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Supported iridium catalysts — a novel catalytic system for the synthesis of toluenediamine

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Abstract

This paper deals with the preparation, characterization, and testing of a new modified iridium catalyst for the selective hydrogenation of dinitrotoluene (DNT) to toluenediamine (TDA) in liquid phase. The new catalyst does thoroughly avoid the formation of ring-hydrogenated and incompletely converted side-products that are frequently observed in the presence of supported palladium catalysts. Moreover, the catalytic hydrogenation of DNT with supported iridium catalysts is also accompanied by an extremely low amount of undesired dimers and oligomers (“tar formation”) in comparison to industrially applied standard Pd/C or Pd-Fe/C catalysts. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Today, aromatic amines are used as important intermediates in the manufacture of polymers, rubber chemicals, agriculture products, drugs as well as photographic chemicals. The production of aniline and toluenediamine (TDA) is an example of slurry phase catalytic hydrogenation for the manufacture of bulk chemicals. TDA is an intermediate for the manufacture of toluenediisocyanate (TDI), a compound predominantly used in flexible polyurethane foams and elastomers. In 1997 a production capacity of more than 1.5 MM tons has been installed for the production of TDI. Although, aniline can be manufactured by either gas phase or liquid phase hydrogenation, TDA is exclusively produced by the catalytic hydrogenation liquid phase of dinitrotoluene (DNT). Suitable catalysts for the manufacture of TDA include palladium or palladium/iron on carbon supports and activated nickel or supported nickel [1]. Although, liquid phase catalysts represent the overwhelming majority of catalysts for the hydrogenation of DNT, fixed bed type systems have also been reported in the literature [2,3]. However, the commercial importance of such processes is limited by the short lifetime of the catalysts, the difficult heat management of the exothermic nitrogroup reduction and the worse overall productivity in comparison to established slurry catalysts. However, a new highly efficient fixed bed process was recently developed for the manufacture of TDA including the use of graphite supported palladium catalysts for that application [4].

Although, supported palladium catalysts are widely used for the liquid phase hydrogenation of aromatic nitrocompounds to the corresponding amines [5], these catalysts undergo a deactivation due to sintering of the metal and/or fouling caused by undesired side-products. Many papers have been published on

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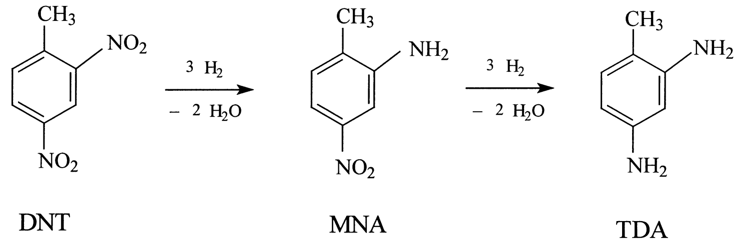


Fig. 1. Stepwise hydrogenation of DNT.

mono-metallic or modified bi- or multi-metallic palladium catalysts supported on activated carbon or carbon black for the hydrogenation of DNT to TDA [6–18]. In general, four different industrial processes have been established for the manufacture of TDA referred in the literature [6–10,19–26].

Both carbon supported palladium as well as skeletal nickel or silica supported nickel catalysts are successfully used in industrial applications. Ongoing research efforts attempt to improve the performance, recyclability and productivity of the existing catalyst systems. However, examples for alternative supported precious metal catalysts could not be found in the literature, even though the formation of side-products, such as oligomers (“tar precursors”), ring-hydrogenated or incompletely hydrogenated derivatives, is still a problem for the industrial manufacture of TDA. Especially, high molecular weight oligomers (“tar”) reduce the yield of TDA and are difficult to separate from the product stream. Inhibiting tar formation is one of the most challenging tasks in the hydrogenation of DNT.

It is known that the hydrogenation of DNT to TDA proceeds stepwise by the sequential hydrogenation of both nitrogroups [12]. The formation of 4-methyl-3-nitro-aniline (MNA) occurs rapidly in the presence of a supported palladium catalyst. The second step nitrogroup has a higher activation energy and less selectivity (Fig. 1).

2. Experimental

2.1. Catalyst preparation and properties

A new modified supported iridium catalyst has been developed [27–29] for the hydrogenation of DNT. Various types of suitable supports, such as aluminum oxide, titanium oxide, silicon dioxide or activated carbon can be used for catalyst preparation in aqueous media using standard impregnation methods [30,31]. Peat or wood based activated carbons are preferably used as supports and have shown the best results. The new multi-metallic catalyst contains iridium and promoters such as manganese, iron, cobalt, nickel, copper and ruthenium. These promoters can be fixed onto the support either by simultaneous or sequential precipitation in the presence of hexachloroiridium(IV)acid. The amount of iridium on the catalyst is kept between 1 and 5 wt.%, typically the total loading of promoters varies in the range of 0.1–1 wt.%. This new catalytic system is characterized by well-reduced precious metal particles that are typically smaller than 5 nm. The dispersion of iridium depends on the type of precious metal precursor, on the velocity of its hydrolysis, and on the reducing agent. As known from the literature, strong reductants used in liquid phase tend to lead to precious metal crystallite growth. Even for iridium catalysts, moderate reductants are required. Details in preparation are already published [32]. The TEM analysis basically indicates a thick-shell character for the most active types as shown in Fig. 2.

For generating comparative data, standard palladium or modified palladium catalysts on activated carbon or carbon black have been prepared according to methods reported in the literature [9,10,15,16,28].

Table 1 gives a brief summary on some physicochemical properties of the supported precious metal catalysts used for the hydrogenation tests.

2.2. Catalytic hydrogenation

The catalytic hydrogenation of DNT was performed in a stirred stainless steel autoclave as a batch process.

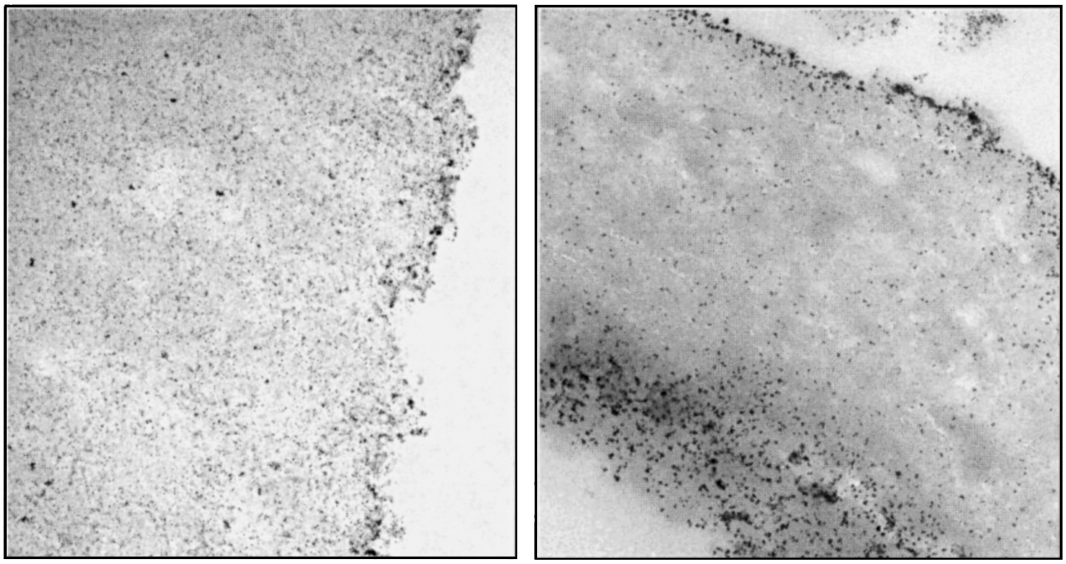


Fig. 2. TEM images of Ir-Fe-Mn/C (right) and Ir-Fe-Co/C (left) (magnification 400 000:1).

For catalyst screening, the following reaction conditions have been applied:

Reactor	1 l autoclave
Pressure (absolute)	20–50 bar
Temperature	100–120°C
Solvent	Methanol or TDA/water
Amount of DNT	50 g
Catalyst/substrate ratio	For 5 wt.% loaded Ir/C or Pd/C types: 0.25 wt.% dry weight For 2 wt.% loaded Pd/C types: 1.25 wt.% dry weight

Details regarding pressure, temperature and catalyst loading are given subsequently. Conversion of DNT, yield of TDA, and the formation of side-products have been detected by GC and HPLC. The side-products observed in the catalytic hydrogenation can be classified as follows:

Side-product 1	Ring hydrogenated monomers of DNT, MNA and TDA
Side-product 2	Incompletely hydrogenated monomers, such as isomers of MNA
Side-product 3	Dimers, oligomers (“tar precursors”)

Table 1
Catalyst properties

Code	Catalyst loading and metal composition (wt.%)	Support type	Specific surface area (m^2/g)
A	5% Ir, 0.15% Mn, 0.15% Fe	Chemically activated carbon	1500
B	5% Ir, 0.15% Fe, 0.15% Co	Chemically activated carbon	1500
C	5% Pd	Steam activated carbon	1200
D	2% Pd, 4% Fe	Steam activated carbon	1200
E	2% Pd, 4% Fe	Oleophilic carbon black	80
F	5% Ir	Chemically activated carbon	1500
G	5% Ir, 0.3% V	Chemically activated carbon	1500
H	5% Ir, 0.3% Fe	Chemically activated carbon	1500
I	5% Ir, 0.3% Ni	Chemically activated carbon	1500
K	5% Ir, 0.15% V, 0.15% Fe	Chemically activated carbon	1500
L	5% Ir, 0.15% Fe, 0.15% Cu	Chemically activated carbon	1500

The samples for GC and HPLC analyses were usually taken from the autoclave 15 min after the apparent 100% conversion of DNT. Each test was replicated four times. All figures given below, represent an average of five tests. Typically, the accepted tolerance for the GC and HPLC analyses was in the range of ±0.15 wt.% (absolute).

3. Results and discussion

The aim of this work was to find a new approach for the synthesis of TDA based on precious metal catalysts that can be distinguished by improved selectivity from known catalyst systems at elevated pressure. The hydrogenation tests were not adapted to a specific industrial process as described earlier.

3.1. Hydrogenation at 50 bar

The new supported iridium catalysts show comparable activities, but superior selectivities to other heterogeneous precious metal catalysts as shown in Table 2.

In comparison to different palladium catalysts — either supported on activated carbon or on carbon black — the iridium based system shows neither ring-hydrogenation nor the formation of incompletely hydrogenated products. Moreover, unlike supported palladium samples, an iron-manganese or iron-cobalt promoted iridium catalyst keeps tar formation significantly below 1 wt.%, as shown in Table 2. These results are in line with the properties of supported palladium systems that catalyze the ring hydrogenation of aromatics at elevated pressure [33].

The modification of the iridium catalysts by the co-precipitation of suitable promoters influences the properties of this precious metal in the selective hydrogenation of DNT. As it is clearly shown in Table 2, the presence of iron, manganese, vanadium, or cobalt on the surface of the support increases the selectivity towards TDA and prevents the formation of undesired oligomers. Unexpectedly, nickel seems to decrease the activity and selectivity of the iridium catalyst. As published by Haber [34] and Blaser et al. [35], the modifiers have to be present in an ionic form, not as zero-valent metal species (Table 3). This allows a facile transfer of electrons from the metal to the phenylhydroxylamine intermediate, and accelerates its disproportionation. This redox process is accompanied by a rapid change of the metal oxidation state. Obviously, iron, cobalt and manganese easily undergo such a change in their typical oxidation state. As already reported [29], the preparation method of the modified supported iridium catalyst leads to transition metal promoters in oxidic form.

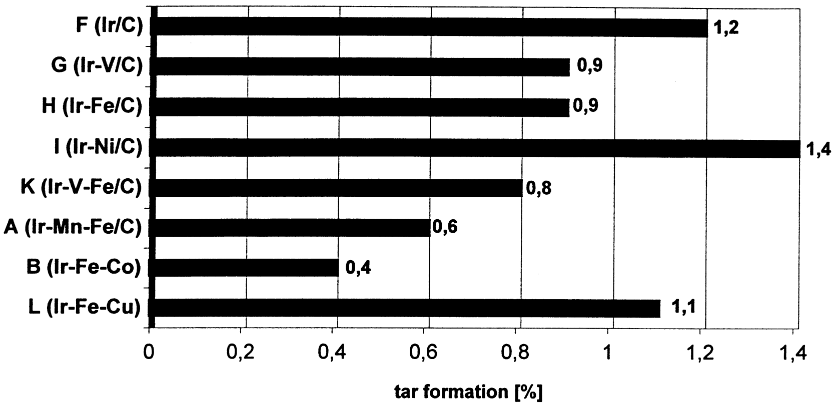
The influence of modifiers, especially iron and vanadium, on the catalytic hydrogenation of an aromatic nitrocompound can be explained according to the following reaction scheme [34,35] (Fig. 3). The disproportionation of the hydroxylamine intermediate in the presence of modifiers (e.g. iron or vanadium) is described as "catalytic by-pass" [36] and prevents the accumulation of phenylhydroxylamine. In parallel to that, the formation of the desired amine is accelerated. Inhibiting the accumulation of phenylhydroxylamine, the di- and oligomerization to azo- and azoxy-compounds can be largely suppressed.

The ratio of the rate constants k_1 and k_2 for the formation of MNA and TDA (refer Fig. 1) have shown that carbon supported palladium catalysts are highly active for the conversion of DNT to MNA, whereas the second step of the reaction requires a longer reaction time [12]. A supported iridium catalyst does not show an enrichment of MNA during this reaction. This can be easily confirmed by comparing the amount of side-product 2 given in Table 4.

Table 2
Hydrogenation of DNT at 50 bar, 120°C, 50 g DNT in 200 g methanol

Catalyst	Reaction time (min)	TDA yield (%)	Side-product 1 (%)	Side-product 2 (%)	Side-product 3 (%)
A	50	99.4	–	–	0.6
B	45	99.5	–	0.1	0.4
C	30	98.0	0.8	0.2	1.0
D	60	98.4	0.2	0.4	1.0
E	40	98.2	0.3	0.3	0.8

Table 3
Comparison of different modifiers on the selectivity of supported iridium



This clearly indicates a “post-reaction” of the 4-methyl-nitro-aniline in the presence of supported palladium catalysts, even if the hydrogen uptake has been completed. These results confirm the kinetic calculations of White [12] with regard to the rate constant ratios r_1 and r_2 for supported palladium and activated nickel catalysts, respectively. It can be concluded that the hydrogenation of DNT in the presence

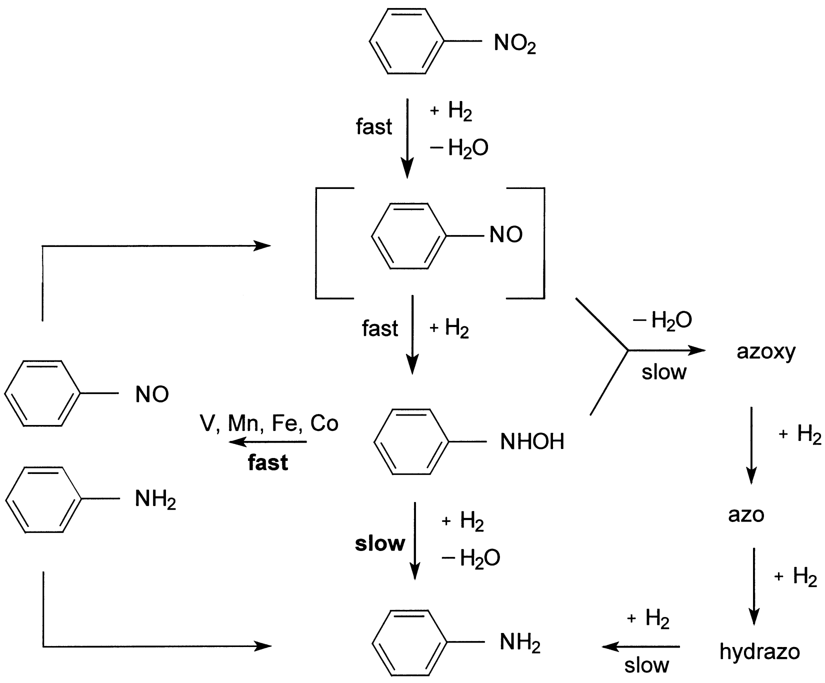


Fig. 3. Reaction scheme for the hydrogenation of nitroarenes in the presence of a supported iridium catalyst.

Table 4
Determination of MNA[a]

Catalyst	Sample taken after		
	0 min	15 min	30 min
Amount of MNA (side-product 2) (wt.%)			
F (iridium on activated carbon)	0	0	0
C (palladium on activated carbon)	0.4	0.25	0.2

[a] Samples were taken immediately after apparent 100% conversion of DNT (0 min), after 15 and 30 min (50 bar; 120°C).

of modified iridium catalysts goes rather in parallel to the kinetics of activated nickel catalysts than supported palladium systems.

3.2. Hydrogenation at 20 bar

Even at moderate reaction conditions, supported iridium catalysts modified by iron, manganese, or cobalt yielded excellent selectivities for the conversion of DNT. In comparison to carbon supported palladium or palladium-iron catalysts, iridium produces lower amount of side-products (Table 5). This confirms its high selectivity for the hydrogenation of DNT.

3.3. Hydrogenation below 10 bar

At a pressure of around 5–10 bar, the excellent selectivity of supported iridium catalysts that was found in the hydrogenation of DNT to TDA at higher pressure, could be also confirmed under moderate reaction conditions.

However, the hydrogenation activity decreases significantly in parallel to the reduction of the process pressure. This is probably caused by the moderate hydrogenation activity of the iridium itself in comparison to palladium or platinum based catalysts associated to a strong interaction between metal surface and reactant. If the catalyst is pre-treated with DNT, it could be unambiguously demonstrated that the hydrogen uptake of supported iridium catalyst is significantly lower than that of supported palladium catalysts.

Therefore, the economical benefit of the Ir/C systems is limited at moderate pressure by a longer reaction time that might not be acceptable for industrial use. However, in comparison to existing TDA manufacturing technologies at elevated pressure (e.g. supported nickel or skeletal nickel catalysts) supported iridium systems are promising options for an alternative catalytic route.

For illustrating these facts, Table 6 underscores the decrease of activity associated to an excellent selectivity.

4. Summary

For the synthesis of TDA, supported iridium catalysts allow a selective hydrogenation of DNT keeping the tar formation significantly below 1 wt.%. Modifiers, such as iron, cobalt, vanadium and manganese

Table 5
Hydrogenation of DNT at 20 bar, 120°C, 50 g DNT in 200 g methanol

Catalyst	Run time (min)	TDA yield (%)	Side-product 1 (%)	Side-product 2 (%)	Side-product 3 (%)
A	90	99.3	–	0.1	0.6
B	90	99.4	–	0.1	0.5
C	40	98.2	0.8	0.2	0.8
E	70	98.2	0.2	0.3	1.3

Table 6
Hydrogenation results for catalyst B at 5 bar, 120°C, 50 g DNT in 200 g methanol

Pressure (bar)	Run time (min)	TDA yield (%)	Side-product 1 (%)	Side-product 2 (%)	Side-product 3 (%)
50	45	99.5	–	0.1	0.4
20	90	99.5	–	0.1	0.4
5	220	99.3	–	0.1	0.6

improve the activity and selectivity of the iridium catalyst by accelerating the formation of amine in the stepwise hydrogenation.

Moreover, in comparison to carbon supported palladium catalysts, other side-products, such as ring-hydrogenated derivatives of DNT, MNA or TDA and incompletely converted monomers (e.g. MNA) are not formed in the presence of the iridium catalyst. Hence, this new catalytic system could be an interesting alternative to the broad variety of conventional supported palladium catalysts due to its outstanding selectivity in the catalytic hydrogenation of DNT.

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