



Reprint of influence of catalyst preparation on the contribution of homogeneous and heterogeneous steps to the selectivity in nitroaliphatic compounds hydrogenation[☆]

V. Dubois^{*}, G. Jannes¹

Chimie Physique & Catalyse, Institut Meurice, 1 Avenue Gryzon, B-1070 Bruxelles, Belgium

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ABSTRACT

2-Methyl-2-nitropropane hydrogenation proceeds along a *rake scheme* that may encompass homogeneous steps, reactions on the support and on the metallic phase as well. This complexity makes it useful as a test reaction. Reaction rates, selectivities and intermediate compounds accumulation provide experimental information on the modification of catalytic parameters such as support functionality and metallic dispersion. Experiments were carried out in homogeneous phase, on bare carbon supports, with mechanical mixtures of bare carbon supports and carbon-supported catalysts, and with catalysts prepared on modified supports. We have shown that hydrogen activation takes place on the metal and that organic reactants and intermediates may be activated on the metal and on the carbon support as well and may react with hydrogen available after spillover and jumpover migrations.

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1. Introduction

Reaction of 2-methyl-2-nitropropane (MNP) with hydrogen to *t*-butylamine (TBA) proceeds through the formation of two intermediate compounds, 2-methyl-2-nitrosopropane (MNO₂P) and *t*-butylhydroxylamine (TBHA), as described in [Scheme 1](#).

The system has some similarities with the reduction of nitrobenzene and is less complex than the reduction of primary and secondary nitroaliphatic compounds thanks to the absence of tautomeric equilibrium between the nitroso and the oxime forms. It is recognized that supported palladium catalysts exhibit a good activity for hydrogenolyses and hence for nitroalkanes reduction [1–3]. The moderate complexity of the reaction makes it useful as a test reaction [4], and we have described its kinetics some years ago [5,6].

In this paper we will focus on the potential localizations of the various reaction steps: metal surface, support surface, or homogeneous phase and on the adsorption-desorption equilibria between them. These equilibria are better described in a so-called *rake scheme* (see [Scheme 2](#)), inspired by a proposal of Montarnal [7,8].

This scheme may be expanded taking into account possible adsorption on the metal and on the support, and envisaging that

each elementary step may occur on both solid surfaces and in solution as well. By similarity with the classical mechanism of nitrobenzene hydrogenation [9–11], we may include hydroxylamine disproportionation and coupling reactions leading to azoxy (coupling C₁) or azo compounds (C₂) to reach [Scheme 3](#).

2. Experimental

2.1. Materials

The solids listed in [Table 1](#) were used in this work, either as such, or after modification.

Carbons JMT1, Darco G60 and Norit, and catalyst JM487 have been modified through nitric acid oxidation according to the following procedure.

- Dispersion of the solid in aqueous nitric acid (typically 0.25 M) at room temperature, at a ratio of 1 g/10 mL for 24 h.
- Rinsing in distilled water at room temperature, at a ratio of 1 g/10 mL, under magnetic stirring for 24 h. Recovery of the solid by filtration or centrifugation.
- Three successive rinsing steps in distilled water at room temperature, at a ratio of 1 g/10 mL, under magnetic stirring for 2 h, separated by filtration or centrifugation.
- Rinsing in methanol at room temperature, at a ratio of 1 g/10 mL, under magnetic stirring for 24 h, separated by filtration or centrifugation.
- Drying under air at 70 °C.

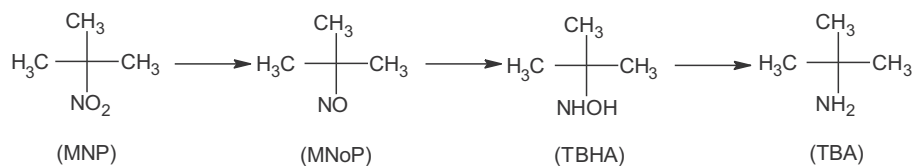
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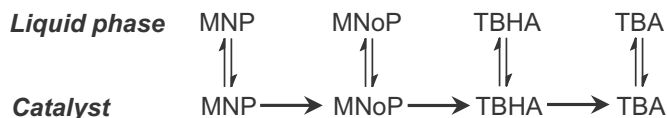
* Corresponding author. Tel.: +32 2 5267311; fax: +32 2 5242170.

E-mail address: vincent.dubois@meurice.heldb.be (V. Dubois).

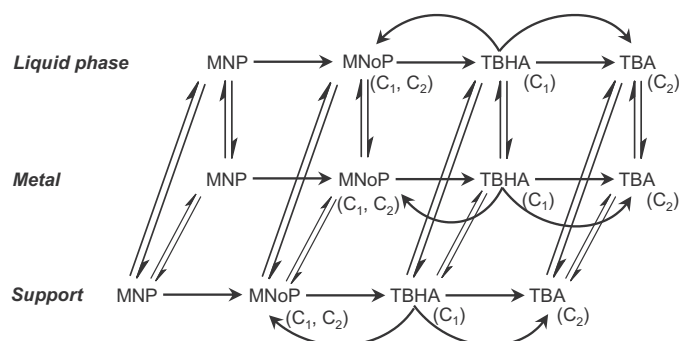
¹ Present address: ICHEC, 2 Boulevard Brand Whitlock, B-1150 Bruxelles, Belgium



Scheme 1. Step by step reduction of 2-methyl-2-nitropropane in *t*-butylamine.



Scheme 2. Simple rake-scheme encompassing adsorption–desorption equilibria of reactant, product and intermediates.



Scheme 3. Complete rake scheme encompassing all potential equilibria and reaction localizations.

Table 1
Solids used in the present work.

Type	Name	Short name	Provider
Pd/C 5%	Type 58	JM 58	Johnson Matthey
Pd/C 5%	Type LR 247B	LR 247	Johnson Matthey
Pd/C 5%	Type 487	JM 487	Johnson Matthey
Pd/C 5%	E10N	E10N	Degussa
Pd/C 5%	CCE SE86	CCE	Catalysts & Chemicals Europe
Active carbon	JMT1	JMT1	Johnson Matthey
Active carbon	Norit A	Norit A	Aldrich (26,001-0)
Active carbon	Darco G60	DG60	Aldrich (24,227-6)
Active carbon	Darco 12-20	D12-20	Aldrich (24,224-1)
Active carbon	Carbopal	Carbopal	Prof. Petró and Tungler ^a

^a We acknowledge the gift of this sample from Prof. Petró (†) and Prof. Tungler, Technical University Budapest.

Some catalysts were prepared, on JMT1 active carbon, in the laboratory in the following ways and are summarized in Table 2:

Catalyst P-1: 0.083 g of palladium chloride in 5 mL of 10% hydrochloric acid are added to 1.03 g of active carbon in suspension in 15 mL of water (pH between 0 and 3). After a 15 min stirring, 2.4 mL of 20% sodium hydroxide are added at once. pH value must reach 12. Then, 2 mL of formaldehyde are added and the stirring is kept for one hour. The suspension is heated to 90 °C for one minute

Table 2
Synthetic overview of the non-commercial catalyst preparation.

Catalyst acronym	Support	Preparation method	Palladium origin	Palladium reduction
P-1	JMT1	Precipitation (NaOH)	H ₂ PdCl ₄	Formaldehyde
P-2	JMT1	Precipitation (HCl)	(NH ₃) ₄ PdCl ₂	Hydrogen
POx-3	JMT1/HNO ₃	Precipitation (NaOH)	H ₂ PdCl ₄	Formaldehyde
IW-4	JMT1	Incipient wetness	H ₂ PdCl ₄	Hydrogen
IWOx-5	JMT1/HNO ₃	Incipient wetness	H ₂ PdCl ₄	Hydrogen
DP-6	JMT1	Dry precipitation (HCl)	(NH ₃) ₄ PdCl ₂	Hydrogen

and then quickly cooled down. pH is adjusted to a value of 5 using hydrochloric acid. Finally, the solid is filtered and washed under a nitrogen atmosphere, with 300 mL of water, poured in six steps.

Catalyst P-2: 0.1151 g of tetraamminepalladium chloride dissolved in 5 mL of water are added to 1.03 g of active carbon in suspension in 15 mL of water. After a 15 min stirring, 2.9 mL of 10% hydrochloric acid are added dropwise over a 15 min time. The stirring is kept for one hour. The suspension is heated to 90 °C during 5 min and then quickly cooled down. The solid is filtered under air and washed with 300 mL of water. Reduction is performed in situ by hydrogen, right before being characterized or used for a reaction.

Catalyst POx-3: The support has undergone a prior treatment with 0.25 M nitric acid. The catalyst is prepared the same way as catalyst P-1, except that the sodium hydroxide is added dropwise over a 25 min time, that the heating at 90 °C is kept during 5 min, and that the filtration and the washing are made under air.

Catalyst IW-4: 0.5 mL of an aqueous solution of palladium chloride, containing 0.05 g of palladium, are added dropwise to 1.03 g of active carbon (incipient wetness). After each addition, the solid is thoroughly mixed. The catalyst is then dried during 4 h, at 130 °C, under a helium flow. It is finally reduced during 1 h, at 150 °C, under a hydrogen flow.

Catalyst IWOx-5: This catalyst is prepared on the support oxidized with nitric acid. The procedure is the same as the one of catalyst IW-4.

Catalyst DP-6: A combination of the precipitation and incipient wetness techniques is tried. Therefore, 0.5 mL of 0.5 M nitric acid is added to 1.03 g of active carbon, which half-fills the pores of the support. 0.5 mL of a solution containing 0.1152 g of tetraamminepalladium chloride is then added. The catalyst is dried in a vacuum oven. It is reduced in situ by hydrogen right before being characterized or used for a reaction.

2.2. Acid–base characterization of the support and textural characterization of the solids

The characterization methods are classical ones for supports (BET surface area, Boehm titrations) and have been described previously [12]. The main characteristics are reported in Table 3 for the raw supports as well as for the oxidized solids.

2.3. Reaction kinetics

We have used the same experimental setups and chemicals as in [4–6]. The results were treated accordingly. It means that 1 L batch reactors are filled with 360 mL of methanol, catalyst when needed (classically 0.3 g of dried solid) and chromatographic

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