

# Hydrogen borrowing methodology for catalytic synthesis of amines and alcohols

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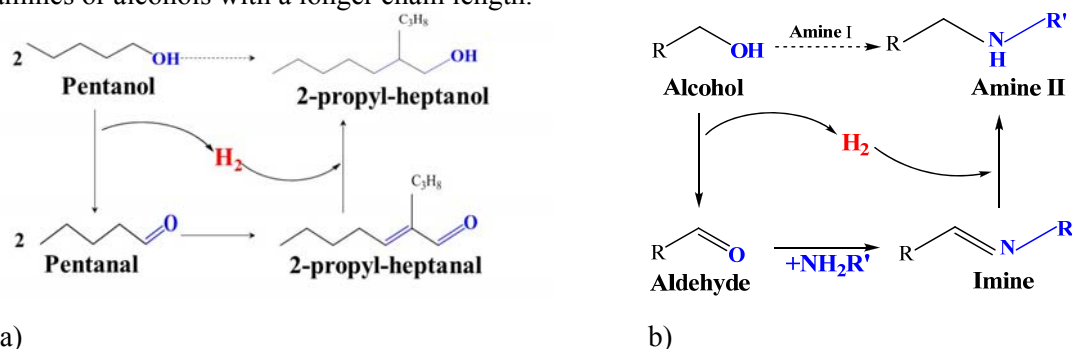
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**Abstract:** Examples to be discussed during the lecture comprise application of supported heterogeneous catalysts for several hydrogen borrowing reactions related to biomass upgrading and synthesis of amines for chemical and life science applications.

**Keywords** Guerbet reaction, *n*-pentanol condensation, 2-propyl-1-heptanol, hydrogen borrowing, amines

## 1. Introduction

Hydrogen borrowing reaction with alcohols is an environmentally friendly way for synthesis of alcohols [1, 2] or secondary amines [3-5], where the first step is the removal of hydrogen from the alcohol by the catalyst to form an aldehyde. In the subsequent step either there is a self-condensation of the aldehyde forming an unsaturated aldehyde and water (Scheme 1a) or an aldehyde is condensed with an amine (Scheme 1b) giving an imine and water. Finally, hydrogen is returned by the catalyst to these intermediates resulting respectively in amines or alcohols with a longer chain length.



**Scheme 1.** General scheme of hydrogen borrowing reactions for synthesis of a) alcohols via the Guerbet reaction with pentanol as an example, b) secondary amines.

## 2. Results and discussion

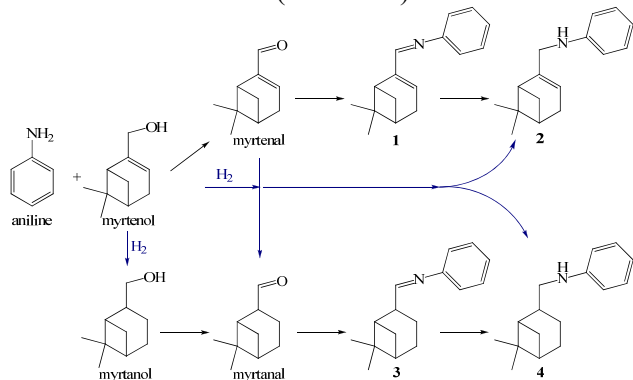
### Solid base assisted *n*-pentanol coupling over VIII group metals.

Liquid phase catalytic coupling of *n*-pentanol (Scheme 1b) over VIII group metals (Pt, Pd, Ir, Ru, Rh) on a range of supports (C, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, CeO<sub>2</sub>, ZrO<sub>2</sub>) doped with different solid bases was studied by varying the reaction temperature and gas atmosphere. Coupling of *n*-pentanol under the selected reaction conditions (180°C, 10 bar of N<sub>2</sub>) mainly resulted in formation of the target product 2-propyl-1-heptanol, whereas other products, such as pentanal, 2-propyl-2-heptenal, 2-propyl-1-heptanal, 2-propyl-1-heptenol were formed in minor quantities. Temperature increase accelerates the reaction and improves selectivity to 2-propyl-1-heptanol. Other parameters influencing conversion and selectivity were acid-base properties of the supports, namely the support base strength. For carbon supported catalysts conversion increases in the row Ir < Ru < Pt < Pd. When a certain amount of valeric aldehyde replaced *n*-pentanol in the initial reaction mixture the main product after 4 h was the one corresponding to aldol condensation. Introduction of the aldehyde decreases the alcohol concentration giving thereby a lower amount of hydrogen compared to the neat Guerbet reaction involving only *n*-pentanol. This confirms that the reaction proceeds through hydrogen borrowing mechanism and that hydrogen transfer plays the dominant role.

Analysis of the reaction mechanism for NaOH/Pt/Al<sub>2</sub>O<sub>3</sub> and relative contribution of various catalytically active phases was done by in-situ FTIR spectroscopy. The results obtained showed that Pt<sup>0</sup> and Pt<sup>δ+</sup> species are present on the surface of Pt/Al<sub>2</sub>O<sub>3</sub>, while NaOH/Pt/Al<sub>2</sub>O<sub>3</sub> exhibited only Pt<sup>δ+</sup>. Based on the correlation of ν(CO) and the positive charge on the platinum atom it can be concluded that the positive charge on platinum in Pt/Al<sub>2</sub>O<sub>3</sub> is higher than for NaOH/Pt/Al<sub>2</sub>O<sub>3</sub>, which is related to the influence of NaOH on the strength of alumina basic sites.

### One-pot myrtenol amination over Au nanoparticles supported on different metal oxides.

The main objective was to study general regularities of one-pot natural terpene alcohol amination with aniline in the presence of gold catalysts over different metal oxides such as ZrO<sub>2</sub>, MgO, Al<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub> as well as to determine a correlation between catalytic activity and the support nature. Myrtenol, which represents a natural terpene alcohol with a primary hydroxyl group, was selected as a model substrate for amination with aniline (Scheme 2).

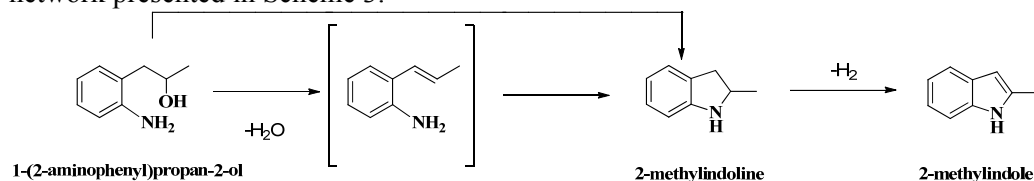


**Scheme 2.** Myrtenol amination with aniline over Au catalysts.

Catalytic activity and product distribution were strongly dependent on the support nature, which could be correlated with the acid-base properties of metal oxides. Basic sites on the metal oxide surfaces are needed for the initial alcohol activation, while availability of protonic groups on the support is important for the target amine formation. The highest activity in one-pot myrtenol amination among the tested catalysts was obtained over Au/ZrO<sub>2</sub> bearing both acidic and basic surface sites.

### Transformations of 1-(2-aminophenyl)propan-2-ol to 2-methylindoline.

Dehydrogenation-cyclization and hydrogen borrowing of 1-(2-aminophenyl)propan-2-ol to 2-methylindoline and 2-methylindoline was investigated. Both products are known to be used as intermediates for syntheses of pharmaceuticals. Transformation of 1-(2-aminophenyl)propan-2-ol was studied at 200 °C under argon pressure. A range of catalysts was applied including carbon, titania and zeolite supported Ru, Pd, Pt, Rh, and Ir, as well as metal free zeolites. Dependence of selectivity to 2-methylindoline and 2-methylindoline on conversion as well as an experimental evidence on 2-methylindoline dehydrogenation to 2-methylindoline are not in line with Scheme 1 for hydrogen borrowing reactions, but rather correspond to an alternative reaction network presented in Scheme 3.



**Scheme 3.** Transformations of 1-(2-aminophenyl)propan-2-ol through dehydration-cyclization and dehydrogenation.

### 3. Conclusions

Synthesis of secondary amines and longer chain alcohols by applying a hydrogen borrowing methodology can allow formation of the target product in appropriate yields. Complications can arise from presence of side processes, such as dehydration leading to cyclization, or because of deactivation.

### References

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