



# Alcohol amination with heterogeneous ruthenium hydroxyapatite catalysts



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## ABSTRACT

The intermolecular amination of alcohols was performed with ruthenium ( $\text{Ru}^{3+}$ ) immobilized on a calcium hydroxyapatite support. No additional base additives were necessary, nor did the catalyst require base treatment prior to reaction. High conversions were obtained with different amine and alcohol reactants.

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## 1. Introduction

The amination of alcohols has gained much interest as the search for environmentally benign routes towards substituted amines continues. The use of alcohols as feedstock is highly attractive due to their availability on a large scale by hydroformylation/reduction or hydration of olefins, direct production from synthesis gas or from sugar fermentation [1]. These alcohols are generally stable, low priced and low in toxicity [2]. The atom efficiency for the amination of alcohols is relatively high, since water is the only stoichiometric by-product from this reaction.

A drawback of working with alcohols is the poor leaving ability of the OH group [3–5]. This is elegantly circumvented in the borrowing hydrogen methodology, also known as the hydrogen autotransfer process. Here, the alcohol is activated by dehydrogenation to a more reactive carbonyl group. The intermediate can undergo dehydrative condensation with an amine nucleophile with relative ease. The corresponding imine is formed, which is then hydrogenated to the amine with hydrogen that was ‘borrowed’ from the starting alcohol (Scheme 1).

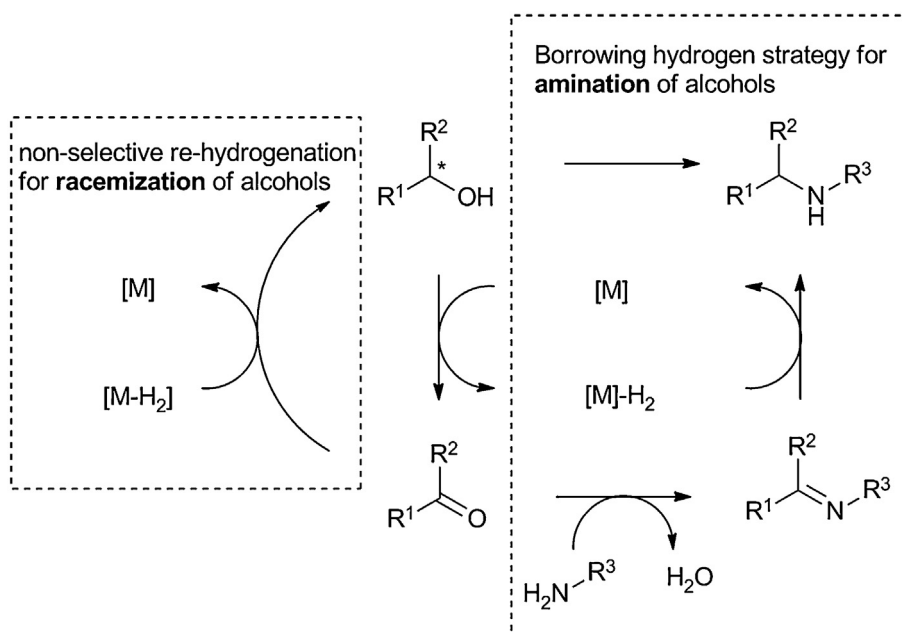
Typically a metal catalyst is employed for this reaction to dehydrogenate the alcohol in a first step, and to hydrogenate the imine in a second step. The groups of Grigg and Watanabe first demonstrated the activity of homogeneous rhodium, ruthenium

and iridium based catalysts for the amination of alcohols in 1981 via the borrowing hydrogen methodology [6,7]. Since then, many homogeneous Ru-catalysts have been developed but often, stabilizing ligands are required and bases are needed as additives, often even in (over)stoichiometric amounts [1,8,9]. Although the exact role of the base additives is still under debate, they are believed to aid in the dehydrogenation of the alcohol [2]. The group of Mizuno reported heterogeneous Ru activated by a base pretreatment supported on alumina or titania [10–12]. In this work, we propose the use of ruthenium immobilized on a calcium hydroxyapatite (HAP) carrier as a heterogeneous catalyst for the alcohol amination via the borrowing hydrogen mechanism, without the need for base co-catalysts, base pretreatment of the catalyst, or ligands.

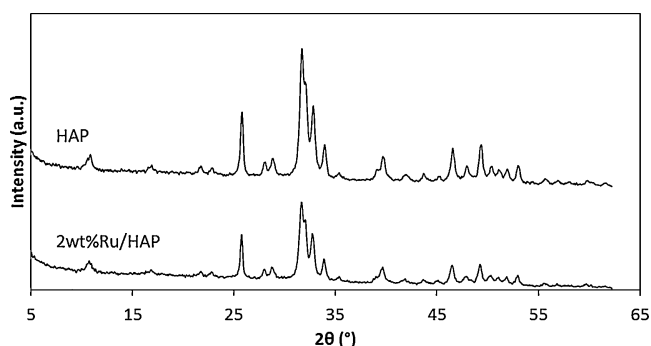
The use of a ruthenium on HAP (Ru/HAP) catalyst has been previously reported for aerobic alcohol or amine oxidation [13–20], Diels–Alder and aldol reactions [21] and racemization of alcohols [22]. For the latter reaction, the following mechanism was proposed by Wuyts et al. [22]. An alcohol can coordinate to the active Ru centre on the Ru/HAP catalyst and it is subsequently oxidized to the corresponding ketone. Racemization occurs when the ketone is hydrogenated back to the corresponding alcohol in a non-selective manner by a Ru hydride species. The intermediately formed ketone, or aldehyde when working with primary alcohols, can however easily react with amine nucleophiles if they are present in the reaction mixture. The strong parallel between racemization and the borrowing hydrogen mechanism for alcohol amination led us to investigate the use of Ru/HAP for these reactions (see Scheme 1).

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**Scheme 1.** Borrowing hydrogen strategy for the amination of alcohols, and the related racemization of alcohols.



**Fig. 1.** XRD pattern of HAP support (top) and 2 wt% Ru/HAP standard catalyst.

## 2. Experimental

### 2.1. Catalyst preparation and characterization

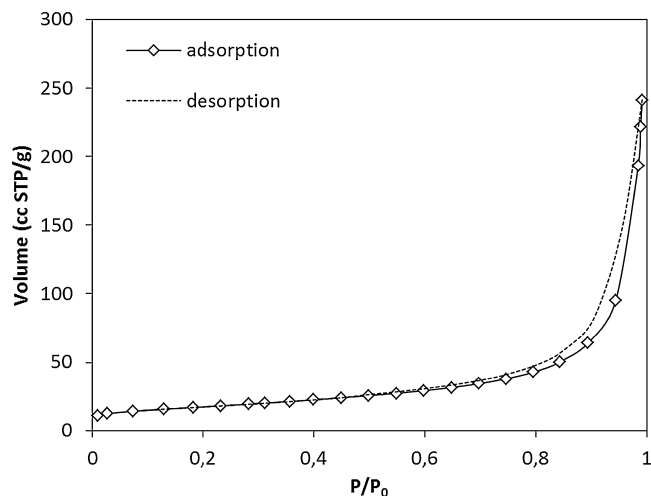
The ruthenium-exchanged hydroxyapatite catalysts were prepared according to a previously reported method [22]. In the standard preparation procedure 1 g of calcium hydroxyapatite ( $[\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2]$ ) is slurried in 50 mL of deionized water containing dissolved  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  (Aldrich). The concentration depends on the desired weight percentage of immobilized ruthenium, which was fixed at 2 wt% as a standard. The black suspension is stirred magnetically for 24 h at room temperature. After centrifugation the supernatant is colourless, indicating that all of the Ru is exchanged and immobilized on the HAP support. The material is washed three times with distilled water and the grey cake is freeze-dried resulting in a fine grey powder. For comparison, a 2 wt%  $\text{RuCl}_x/\text{alumina}$

**Table 1**  
ICP analysis of Ru/HAP catalysts and support.

Sample	Ru (wt%)	Ru/(Ru + Ca)
HAP	0	0
1 wt% Ru/HAP	1.03	0.0098
2 wt% Ru/HAP	2.11	0.0217
5 wt% Ru/HAP	5.09	0.051

was prepared by slurring 1 g of  $\gamma$ -alumina (Saint-Gobain Norpro, 200  $\text{m}^2/\text{g}$ ) in 50 mL of deionized water containing the appropriate amount of dissolved  $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$  at room temperature for 24 h, without any pH control. After washing three times with deionized water, the grey powder was dried at 60 °C.

The basicity of the HAP carrier was determined by titration. A 0.2 g powder sample was dried at 423 K overnight and suspended in 2 mL of an indicator solution (0.1 mg/mL bromothymol blue in toluene). This suspension was left to stir for approximately 2 h and was subsequently titrated with a 0.01 M benzoic acid solution in toluene. The titration experiment was reproduced thrice with good reproducibility. X-ray powder diffraction measurements were performed on a STOE StadiP, with  $\text{Cu K}\alpha$  radiation. Scanning electron microscopy was carried out on a Philips XL 30 FEG microscope after coating with Au. Elemental analysis was carried out using a Jobin Yvon Ultima spectrometer and a TJA Solaar 969 AA spectrometer. Nitrogen sorption measurements were performed on a Micromeritics 3Flex surface analyser at 77 K. Prior to measurement, the 400 mg samples were outgassed at 473 K overnight under  $\text{N}_2$  flow.



**Fig. 2.** Nitrogen adsorption–desorption isotherms of 2 wt% Ru/HAP catalyst.

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