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Selective reductive coupling of nitro aliphatic compounds with aldehydes in hydrogen using gold catalyst

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ABSTRACT

Nitrones were synthesized in good yields directly from nitro aliphatic compounds, aldehydes, and H₂ using highly dispersed gold nanoparticles on titania. The high selectivity for nitron synthesis contrasts with the platinum supported on carbon and corresponds to an increase from roughly 50% to 90%. The catalytic performance is tuned by precise control of the structure of the active sites, the characteristics of the support and reaction conditions.

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1. Introduction

Nitrones are organic molecules that found wide applications for the synthesis of important organic molecules such as isoxazolidines, isoxazolines and β -amino alcohols [1] and, in general as precursors for some nitrogen-containing derivatives. Furthermore, their radical trapping abilities have found applications as antioxidants [2], spin-traps [3], and enzymes inhibitors [4]. Their reactant abilities have shown to have anti-cancer activity in several experimental cancers models and potential therapeutics in some cancers [5–7].

The most common methods for the synthesis of nitrones involve the synthesis of hydroxylamines or oximes which are then reacted with aldehydes or N-alkylation respectively. The first step of the process named above requires the synthesis of hydroxylamines or oximes by partial hydrogenation with re-

ducing agents. Though Zn dust can act as reducing agent in stoichiometric amounts for producing the hydroxylamine intermediate in the presence of acetic acid or ammonium chlorides, the use of solid acids is desired. Nevertheless, one should also take into account that hydroxylamines are unstable under storage and potentially explosive, and consequently the number of hydroxylamines commercially used is very limited (Scheme 1(a)).

Oximes can be synthesized by hydrogenation of α,β -unsaturated nitro compounds, with a chemoselective catalyst that avoids the reduction of the C=C bond [8]. Nevertheless, the synthesis of nitrones from oximes requires several steps since α,β -unsaturated nitro compounds should be first prepared from nitroalkanes and an aldehyde or ketone, followed by hydrogenation of a conjugated nitro group and N-alkylation of the resultant oxime (Scheme 1(b)). There is a third route,

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a) Condensation of carbonyl compounds with hydroxylamines

b) N-alkylation of oximes

c) Oxidation of secondary amines, hydroxylamines or imines

Scheme 1. Some representative routes for the synthesis of nitrones.

able to produce nitrones by oxidation of imines or secondary amines which also involve a multi-step process, most of the times starting with the reduction of a nitro compound (Scheme 1(c)).

It should be noticed that complexity of the preceding routes increases when the desired nitrones involve groups sensitive to oxidation or reduction, such as aldehydes, alcohols, cyano, olefinic or acetylenic bonds. In those circumstances chemoselectivity has been often achieved in the past by using stoichiometric oxidation or reduction agents, with the corresponding generation of residues.

An efficient way to produce nitrones could be envisaged by

considering a cascade-type reaction whereby hydroxylamine generated *in situ* by partial hydrogenation of the nitro group would be rapidly reacted with a carbonyl compound. It is clear that if one could find a selective catalyst able to produce the above cascade reaction, the new process would avoid problems associated to hydroxylamine storage and will reduce the number of steps. Notice that such catalyst should prevent: (a) a complete reduction of the nitro group into the corresponding amine, (b) hydrogenation of the carbonyl group from the aldehyde, and (c) the degradation of the nitron via secondary reaction paths (Scheme 2). For doing that, we found that there was one route of hydrogenation of nitrobenzene and substituted

nitrobenzenes that goes through the hydrogenation to nitrosobenzene, followed by formation of the corresponding hydroxylamine that can be further hydrogenated to the amine.

Moreover, it was also observed that depending on the nature of the support it was possible to stabilize in a higher extend the concentration of the intermediate nitroso compound and hydroxylamine on the catalyst surface [9]. If this is so, one could then optimize a catalyst that rapidly reacts the intermediate nitroso compound species with other molecules in a cascade mode to give products other than amines or amino derived products when starting from nitrobenzene. For instance, one could react the intermediates nitrosobenzene to produce the azoxy and azo compounds directly or by reacting with the corresponding hydroxylamine (Scheme 3).

The objective can be achieved by means of an Au/CeO₂ catalyst; that gives high conversion and selectivity to azo compounds, starting from substituted nitro aromatics [9]. However, if one could react the nitrosobenzene and the corresponding hydroxylamine with an aldehyde, it should be possible to obtain the corresponding nitron (Scheme 4).

Nevertheless, to achieve the nitron in high yields, the consecutive hydrogenation of the nitron to the imine and secondary amine should be avoided (Scheme 5).

Recently, we showed that a carbon-decorated platinum catalyst was able to synthesize aromatic nitrons in high yields provided by a precise control of the structure of the active sites and the characteristics of the support. Particularly, platinum on carbon is a suitable catalyst due to: (a) it is arranged in the form of nanoparticles that lack metal sites located in cristal terraces accessible to the reactants, (b) the support is a high surface area mesoporous active carbon, and (c) the nitro compound has an aromatic character. Due to this, good yields to nitrons were obtained with the Pt/C catalyst with

Scheme 4. Reductive coupling of nitrobenzene and aldehyde.

Scheme 5. Consecutive hydrogenation pathway for the reductive coupling of nitrobenzene and aldehyde.

substituted nitroaromatic compounds and substituted aromatic aldehydes. The concept could also be extended to other metals such as Pd and Ru. We reported, however, that the selectivity was only moderate when the reaction involved a nitroalkane or nitro cycloalkanes as a starting reactant, mainly because then a parallel (undesired) reduction of the aldehyde compound occurred [12]. Nevertheless, there is an interest in the design of a selective, efficient and eco-friendly catalyst for the preparation of this type of products not only to expand the scope of synthetic possibilities, but also because some relevant families of nitrons, derive from non-aromatic nitro compounds, are particularly relevant as potential therapeutic molecules for some cancers (e.g. PBN).

Since Au/TiO₂ was able to perform the hydrogenation of nitro aromatic compounds in the presence of aldehydes and ketones into the amines through a route that involve the hydroxylamine as intermediate, we thought that, conveniently tuned, Au/TiO₂ catalyst could be an adequate catalyst for producing nitrons starting from nitro compounds, aldehydes and H₂. Herein we have explored the possibilities of gold catalysts as an alternative for one pot synthesis of the most reluctant aliphatic nitrons.

2. Experimental

2.1. Catalyst preparation

Precipitation of gold nanoparticles on TiO₂ (P-25, Degussa) was done from an aqueous solution of HAuCl₄ that was neutralized with NaOH (0.2 mol/L) to have a final pH of 7 [13–15]. TiO₂ and the HAuCl₄ solution were contacted at room temperature and the resultant slurry was vigorously stirred for 5 h. The pH of this slurry was maintained at 7 during the process. The catalyst was then filtered and washed thoroughly to remove chlorides from the catalyst surface. After drying the solid powder for 12 h at 373 K, the sample was calcined in a fix bed reactor with air flowing (50 mL/min) at 673 K and 1 bar for 3 h. To get 1 wt% of Au loading, it must be considered that only ~70% of the nominal gold is deposited on the surface of TiO₂ at a pH of 7.

Scheme 3. Proposed reaction pathways for the reduction of an aromatic nitro compound to the corresponding aniline [10,11].

Deposition of platinum or palladium on gold catalyst was done from aqueous solutions of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (Aldrich, > 37.5% as Pt); or PdCl_2 (Aldrich, 99%). Gold catalyst was impregnated with the solution containing the desired amount of metal to form a thick paste (incipient wetness impregnation). After a perfect mixing of the wet solid, samples were dried at 373 K for 12 h. The resultant powders were reduced in fix bed reactor using 50 mL/min of H_2 at the selected temperature for 3 h before reaction.

Deposition of platinum was done from aqueous solutions of H_2PtCl_6 . Supports (Active carbon Darco KB-B, Aldrich) were impregnated with the solution containing the desired amount of metal to form a thick paste (incipient wetness impregnation). As an example, 1.2 mL of an aqueous solution containing 10.62 mg of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ were contacted with 2 g of carbon Darco to prepare the 0.2 wt% Pt/C catalyst. After a perfect mixing of the wet solid, samples were dried at 373 K for 12 h. The resultant powders were reduced in fix bed reactor using 50 mL/min of H_2 at the selected temperature for 3 h before reaction.

2.2. Catalytic performance

Catalytic reactions were performed in a reinforced glass reactor (2 mL) with temperature and pressure control, and stirred magnetically. The feed composition was (mol): 90.5% solvent, 6% nitro compound, 3% aldehyde, 0.5% *o*-xylene (internal standard). Typically, 100 mg of catalyst were used for 900 mg of feed. Reaction pressure and temperature are indicated in the corresponding table of the main text. Conversion and selectivities were determined using a gas chromatograph (Varian 3900) equipped with an FID detector and a 30-m HP-5 capillary column. The products were identified by mass spectrometry using a GC/MS device (Agilent MDS-5973) equipped with a quadrupole electron-impact ionization detector.

3. Results and discussion

In this paper, we have designed a catalyst that affords nitrones in higher yields than any preceding process, starting from aliphatic nitro compounds, aldehydes (aromatic or aliphatic) and H_2 in a single step process, for doing that the catalyst should hydrogenate selectively nitroaromatic compounds, without causing reduction of other sensitive groups such as carbonyls. This is a necessary condition for obtaining nitrones via a cascade-type reaction. The condition is, however, not sufficient and previous attempts to accomplish this reaction with gold catalysts were fruitless [12]. Despite the tolerance of the carbonyl function, the Au/TiO₂ catalyst required higher temperatures to dissociate H_2 and the catalyst gives lower selectivity to the nitrone **3** when reacting with 5-methylfurfural **2** (Table 1) since, the imine **4** (formed by condensation of aniline and the 5-methylfurfural **2**) is obtained in high yields (the corresponding imine forms according to the sequence of reactions in Schemes 2 and 5).

A first series of experiments show that the selectivity to nitrone compounds with Au/TiO₂ is largely dependent on the

Table 1

Effect of temperature on the selectivity to nitrone **3** formed from nitrobenzene **1**, 5-methylfurfural **2** and H_2 (5 bar) using the different types of catalysts [12].

Catalyst	Temperature (K)	Conversion (%)	Selectivity to nitrone (%)
1 wt% Au/TiO ₂	393	99	0
1 wt% Au/TiO ₂	373	99	15
1 wt% Au/CeO ₂	333	88	12
0.2 wt% Ru/C	308	95	84
0.2 wt% Ru/C	333	73	73

reaction temperature, and the nature of solvent. More particularly, higher reaction temperatures imply, in general, lower selectivities to the nitrones, not only with the Au/TiO₂ catalyst, but also with other metals (Table 1).

It was presented before that while Au/TiO₂ was not selective enough for producing nitrones from nitro aromatics compounds since this catalyst must operate at higher temperatures to achieve practical reaction rates; with Pt on carbon the rate of H_2 dissociation could be enhanced and the catalyst can work at lower temperature, showing very high selectivity to aromatic substituted nitrones [12]. Unfortunately, Pt/C catalyst, used to obtain nitrones in high yields from nitroaromatic compounds and aldehydes, is less selective when nitroalkanes were reacted, due to the concomitant formation of the corresponding alcohol (Table 2). On the other hand, we realized that nitrones coming from nitro aliphatic compounds were more stable to reaction temperature and the Au/TiO₂ catalyst (that requires higher reaction temperatures) could be a suitable option.

With the objective to analyze the mechanism of interaction between active centers and different functional groups with Pt/C and Au/TiO₂ catalysts, activation of nitrobenzene and styrene was studied in a situation of competitive adsorption. Fig. 1(a) shows presence of nitrobenzene avoiding double bond reduction with Au/TiO₂ and also with Pt/C catalysts; even though with Pt/C catalyst a higher hydrogenation rate is observed. Competitive adsorption shows an important diminish in styrene activity due to strong adsorption of nitro aromatic compound on the surface avoiding styrene activation on active centers, because of this, there is not an important reduction of double bond until more than 90% of nitrobenzene has been consumed.

An equivalent experiment with a nitro aliphatic compound, like nitrobutane, in the presence of styrene (Fig. 1(b)) was done and the results show a much higher rate of disappearance of double bond with Pt/C catalyst, meanwhile good selectivity to nitrobutane compound is preserved with Au/TiO₂ catalyst. In conclusion, reduction of double bond on Pt/C catalyst is much faster when there is a nitro aliphatic compound in the reaction media and the highest selectivity of Au/TiO₂ catalyst showed in this paper can be explained because the strong activation of $-\text{NO}_2$ group in the interface Me-Ti [16].

Table 2Catalytic performance of various catalysts for the reductive coupling of nitrobutane **7** and 5-methyl furfural **2**.

Catalyst ^a	Solvent	Time (h)	Conversion (%)	Selectivity (%)				
				N	I	A	TA	OH
1%Au/TiO ₂	Ethanol	3.5	97	90	5	2	3	0
0.2%Pt/C ^b	Ethanol	6.5	90	50	10	10	0	30
1%Au/TiO ₂	Toluene	6	93	70	22	3	4	0
50 ppm Pt-Au/ TiO ₂	Ethanol	1.5	95	57	8	10	25	0
50 ppm Pd-Au/ TiO ₂	Ethanol	2	97	53	11	11	25	0
100 ppm Pt-Au/ TiO ₂	Ethanol	3	99	46	16	13	23	0
50 ppm Pt-Au/ TiO ₂	Toluene	12	94	25	35	12	21	0
50 ppm Pd-Au/ TiO ₂	Toluene	15	98	25	40	8	23	0

N: Nitrone **8**; I: Imine **9**; A: Secondary amine **10**; TA: Tertiary amine **11**; OH: Alcohol **6**.^a Reactions performed at 333 K and 10 bar of H₂, unless otherwise indicated. Feed composition (mol): 90.5% solvent, 6% nitrobutane, 3% 5-methyl furfural, 0.5% *o*-xylene. Metal content given as a nominal weigh percent. Balance corresponds to small amounts of unidentified products.^b Reactions performed at 313 K and 5 bar of H₂.

Taking into account these results, behavior of gold nanoparticles supported on titania in the formation of aliphatic nitrones was studied. When reacting nitrobutane **7** and 5-methyl furfural **2**, a high selectivity to nitrone **8** was obtained, and only gives small yields of the imine **9** and amine **10** (Table 2). Notice that the Au/TiO₂ catalyst was not forming the 5-methyl furfural alcohol **6** (Fig. 2). Other important information is that changing the solvent to a non-polar (toluene), imine **9** formation was favored, resulting in a slight decrease in the formation of nitrone **8**. Meanwhile the 0.2 wt% Pt/C not only produces 5-methyl furfural alcohol **6** but also large amounts of by-products **9** and **10**, when working under conditions that was selective for producing aromatic nitrones. A first series of experiments have shown that selectivity to nitrone with Au/TiO₂ catalysts is largely dependent on the reaction temperature and the nature of solvent.

At this point, in an attempt to increase the activity of gold catalyst, a series of bimetallic Me-Au/TiO₂ catalysts were prepared with the objective of increasing the rate of hydrogenation while preserving high chemoselectivity. With this purpose, small amounts of Pt or Pd were introduced to the Au/TiO₂ cat-

alyst to accelerate the rate of H₂ dissociation. The resultant catalysts were tested at 333 K and the results show that it is, indeed, possible to increase the reaction rate in the presence of a polar solvent (ethanol). However, though the rate of H₂ disso-

Fig. 2. Kinetic curve correspond to conversion of 5-methyl furfural and selectivities to nitrone, imine, amine and tertiary amine (circles) during the reductive coupling of nitrobutane and 5-methyl furfural at 353 K and 10 bar with Au/TiO₂ catalyst. **Fig. 1.** Evolution of the conversion of styrene and nitro compounds in terms of competitive reactivity (equimolecular blend) using Au/TiO₂ and Pt/C catalysts. Reaction mixture composition: 4.25% nitro compound, 4.25% styrene, 0.005% *o*-xylene and 91.495% ethanol. Reaction conditions: Au/TiO₂ 353 K, 10 bar H₂ and 100 mg 1%Au/TiO₂; Pt/C: 313 K, 5 bar H₂ and 50 mg 0.2%Pt/C.

ciation was increased, the selectivity to nitron **8** was not improved due to the formation of a new by product, i.e. tertiary amine **11**. When 50 ppm Pt on Au/TiO₂ catalyst was tested using ethanol as solvent, the selectivity to nitron **8** was only 57% (Table 2), and increasing the amount of Pt to 100 ppm resulted in a slight decrease to nitron **8** (46%). Changing to a non-polar solvent (toluene), imine **9** is the main product with 50 ppm Pt-Au/TiO₂ and 50 ppm Pd-Au/TiO₂ catalysts. From results of Table 2 we can conclude that the activity towards hydrogenation was increased considerably with Pt-Au/TiO₂ and Pd-Au/TiO₂ catalysts, in order to have good selectivity to nitron **8** not only a chemoselective catalyst is needed, but a polar solvent is also required.

When a nitro cycloaliphatic is used, like nitro cyclohexane **12**, the polymerization reaction to tertiary amine is minimized and using a proper amount of Pt (50 ppm Pt-Au/TiO₂) selectivity to nitron **13** could be increased up to 85%. The bimetallic Pd-Au/TiO₂ catalyst is also selective to the nitron **13**, though it is less selective than the equivalent Pt-Au/TiO₂ catalyst but both of them are more selective than the commercial Lindlar catalyst. As showed in Table 3, we can conclude that when only small amounts of highly dispersed Pt are added to the catalyst, the activity towards hydrogenation increases considerably while the chemoselectivity of Au/TiO₂ catalyst is maintained, kinetic profiles are shown in Fig. 3.

Au/TiO₂ catalyst was tested for reacting various nitro aliphatic compounds and aromatic aldehydes in the presence of H₂. Nitrones coming from the nitro aliphatic compounds, which are more stable to reaction temperature, were observed. Showing that the gold based catalyst allows obtaining higher selectivities to the corresponding aliphatic nitron (87%–67%) than Pt/C catalyst (Table 4). Regenerability of Au/TiO₂ catalyst was tested during three cycles without losing activity and selectivity, in order to recover catalytic activity after each cycle it should be washed with ethanol and water and then calcined at 673 K.

Table 3

Catalytic performance of various catalysts for the reductive coupling of nitro cyclohexane **12** and 5-methyl furfural **2**.

Catalyst ^a	Solvent	Time (h)	Conversion (%)	Selectivity (%)				
				N	I	A	TA	OH
1%Au/TiO ₂	Ethanol	14	99	90	3	3	4	0
1%Au/TiO ₂	Toluene	9	99	71	22	5	3	0
50 ppm Pt-Au/TiO ₂	Ethanol	6	97	85	11	4	0	0
50 ppm Pt-Au/TiO ₂	Toluene	8	95	16	79	5	0	0
100 ppm Pt-Au/TiO ₂	Ethanol	5.5	99	42	32	10	13	2
50 ppm Pd-Au/TiO ₂	Ethanol	9	99	71	21	3	5	0
5%Pd-Pb/CaCO ₃	Toluene	4	99	62	5	30	3	0
0.2%Pt/C ^b	Toluene	24	99	39	8	18	13	22

N: Nitron **12**; I: Imine **13**; A: Secondary amine **14**; TA: Tertiary amine; OH: Alcohol **6**.

^a Reactions performed at 333 K and 10 bar of H₂, unless otherwise indicated. Feed composition (mol): 90.5% solvent, 6% nitrobutane, 3% 5-methyl furfural, 0.5% *o*-xylene. Metal content given as a nominal weigh percent. Balance corresponds to small amounts of unidentified products.

^b Reactions performed at 313 K and 5 bar of H₂.

Fig. 3. Kinetic curve correspond to conversion of 5-methyl furfural and selectivities to nitron, imine and tertiary amine during the reductive coupling of nitro cyclohexane and 5-methyl furfural at 353 K and 10 bar with Au/TiO₂ catalyst.

Special mention should be made to the reaction between an aliphatic nitroalkane and an aliphatic aldehyde, i.e. nitrobutane **7** and valeraldehyde **16** (Scheme 6).

In this case, besides the nitron **17**, the hydroxyl secondary amine **18** is also obtained. Results in Table 5 show again that gold catalyst is more selective to the nitron **17** than the bimetallics and Pt/C catalysts, being Au/TiO₂ catalyst the most selective. When different amounts of Pt were added to Au/TiO₂ catalyst, the distribution of byproducts changed, but in all cases the selectivity to nitron **17** was similar. Results can be extended to aldehydes with longer aliphatic chains (i.e. heptaldehyde) indicating that this kind of substrates are not as sensitive to changes in the properties of metal-support interface as the aromatic aldehydes. According with results showed in Table 5, this behavior is not observed with nitro *tert*-butane and valeraldehyde **16** and we can suggest that the low reactivity of the reactants above are due to the high steric hindrance of nitro compound.

Due to anti-cancer activity of PBN (*a*-phenyl-*tert*-butylnitron) many efforts have been done in order to synthesis this

Table 4

Catalytic performance for the reductive coupling of various nitro aliphatic compounds and aromatic aldehydes.

Nitro compound	Aldehyde	Catalyst ^a	Conversion (%)	Selectivity (%)			
				N	I	A	OH
1%Au/TiO ₂	99	87	23	0	0
		0.2%Pt/C ^b	97	55	17	10	18
1%Au/TiO ₂	97	77	18	5	0
		0.2%Pt/C ^b	99	49	10	8	33
1%Au/TiO ₂	99	76	24	0	0
		0.2%Pt/C ^b	94	46	7	16	19
1%Au/TiO ₂	93	67	17	6	5
		0.2%Pt/C ^b	98	40	18	25	17

N: Nitron; I: Imine; A: Secondary amine; OH: Alcohol.

^a Reactions performed at 353 K, 10 bar of H₂, unless otherwise indicated. Feed composition (mol): 6% nitro compound, 3% aldehyde, 0.5% *o*-xylene and 90.5% ethanol. Metal content given as a nominal weigh percent. Balance corresponds to small amounts of unidentified products.^b Reactions performed at 333 K and 5 bar of H₂.**Table 5**

Catalytic performance for the reductive coupling of various aliphatic nitro compounds and aliphatic aldehydes.

Nitro compound	Aldehyde	Catalyst ^a	Conversion (%)	Selectivity (%)				
				N	HAS	I	A	TA
1%Au/TiO ₂	97	82	11	0	0	7
		100 ppm Pt-Au/TiO ₂	94	65	13	0	0	22
		50 ppm Pt-Au/TiO ₂	90	69	0	8	14	9
		50 ppm Pd-Au/TiO ₂	97	68	0	10	20	2
		0.2%Pt/C ^b	98	4	77	3	0	17
		1%Pt/C Commercial	96	14	39	0	15	25
		Au/Al ₂ O ₃ ^b	95	71	12	7	0	10
1%Au/TiO ₂ ^b	95	10	7	18	31	30
		100 ppm Pt-Au/TiO ₂ ^b	97	8	5	35	21	27
		0.2%Pt/C ^c	95	26	45	7	18	4
1%Au/TiO ₂ ^b	93	85	9	3	2	1
		50 ppm Pt-Au/TiO ₂ ^b	93	68	10	7	8	5
		2%Pt/C ^c	95	26	45	4	11	10

N: Nitron; I: Imine; A: Secondary amine; HAS: Hydroxyl secondary amine; TA: Tertiary amines.

^a Reactions performed at 353 K and 10 bar of H₂, unless otherwise indicated. Feed composition (mol%): 90.5% toluene, 6% nitro compound, 3% aldehyde, 0.5% *o*-xylene. Metal content given as a nominal weigh percent. Balance corresponds to small amounts of unidentified products.^b Reactions performed at 5 bar of H₂. Feed composition (mol): 90.5% ethanol, 6% nitro compound, 3% aldehyde, 0.5% *o*-xylene.^c Reactions performed at 313 K and 5 bar.**Table 6**Catalytic performance of various catalysts for the reductive coupling of nitro-*tert*-butyl and benzaldehyde.

Nitro compound	Aldehyde	Catalyst ^a	Conversion (%)	Selectivity (%)		
				Nitron	Imine	Alcohol
0.2%Pb-Pt/C	96	40	40	2
		0.2%Pt/C	87	2	21	41
		1%Au/TiO ₂	83	0	39	14

Reactions performed at 10 bar of H₂ and 353 K, unless otherwise indicated. Feed composition (mol): 90.5% toluene, 6% nitro compound, 3% aldehyde, 0.5% *o*-xylene. Metal content given as a nominal weigh percent. Balance correspond to products not considered for this purpose.

important nitron with Au/TiO₂ and Pt/C catalysts but were fruitless; only doping Pt/C catalyst with Pb according to Siegrist procedure [17] was possible to obtain a certain selectivity to PBN nitron (Table 6).

Scheme 6. Catalytic performance of reductive coupling of nitrobutane 7 and valeraldehyde 16.

4. Conclusions

It is possible to produce nitrons from nitro compounds, aldehydes and H₂ in a one-pot system, provided that chemoselective hydrogenation metals are used as catalysts. Selective formation of nitrons from nitroaromatic compounds can be achieved with platinum on carbon catalyst with a high proportion of unsaturated Pt sites, but, when reacting nitroalkanes, Pt on carbon gives low to moderate selectivity to nitrons due to the concomitant formation of the corresponding alcohol. How-

Graphical Abstract

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Selective reductive coupling of nitro aliphatic compounds with aldehydes in hydrogen using gold catalyst

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Nitrones were synthesized in high yields directly from nitro aliphatic compounds, aldehydes and H₂ using highly dispersed gold nanoparticles on titania in a single step process. The high selectivity contrasts to the selective platinum nanoparticles.

ever, Au/TiO₂ catalyst is able to afford nitrones from aliphatic nitro compounds, aldehydes (aromatic or aliphatic) and H₂ in higher yields than any preceding solution, when reaction temperature is increased. A proper amount of Pt or Pd introduced into the Au/TiO₂ catalyst is able to increase the rate of hydrogenation reaction of the nitro groups, while preserving high chemoselectivity.

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金催化剂上脂肪族硝基化合物与醛在氢气中选择还原耦合

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摘要: 采用TiO₂上高度分散的金纳米粒子做催化剂, 从脂肪族硝基化合物、醛和氢气可高选择性合成硝酮。与碳负载Pt催化剂相比, 该催化体系上硝酮的选择性从50%增加到90%。其催化性能可有活性位结构、载体特性和反应条件精确调节。

关键词: 金催化剂; 硝基化合物; 串联反应; 加氢; 硝酮

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