **1** and **2** in toluene are presented in Fig. 1.

The two types of nickel catalysts exhibited very similar performances during the recycling experiments promoting 100% desulfurization of DBT, only in the first run. After the first recycle the activity of the catalysts dropped to 70% and 50%, respectively, pro-

Table 1

Catalytic desulfurization of dibenzothiophene with nickel supported catalysts.



Entry	Catalyst (equiv.)	Thiophene (equiv.)	Grignard (equiv.)	Solvent	Organics (%)
1	1 (1)	DBT (1000)	MeMgBr (2000)	Toluene	MePh-PhMe (100)
2	1 (1)	DBT (100)	MeMgBr (200)	THF	DBT (100)
3	1 (1)	DBT (1000)	MeMgBr (2000)	<i>o</i> -Xylene	MePh-PhMe (100)
4	1 (1)	DBT (1000)	MeMgBr (2000)	Mesitylene	MePh-PhMe (100)
5	2 (1)	DBT (1000)	MeMgBr (2000)	Toluene	MePh-PhMe (100)
6	2 (1)	DBT (100)	MeMgBr (200)	THF	DBT (100)
7	2 (1)	DBT (1000)	MeMgBr (2000)	<i>o</i> -Xylene	MePh-PhMe (100)
8	2 (1)	DBT (1000)	MeMgBr (2000)	Mesitylene	MePh-PhMe (100)

All reactions were carried out under reflux of their corresponding solvent for 5 days, typically using 6.600 μmol of the corresponding nickel catalyst. All yields were quantified by GC-MS, after work up.

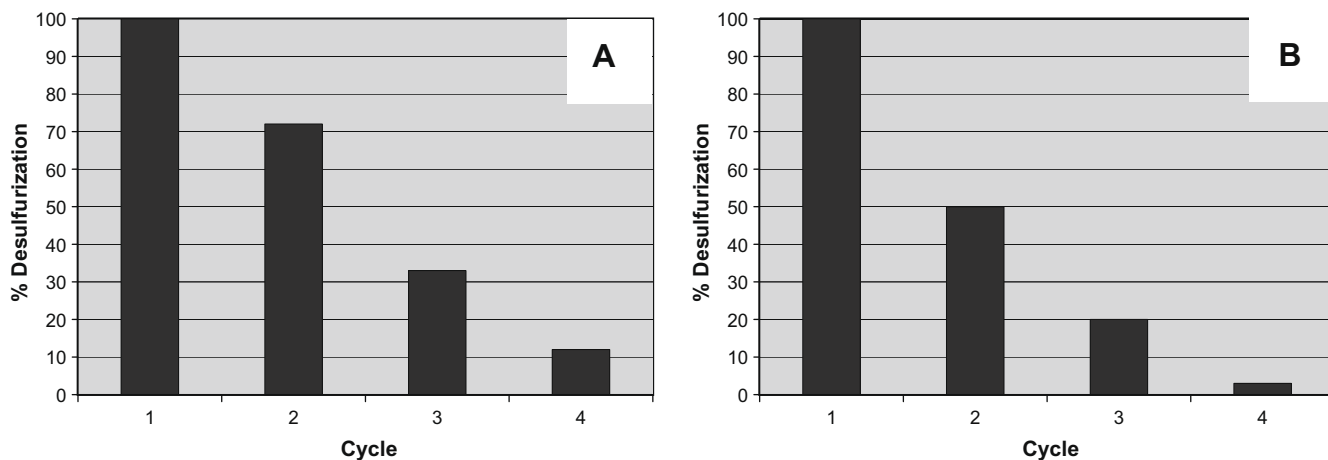


Fig. 1. Catalytic desulfurization of DBT using nickel supported catalysts (0.1 mol% Ni), in toluene. (A) Ni(0) catalyst (1); (B) Ni(II) catalyst (2).

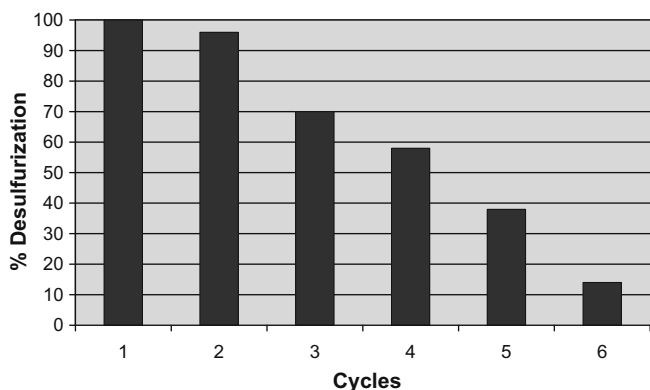
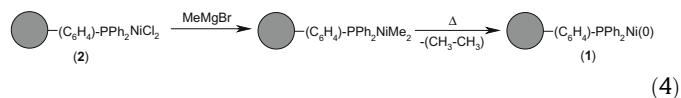


Fig. 2. Catalytic desulfurization of DBT using the nickel(0) supported catalyst, 1, in mesitylene.

gressively resulting in smaller conversions of 33% and 20% and 12% and 3% in the third and fourth runs.

A rationale for the similarities in performance exhibited by both catalysts can be established in terms of the reactivity that the nickel(II) centers exhibit when exposed to the presence of Grignards, from which the nickel (II) catalyst (2) may produce a dimethylated compound by metathesis with 2 equiv. of MeMgBr that decomposes to an active nickel(0) entity, namely 1, as a result of reductive elimination of ethane (Eq. (4)), implying that both systems evolve to common intermediates for the desulfurization process, thereafter. To note, a closely related proposal for the synthesis of Ni(0) moieties from Ni(II) precursors has been reported by Pörschke and co-workers [12].



Also worth to note, the use of solvents with higher boiling point such as mesitylene for the catalytic desulfurization experiments starting with compound 1 (0.1 mol% Ni) allowed us to increase

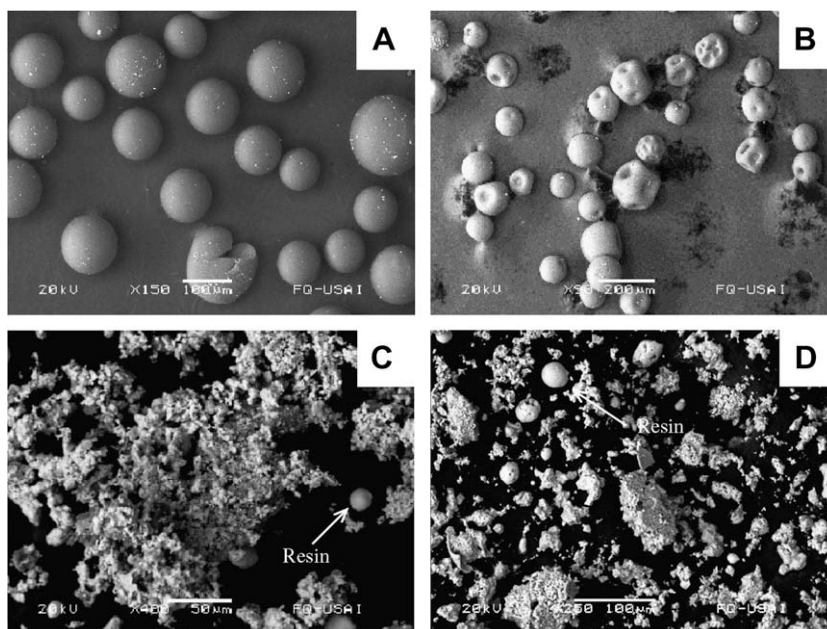


Fig. 3. SEM images of the supported nickel catalysts before, (A) 1, (B) 2, and after 4 desulfurization cycles using toluene as solvent, (C) 1 (D) 2.

the number of recycled runs to a total of six (see Fig. 2), a result that may be derived from a temperature-enhanced mass transfer process that adds for the overall system's efficiency.

2.3. Scanning electron microscopy studies of the catalysts

Scanning electron microscopy (SEM) studies of the nickel supported catalysts, **1** and **2**, were carried out before and after the desulfurization experiments in order to understand the decrease in the catalytic activity encountered during the recycling experiments. Fig. 3 illustrates representative micrographs of the resemblance of polymer particles in these two circumstances.

Before the desulfurization process was undergone, the two catalysts exhibited a particle size distribution ranging between 60 and 150 μm , labeled as **A** and **B** in Fig. 3. However, after the recycling process (4 cycles) using toluene as solvent, the same catalyst particles presented a dramatically different particle size, decreasing to less than 20 μm in both cases (indicated as **C** and **D**). The change in particle size has been attributed to the dissolution of the supporting polymer in the organic phase while undergoing desulfurization, thereby also enabling the loss of active metal centers as a result of leach of nickel into the reaction media, ultimately resulting in the progressive diminishment of the catalytic activity that is reflected over time after continuous recycling runs.

3. Conclusions

The current report presents the catalytic desulfurization process of DBT using polymer supported nickel catalysts in two different oxidation states (0 and II), which in conjunction with MeMgBr yield the formation of 2,2'-dimethylbiphenyl, selectively. The recycling ability of these systems was assessed, allowing at least four consecutive catalytic runs before complete loss of activity. The use of higher boiling point non-coordinating solvents such as mesitylene permitted to extend the effective lifetime of the catalysts, resulting in a larger amount of recycles. SEM studies of the catalysts before and after the desulfurization process allowed to conclude that a reduction of the particle's size takes place during the desulfurization process as a result of progressive dissolution of the polymer matrix, which is directly related with the loss of catalytic activity exhibited by the heterogenized catalysts within consecutive runs in recycling experiments. Studies are underway to extend this methodology to other sterically hindered DBT analogues.

4. Experimental

All manipulations were carried out using standard Schlenk and glovebox techniques under argon (Praxair, 99.998). THF (J.T. Baker) was dried and distilled from dark purple solutions of sodium/benzophenone ketyl. Toluene, *o*-xylene and mesitylene (J.T. Baker) were dried and distilled from sodium. Acetone was dried and distilled over K_2CO_3 . Ethanol was dried and distilled over magnesium. Triphenylphosphine polystyrene bound resin (cross-linked with 2% DVB; 200–400 mesh; 1.6 mmolPPh₃/g resin), DBT and $[(\text{COD})_2\text{Ni}]$ were purchased from Aldrich, dried *in vacuo* and used without further purification. MeMgBr (3.0 M in diethyl ether solution) was purchased from Aldrich and used as received. PPh₃ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ were purchased from Aldrich and were also used without further purification. GC–MS determinations were performed using a Varian Saturn 3 on a 30 m DB-5MS capillary column. Catalysts were characterized by SEM analyses, undertaken using a Jeol JSM 5900 LV microscope. Atomic absorption spectroscopy (AAS) analyses of the nickel content were undertaken on a Varian Spectra AA 220 instrument.

4.1. Preparation of **1**

To a 50 mL Schlenk flask was added $[(\text{COD})_2\text{Ni}]$ (0.11 g, 0.4 mmol) and dissolved with 10 mL of dry THF. The PPh₃ polymer bound resin (1 g, 1.6 mmol) was added to the mixture under constant stirring and was left to stir for 4 h, during which time the color of the solution changed from pale-yellow to becoming almost colorless, the suspended resin also turning red-wine. The latter was filtered and washed 5 times with dry THF (5 mL) and then dried for 5 h under *vacuo*. The nickel content (3.87%) was determined by AAS digesting the sample in a microwave oven reactor using H_2SO_4 and then HNO_3 .

4.2. Preparation of **2**

A 50 mL Schlenk flask was charged with $[(\text{PPh}_3)_2\text{NiCl}_2]$ (0.26 g, 0.4 mmol) and dissolved with 10 mL of a mixture of acetone:EtOH (2:1) to give a green solution. The PPh₃ polymer bound resin (1 g, 1.6 mmol) was added to the solution under constant stirring following the procedure described above, during which the resin turned dark-brown and the remaining solution became almost colorless. The resin was filtered and washed 5 times with a mixture of acetone:EtOH (2:1 v/v, 5 mL) and then dried for 5 h *in vacuo*. The nickel content (2.61%) was determined by AAS following the previous procedure.

4.3. Catalytic desulfurization experiments

A 50 mL Schlenk flask was charged in a glovebox with the corresponding supported nickel catalyst (6.59 μmol Ni) and suspended in 8 mL of dry solvent. Then, to it was added DBT (6.59 mmol) and allowed to stand at room temperature for 30 min under constant stirring. After complete mixing a solution of the Grignard reagent (13.18 mmol) was added; no changes in color were observed. The reaction mixture was heated to reflux under argon in a gas/vacuum line, constantly stirred during 5 d. During this time a beige precipitate was observed. The heating was stopped and the sample hydrolyzed at room temperature with HCl (10 mL, 10% vol.). A strong effervescence was observed with the immediate release of H_2S (*Caution, poisonous gas!*), which was usually bubbled into a trap with 50 mL of an aqueous concentrated solution of $\text{Pb}(\text{CH}_3\text{COO})_2$. After bubbling and venting all the gases, all organics proceeding from the reaction mixture were extracted using CH_2Cl_2 (3 \times 5 mL) and the organic layer analyzed by GC–MS. The samples prepared for SEM analysis were not hydrolyzed but centrifuged during a period of 10 min at 5000 cycles/min. Then, the supernatant solution was decanted leaving a grayish solid residue that was further dried for 5 h *in vacuo*.

4.4. Recycling desulfurization experiments

A 50 mL Schlenk flask was charged in a glovebox with the corresponding nickel catalyst (6.59 μmol Ni) and suspended with 8 mL of dry solvent, adding DBT (6.59 mmol) with constant stirring during 30 min. After complete mixing a solution of the Grignard reagent (13.18 mmol) was added; no changes in color were observed. The reaction mixture was heated to reflux under argon in a gas/vacuum line, constantly stirred during 5 d; a beige precipitate was observed during this time. The heating was stopped and the solution filtered *via* cannula and the solid residue washed 3 \times 10 mL with the corresponding solvent (toluene or mesitylene). The solution was analyzed by GC–MS. Then, the reaction was reconstituted with DBT (6.59 mmol), and MeMgBr (13.18 mmol) using 8 mL of dry solvent and heated again to reflux under argon in a gas/vacuum line, constantly stirred for 5 d. The same procedure was repeated until complete loss of catalytic activity.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.12.019.

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