



Gold catalysts for the synthesis of aromatic azocompounds from nitroaromatics in one step



D. Combita, P. Concepción, A. Corma*

Instituto de Tecnología Química (UPV-CSIC), Avenida de los Naranjos s/n, 46022 Valencia, Spain

ARTICLE INFO

Article history:

Received 23 October 2013

Revised 23 December 2013

Accepted 30 December 2013

Available online 31 January 2014

Keywords:

Azocompounds

Nitroaromatics reduction

Heterogeneous catalysts

Gold catalysts

Hydrogenation

ABSTRACT

One-step selective hydrogenation of nitroaromatics to obtain symmetric azocompounds with high yields has been performed with a gold supported on cerium oxide catalysts. Au/TiO₂ and Au/CeO₂ catalysts direct the reaction by two different pathways and with different selectivities. In situ FTIR studies reveal that the surface concentration of the intermediate nitrosobenzene is decisive in directing the reaction through the different reaction pathways. In this way, while on Au/TiO₂ a fast hydrogenation of the nitrosobenzene intermediate leads to a low surface concentration of the nitroso compound, on Au/CeO₂ nitrosobenzene is more stabilized on the catalyst surface leading to a lower hydrogenation and a higher coupling rate, resulting in high selectivities to azobenzene. On Au/CeO₂, the relative weak adsorption of the azo with respect to the azoxy compound on the catalyst surface avoids the consecutive hydrogenation of azocompounds to the corresponding anilines until all the azoxy has been consumed. Asymmetric azobenzenes have also been obtained with very high yields on TiO₂, through the Mills reaction.

© 2014 Elsevier Inc. All rights reserved.

1. Introduction

Aromatic azocompounds are widely used [1] as dyes [2], food additives [3] and drugs [4]. A major industrial process for their synthesis involves the azocoupling reaction between a diazonium salt and an activated arene [5]. The diazonium salt is prepared in situ, oxidizing an aromatic amine with sodium nitrite and a strong acid [6]. Other processes involve the oxidation of anilines to nitroso compounds, which furthermore react with aromatic amines in glacial acetic acid (Mills reaction) [7], or the rearrangement of an aromatic azoxy compound, obtained by nitro compounds reduction using concentrated acids (Wallach reaction) [8]. Even if all these processes are quite effective, they involve several steps and generate a considerable amount of by-products (see Scheme 1).

An alternative for the synthesis of symmetric azocompounds is the reductive coupling of aromatic nitro compounds using different types of reductive agents [9]. However, this process also generates a large amount of by-products implying intensive post-treatments. There is, therefore, a great interest to develop catalytic heterogeneous methods to directly produce azocompounds from aromatic nitro compounds.

Along these lines, we recently reported a two-stage waste-free process catalyzed by Au/TiO₂ to obtain symmetric and asymmetric azocompounds starting from nitrobenzene and substituted nitrobenzenes, reaching high conversion and selectivity to the

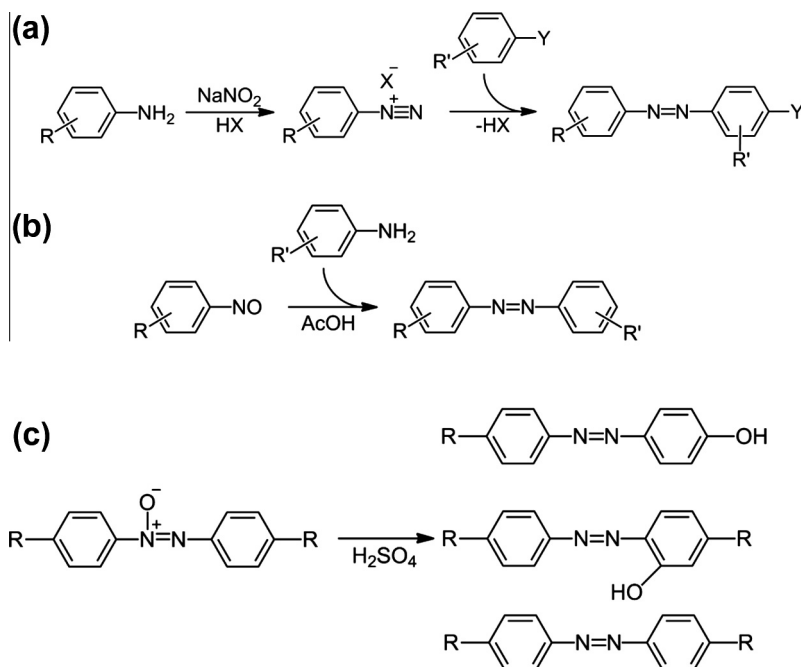
azocompounds [10]. Later, Zhu et al. using a photocatalytic reaction with Au/ZrO₂ as catalyst, in alkaline media (KOH) and room temperature, have reported high nitro compound conversions with moderate to good yields to symmetric azocompounds [11]. However, it should be noticed that the ratio of solvent to reactant in this process is 392/3 mmol. Similarly, Hu et al. have prepared Pt and Pd nanowire catalysts to obtain, in the presence of KOH, symmetric and asymmetric azocompounds with moderate to good yields [12]. Very recently, selectivities to azocompounds close to 15% have been achieved with supported gold catalysts pointing to the importance of the support on the final selectivity [13].

If one considers the general reaction scheme proposed by Haber [14] to reduce nitroaromatics, it should be possible to prepare azocompounds from nitrobenzenes in a single pass via the corresponding azoxy compounds, provided that a catalyst could be found which is able to direct the reaction via the intermediate nitroso compound and aromatic hydroxylamine (routes a.1 and a.2 in Scheme 2) and to avoid the total hydrogenation to aniline. It should also be possible to produce azocompounds by reacting the intermediate nitroso compound with aniline (see route b in Scheme 2). This last route would require a relatively slower reduction of nitroso compound to aniline, and a very fast reaction between nitrosobenzene and aniline.

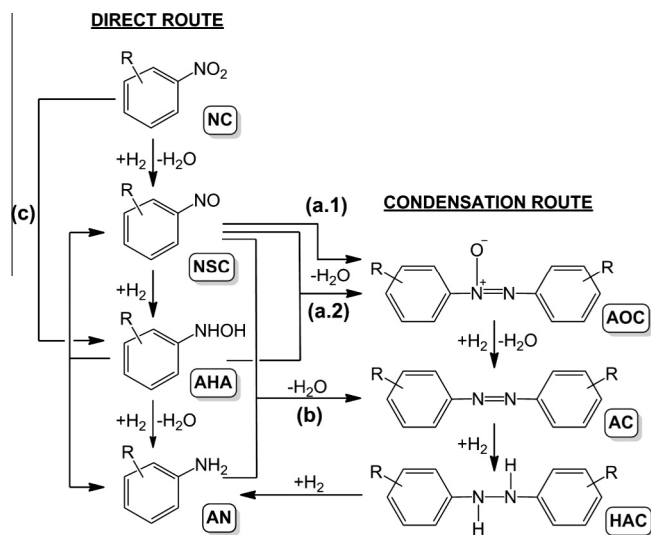
In the present work, we show that it is possible to produce azocompounds with more than 98% yield from nitrobenzene in a single pass with a catalyst able to preferentially direct the process toward the coupling of nitrosobenzene intermediate (condensation route a.1 in Scheme 2). In this way the azoxy compound is formed

* Corresponding author.

E-mail address: acorma@itq.upv.es (A. Corma).



Scheme 1. Azocompounds synthesis: (a) Azocoupling reaction; (b) Mills Reaction and (c) Wallach reaction.



Scheme 2. Reaction pathways for the hydrogenation of nitrocompounds to anilines. NC: nitrocompound, NSC: nitrosocompound, AHA: aromatic hydroxylamine, AN: aniline, AOC: azoxycompound, AC: azocompound, HAC: hydrazocompound. Adapted from Richner et al. [15].

that selectively evolves to the desired azocompound. This is achieved with gold on nanoparticulated CeO_2 where the subsequent hydrogenation of the azocompound to produce aniline is inhibited. With this catalyst, it is possible to reach very high conversion and selectivity while with Au/TiO_2 the full hydrogenation to aniline is favored and the azocompound is not formed.

In the second part of the work, we will present that while Au/CeO_2 is not a selective catalyst to produce asymmetric azocompounds, TiO_2 is a selective catalyst to perform the coupling between nitrosocompounds and anilines, yielding asymmetric azocompounds with high selectivities.

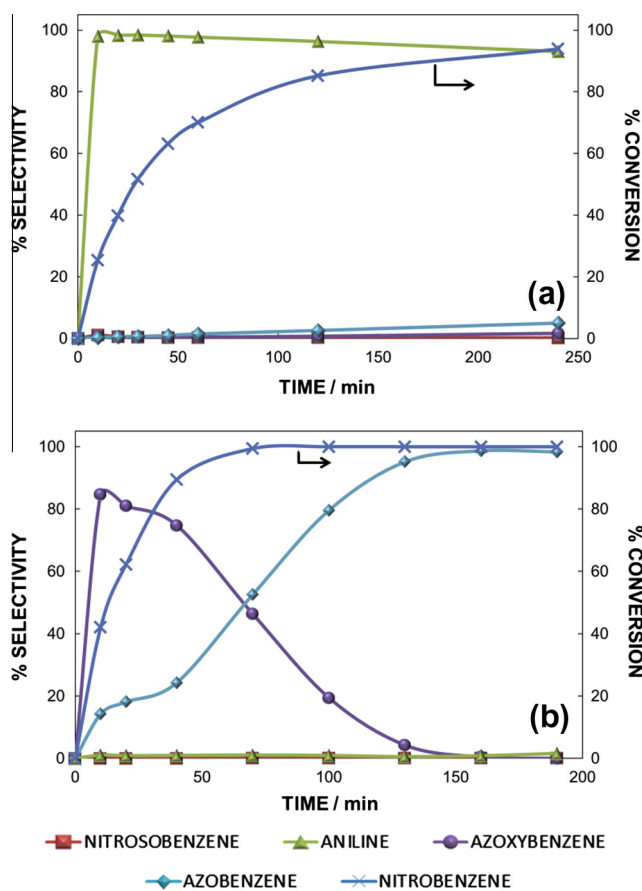


Fig. 1. Nitrobenzene reaction profile over (a) Au/TiO_2 , 1.5 wt% Au and (b) Au/CeO_2 , 1.5 wt% Au. [Nitrobenzene] = 0.25 M in toluene; Au = 1 mol%; $T = 120^\circ\text{C}$; $P_0 = 4$ bar H_2 .

Download English Version:

<https://daneshyari.com/en/article/6527573>

Download Persian Version:

<https://daneshyari.com/article/6527573>

[Daneshyari.com](https://daneshyari.com)