

Alcohol amination with heterogeneous ruthenium hydroxyapatite catalysts



Annelies Peeters, Laurens Claes, Inge Geukens, Ivo Stassen, Dirk De Vos*

KU Leuven, Centre for Surface Chemistry and Catalysis, Kasteelpark Arenberg 23, 3001 Leuven, Belgium

ARTICLE INFO

Article history:

Received 2 July 2013

Received in revised form

23 September 2013

Accepted 26 September 2013

Available online 8 October 2013

Keywords:

Amination

Ruthenium

Hydroxyapatite

N-alkylation

Borrowing hydrogen

ABSTRACT

The intermolecular amination of alcohols was performed with ruthenium (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.

© 2013 Elsevier B.V. All rights reserved.

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).

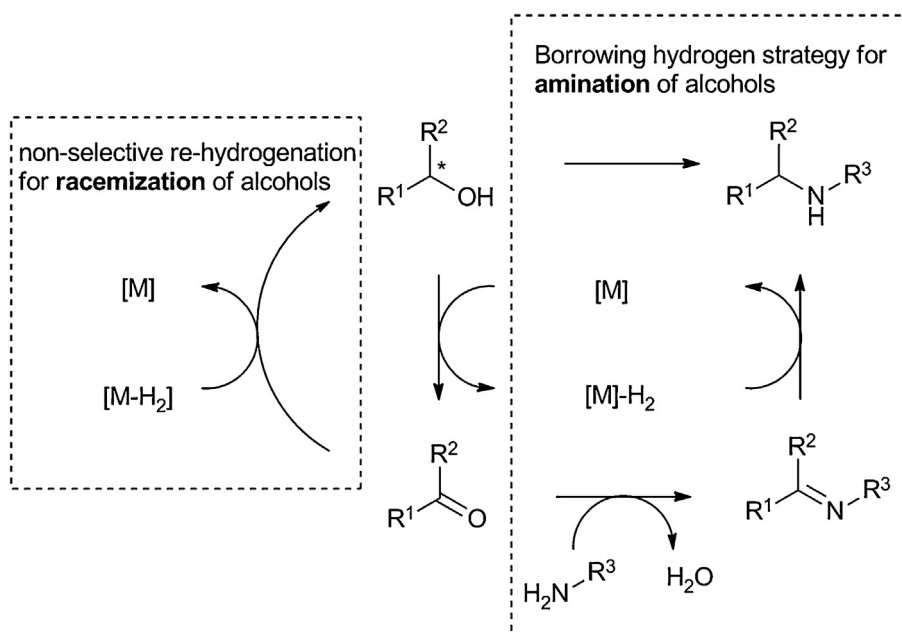
Typically a metal catalyst is employed for this reaction to dehydrogenate the alcohol in a first step, and to hydrogenate the imine in a second step. The groups of Grigg and Watanabe first demonstrated the activity of homogeneous rhodium, ruthenium

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).

* Corresponding author. Tel.: +32 16 321639.

E-mail address: dirk.devos@biw.kuleuven.be (D. De Vos).



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

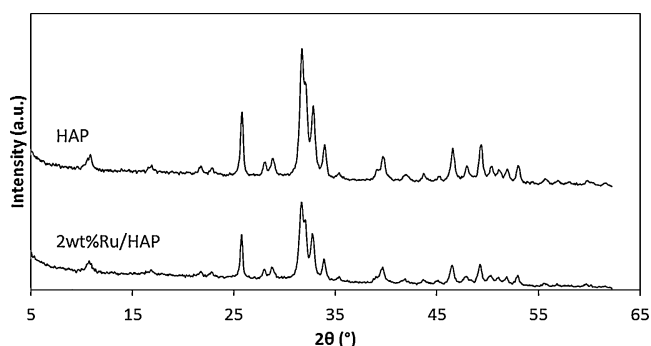


Fig. 1. XRD pattern of HAP support (top) and 2 wt% Ru/HAP standard catalyst.

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 γ -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 N_2 flow.

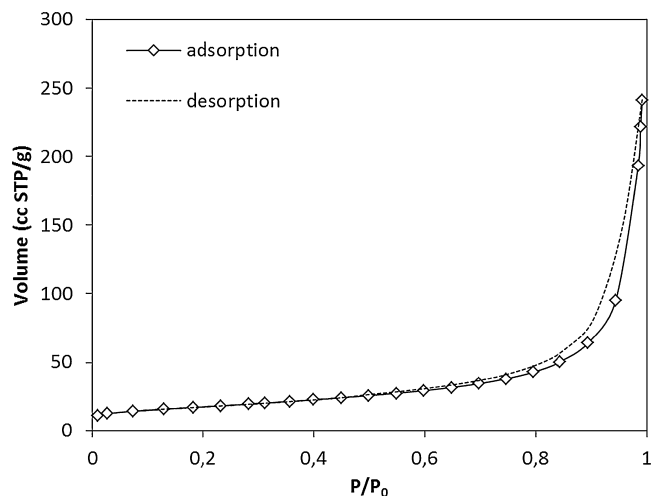
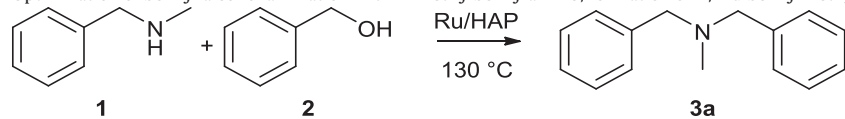


Fig. 2. Nitrogen adsorption–desorption isotherms of 2 wt% Ru/HAP catalyst.

Table 2
Optimization of benzyl alcohol amination with *N*-methylbenzylamine; formation of *N,N*-dibenzylmethylamine^a

Entry	Solvent	Amine/alcohol	Time (h)	Y% 3a
1	Mesitylene	2:1	3	5
			6	9
			24	23
2	Mesitylene	1:1	3	7
			6	11
			24	24
3	Mesitylene	1:2	3	20
			6	33
			24	71
4	Mesitylene	1:4	3	43
			6	74
			24	>99
5	Benzyl alcohol	-	3	67
			6	82
			24	>99
6	DMF	1:4	3	4
			6	7
			24	17
7	Nonane ^b	1:4	3	48
			6	77
			24	>99

^a Reaction conditions: 0.5 mmol of *N*-methylbenzylamine (for entries 2–7), 0.5 mmol of benzyl alcohol (for entry 1), 1 mL solvent, catalyst 2 wt% Ru/HAP (3 mol% with respect to the understoichiometric reactant; 15 μmol Ru; 75 mg catalyst), under Ar atmosphere, 130 °C. GC yield (Y%) based on amine (entries 2–7) or on alcohol (entry 1), calibrated with tetradecane internal standard (0.25 mmol).

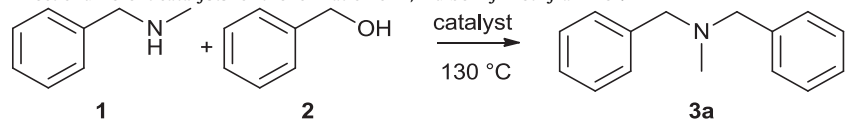
^b 0.5 mL of mesitylene co-solvent needed for dissolution of reactants.

2.2. Catalytic experiments

All reactions were performed in glass batch reactors under inert argon atmosphere and were stirred magnetically. Ru/HAP is used without further activation. Unless stated otherwise, a Ru/HAP with 2 wt% Ru was used. For a standard reaction 1 mL of mesitylene solvent, 0.5 mmol of amine and 2 mmol of alcohol were added to the vial containing 3 mol% of Ru/HAP (15 μmol Ru, 75 mg of the 2 wt% catalyst). As an internal standard tetradecane (0.25 mmol) was added and appropriate response factors were determined. The batch reactor was then thoroughly flushed with argon to minimize

oxidation of substrates with residual oxygen, before the reaction was started at 130 °C.

Small aliquots were removed from the reaction mixture at different time intervals. The heterogeneous catalyst was removed by filtration or centrifugation. The samples were diluted in toluene and analysed on a Shimadzu 2014 GC equipped with a CP-Sil-8 or CP-Sil-5 CB capillary column and a FID detector. The identity of the reaction products was verified by GC–MS with an Agilent 6890 gas chromatograph, equipped with a HP-5ms or HP-1ms column, coupled to a 5973 MSD mass spectrometer.

Table 3
Effect of different catalysts for the formation of *N,N*-dibenzylmethylamine^a.

Entry	Catalyst	Time (h)	Y% 3a
1	None	24	n.d.
2	HAP ^b	24	n.d.
3	2 wt% Ru/HAP	3	43
		6	74
		24	>99
4	RuCl ₃ · <i>n</i> H ₂ O	24	90 ^c
		3	42
		6	67
5	RuCl ₃ /γ-alumina	24	79
		3	8
		6	16
		24	42

n.d. = not detected.

^a Reaction conditions: 0.5 mmol of *N*-methylbenzylamine, 2 mmol of benzyl alcohol, 1 mL mesitylene, Ru catalyst (3 mol% Ru with respect to the understoichiometric reactant; 15 μmol Ru), under Ar atmosphere, 130 °C. Yield (Y%) based on amine, calibrated with tetradecane internal standard (0.25 mmol).

^b 75 mg.

^c Reuse experiment.

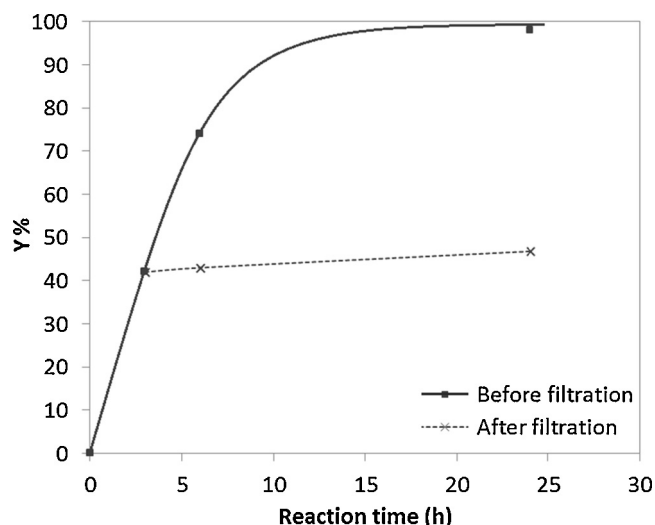


Fig. 3. Hot filtration test: yield (Y%) of *N,N*-dibenzylmethylamine before and after filtration of reaction mixture after 3 h of reaction time (Reaction conditions: 0.5 mmol of *N*-methylbenzylamine, 2 mmol of benzyl alcohol, 1 mL mesitylene, 2 wt% Ru catalyst (3 mol% Ru with respect to the understoichiometric reactant; 15 μ mol Ru; 75 mg catalyst), under Ar atmosphere, 130 °C. GC yield based on amine, calibrated with tetradecane internal standard (0.25 mmol)).

3. Results and discussion

3.1. Catalyst characterization

Hydroxyapatite [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] is a naturally occurring mineral that has gained interest in heterogeneous catalysis during the past decade as basic support material. The Ca^{2+} -ions in the lattice can be partially replaced by other, catalytically active metal ions, such as ruthenium. High catalytic activity of Ru/HAP for oxidations has been ascribed to the combination of redox active Ru sites with basic sites in the lattice [14]. The amination of alcohols via the borrowing hydrogen mechanism has similar catalyst requirements, since a redox site is needed to dehydrogenate the alcohol and hydrogenate the imine, and base additives are known for their co-catalytic effect on e.g. the dehydrogenation.

Since the basicity of the support presumably contributes to the overall activity of the Ru/HAP catalyst, it was studied by acid titration with bromothymol blue ($\text{pK}_a = 7.2$) as pH indicator [23,24]. The titrated number of basic sites was determined to be 0.14 mmol/g.

The HAP support material and a material with 2 wt% Ru were investigated with XRD (Fig. 1). Both before and after ion exchange HAP is the only structure that could be detected. The patterns are in good agreement with literature data, with strong reflections at 25.9°, 31.8°, 32.2°, 32.9°, 46.7° and 49.5° 2θ which are assigned to Miller indices (0 0 2), (2 1 1), (1 1 2), (3 0 0), (2 2 2) and (2 1 3) of the hexagonal crystal system of HAP [25,26].

The elemental compositions of the HAP support and of the Ru-exchanged materials were investigated with ICP and AAS. The Ca/P ratio of the carrier HAP was 1.65, which is slightly below the stoichiometric amount of 1.67 for $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$. The ruthenium amount was determined and is shown in Table 1.

Nitrogen adsorption and desorption isotherms were measured for a 2 wt% Ru/HAP sample and they are shown in Fig. 2. It can be concluded that hardly any microporosity is present in the HAP. The BET surface area was calculated to be 61 m^2/g , while the HAP support itself was found to have a surface area of 59 m^2/g . This indicates that the ion exchange procedure had no significant effect on the surface area.

The morphology of the samples was investigated with SEM and this showed no alterations in morphology of the powder after Ru exchange (see Supporting Information). The surface composition

of the material was examined with EDX after sputtering with carbon. This analysis showed that no chlorine could be detected with EDX, even for the 5 wt% Ru/HAP sample. This is in accordance with literature. Chlorine was found to be absent in samples with a low ruthenium content and only at higher loadings (>15 wt%) it was detected [13,22,27]. The nature of the Ru sites in Ru/HAPs has been debated in literature; most likely a simple ion exchange is not the only mechanism determining the speciation in metal loaded HAPs [18]. EXAFS studies showed evidence for hydroxy-ligands on the Ru sites [16], and later investigations by the same group using DRIFT spectroscopy of adsorbed CO and ATR-IR spectroscopy revealed the presence of two different species: isolated Ru^{3+} ions and a hydrated Ru^{3+} -oxide like phase (Ru^{3+} hydroxide) with high redox activity [14,18].

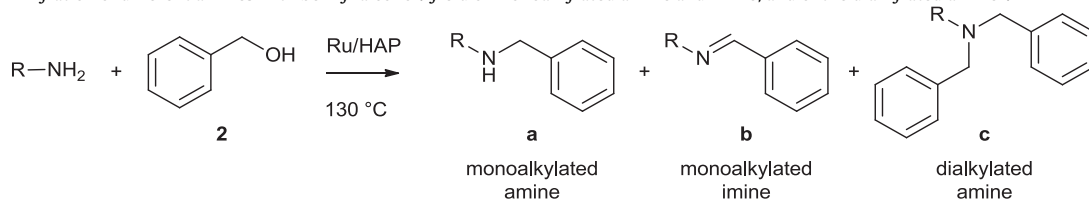
3.2. Amination of benzyl alcohol with *N*-methylbenzylamine

The reaction of *N*-methylbenzylamine with benzyl alcohol was chosen as a test reaction to optimize the reaction conditions with a 2 wt% Ru/HAP catalyst. With this secondary amine, only the mono-*N*-alkylation product can be formed, i.e. *N,N*-dibenzylmethylamine (**3a**, reaction outline, Table 2). Hardly any benzaldehyde was observed, indicating that the first step in the sequence, leading to benzaldehyde, is the slowest one. All subsequent steps in the sequence, i.e. imine formation and reduction must be fast for the model reaction used in Table 2. Primary amines can be alkylated twice with an alcohol generating both secondary and tertiary amine products. The imine formed in the second step of the borrowing hydrogen mechanism is relatively stable when working with a primary amine and is often detected in large quantities in the reaction mixture. This is avoided in the test reaction.

When varying the ratio of amine and alcohol reactants, it became clear that an excess of alcohol has a beneficial effect on the yield of **3a**. With an excess of amine, or a stoichiometric amount of alcohol and amine, the yield did not exceed 24% after 24 h of reaction at 130 °C (Table 2, entries 1 and 2). A 1:2 or 1:4 alcohol excess results in high yields of the desired product (Table 2, entries 3 and 4). When benzyl alcohol is used as solvent (1 mL) the reaction is improved even further. Working in a polar aprotic solvent such as DMF had a detrimental effect on the reaction, most likely due to a stronger coordination of this solvent on the active sites of the catalyst. In the nonpolar solvents mesitylene and nonane the reaction proceeded with ease. For nonane however some mesitylene co-solvent had to be utilized to dissolve all products due to poor solubility of the alcohol and amine in this solvent.

Blank reactions were performed to assess the need for an efficient catalyst. When working without any additives, no product was detected even after 24 h of reaction at 130 °C (Table 3, entry 1). When the HAP support was added to the reaction mixture, still no product was formed (Table 3, entry 2). The Ru precursor $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ was used as a homogeneous catalyst under the same reaction conditions, and while initially good yields of **3a** were obtained with the homogeneous analogue, the yields obtained after long reaction times are clearly inferior to those for the heterogeneous Ru/HAP, which is due to inactivation of the homogeneous catalyst; the Ru salt formed a black precipitate in the reaction mixture after 24 h.

$\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ was supported on a high-surface alumina support; however, reaction yields were moderate in comparison to the Ru/HAP (Table 3, entry 5). On HAP the simultaneous presence of the Ru^{3+} redox site and intrinsic basicity is an excellent combination to obtain high conversions for this *N*-alkylation. Yamaguchi et al. obtained a functional catalyst by treating the suspension of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ and alumina or titania with 1 M of NaOH until the suspension reached a pH of 13.2 [11]. With HAP as support this harsh base treatment of the catalyst is not necessary, since the support has intrinsic basicity.

Table 4Alkylation of different amines with benzyl alcohol: yield of monoalkylated amine and imine, and of the dialkylated amine^a.

Entry	Amine	Time (h)	X%	Y% a	Y% b	Y% c
1		24	>99	70	26	4
2		48	>99	55	25	20
		24	94	53	41	n.d.
3		48	>99	64	35	n.d.
		24	92	14	71	n.d.
4		24	83	17	25	n.d.
		48	>99	26	29	n.d.

^a Reaction conditions: 0.5 mmol of amine, 2 mmol of benzyl alcohol, 1 mL mesitylene, catalyst 2 wt% Ru/HAP (3 mol% with respect to the amine; 15 μmol Ru; 75 mg catalyst), under Ar atmosphere, 130 °C. Conversion (X%) and GC yield (Y%) based on amine, calibrated with tetradecane internal standard (0.25 mmol).

Further, the catalyst was proven to be heterogeneous with a hot filtration test (Fig. 3). After 3 h reaction the yield of **3a** reached 42%. At this point, part of the reaction mixture was removed, filtered while the suspension was still hot, and allowed to stir at reaction temperature. After 3 h another sample was taken, and the yield of **3a** in vial containing the original reaction mixture with catalyst had risen to 74%, while the filtered reaction mixture showed no increase in yield of **3a**. Even after 24 h of reaction the increase in yield of the filtered reaction mixture was minimal, indicating that the catalyst is truly heterogeneous. This was confirmed with a reuse experiment, where the yield after the second run reached 90% (Table 3, entry 3).

3.3. Examination of substrate scope

The scope of the catalytic reaction was successfully expanded to primary amines (Table 4). High conversions were obtained. In all cases the intermediately formed imine was detected and with benzylamine also the dialkylated product was obtained.

Interestingly, the reactions with aliphatic amines 1-hexylamine and 1-octylamine (not shown) yielded moderately low yields of the monoalkylated amine and imine products, although the conversion of the amine is quite high. This is because of alkyl group scrambling, or transalkylation which can occur when the amine or formed diamine can be dehydrogenated to the

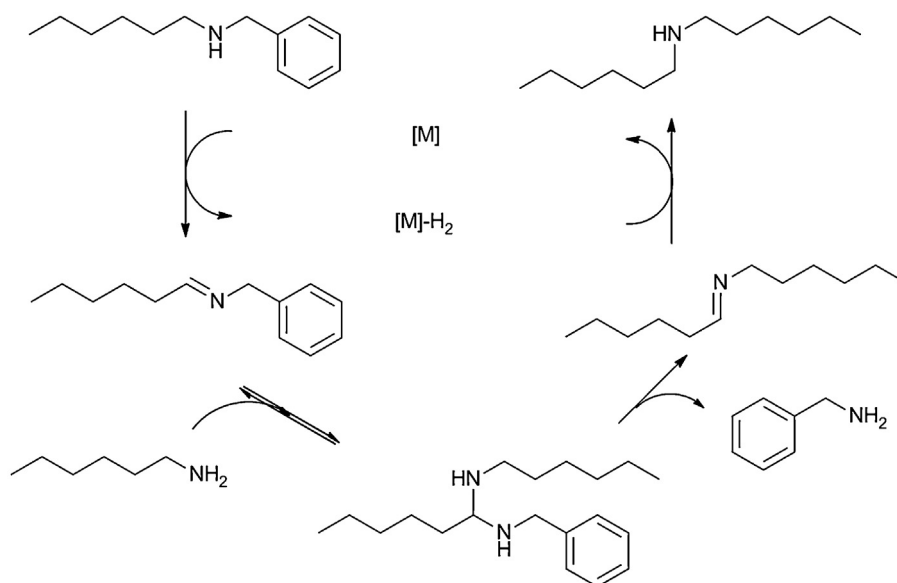
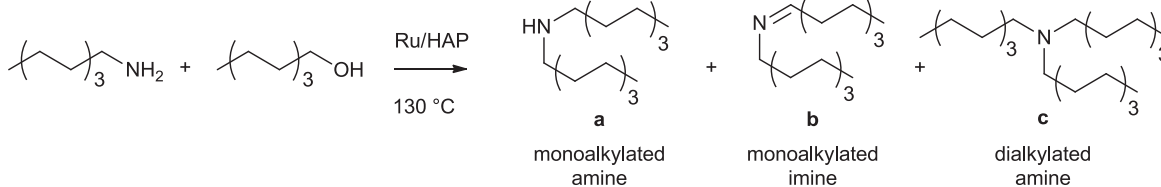
**Scheme 2.** Amine scrambling through transalkylation.

Table 5
Alkylation of 1-octylamine with 1-octanol: yield of monoalkylated amine and imine, and dialkylated amine^a.



Entry	Solvent	Time (h)	X%	Y% a	Y% b	Y% c
1	Mesitylene	3	51	41	10	n.d.
		24	97	20	2	75
2	Nonane	3	63	53	10	n.d.
		24	>99	3	<1	97
3	1-Octanol	3	>99	48	2	50
		24	>99	n.d.	n.d.	>99

^a Reaction conditions: 0.5 mmol of 1-octylamine, 2 mmol of 1-octanol, 1 mL of solvent, catalyst 2 wt% Ru/HAP (3 mol% with respect to the amine; 15 μ mol Ru; 75 mg catalyst), under Ar atmosphere, 130 °C. Conversion (X%) and GC yield (Y%) based on amine, calibrated with tetradecane internal standard (0.25 mmol).

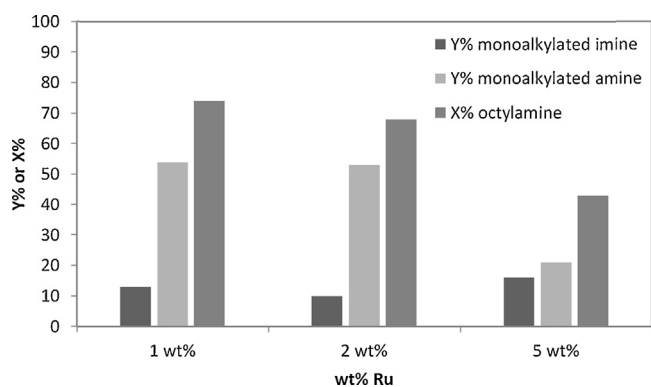


Fig. 4. Influence of Ru loading on conversion (X%) of 1-octylamine and yield (Y%) of the monoalkylated imine and amine in the reaction of 1-octylamine with 1-octanol (Reaction conditions: Ru/HAP (=3 mol% Ru with respect to the amine; 15 μ mol Ru) in 1 mL of solvent, 0.5 mmol of 1-octylamine, 2 mmol 1-octanol, 0.25 mmol tetradecane internal standard, inert atmosphere, 130 °C, 3 h).

corresponding imine [28–30]. For 1-hexylamine, by-products such as *N,N*-dihexylamine, *N,N,N*-trihexylamine, *N,N*-dibenzylamine and *N*-benzylidenebenzylamine could be detected. An example of this mechanism is shown in Scheme 2 for attack of a residual hexylamine on the formed monoalkylated amine, through the intermediate formation of an imine by a comparable borrowing hydrogen mechanism. Theoretically this is also possible for benzylamine, which also easily forms the corresponding imine, but due to the symmetry of the desired mono- and dialkylated products no transalkylation can be detected. With cyclohexylamine this does not occur to a high extent; with aniline this was not observed at all. This is due to the more difficult formation of the corresponding imine with these amines.

With 1-octanol the reaction proceeds as well (Table 5). With 1-octylamine transalkylation is not an issue, and high yields of the monoalkylated amine are generated after short reaction times; after longer reaction times the dialkylated amine is formed (entry 1). In nonane the reaction proceeds faster and almost stoichiometric amounts of the dialkylated amine can be formed after 24 h (Table 5, entry 2). By using 1-octanol as solvent, even after 3 h the dialkylated product is formed, with near stoichiometric yields after 24 h.

For the latter reaction of 1-octylamine and 1-octanol in nonane, the influence of the catalyst's Ru content was investigated. For the above reactions, a 2 wt% Ru catalyst was used. To compare the Ru loading, a 1 wt% and 5 wt% Ru/HAP catalyst were prepared and the

same reaction was performed, keeping the amount of Ru constant at 3 mol% with respect to the amine (Fig. 4). Interestingly, when the Ru-loading is high (5 wt%) the conversion of octylamine decreases. This is in good agreement with Wuyts et al. who also found a low Ru content of the catalyst to be beneficial for the reactivity [22]. It appears that an optimal balance between Ru sites and basic support is needed to obtain optimal activity of the catalyst. The number of weak and strong basic sites on the surface was estimated by a titration with benzoic acid to be 0.14 mmol/g (vide supra). A 2 wt% Ru loading amounts to about 0.2 mmol/g of Ru³⁺. A similar number of active ruthenium sites and basic support sites thus seems to lead to the highest activity. The basicity after Ru loading could not be determined by visual indicators, but future work will be performed to characterize the basicity further.

4. Conclusion

Ruthenium immobilized on an basic hydroxyapatite support was found to be an active heterogeneous catalyst for the amination of alcohols via the borrowing hydrogen mechanism. The catalyst was found to be heterogeneous, as indicated by a hot filtration test, and can be easily separated from the reaction mixture. The basic support was found to be an ideal carrier for the redox active ruthenium centres. An optimal balance between immobilized ruthenium and basic sites is required for activity. Higher loadings of ruthenium therefore led to lower activities. Both secondary and primary amines can be used as reactants and low catalyst amounts are used (3 mol% Ru) without the use of any co-catalysts or additives, nor did the catalyst require any pretreatment before reaction.

Acknowledgements

A.P., I.G. and I.S. acknowledge the Fund for Scientific Research Flanders (FWO-Vlaanderen) for financial support (Aspirant of FWO). L.C. thanks the IWT-Vlaanderen for support. D.E.D.V. thanks the Belgian Science Policy (BELSPO) for financing the Interuniversity Attraction Poles (IAP-PAI P7/05) and the Flemish government for long-term structural funding (Methusalem).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcata.2013.09.051>.

References

- [1] S. Bahn, S. Imm, L. Neubert, M. Zhang, H. Neumann, M. Beller, *ChemCatChem* 3 (2011) 1853–1864.
- [2] C.Z. Liu, S.H. Liao, Q. Li, S.L. Feng, Q. Sun, X.C. Yu, Q. Xu, *J. Org. Chem.* 76 (2011) 5759–5773.
- [3] A.J.A. Watson, J.M.J. Williams, *Science* 329 (2010) 635–636.
- [4] A. Baiker, J. Kijenski, *Catal. Rev. Sci. Eng.* 27 (1985) 653–697.
- [5] Y. Pouilloux, V. Doidy, S. Hub, J. Kervennal, J. Barrault, *J. Mol. Catal. A: Chem.* 115 (1997) 317–327.
- [6] R. Grigg, T.R.B. Mitchell, S. Sutthivaiyakit, N. Tongpenyai, *J. Chem. Soc., Chem. Commun.* 12 (1981) 611–612.
- [7] Y. Watanabe, Y. Tsuji, Y. Ohsugi, *Tetrahedron Lett.* 22 (1981) 2667–2670.
- [8] G. Guillena, D.J. Ramon, M. Yus, *Chem. Rev.* 110 (2010) 1611–1641.
- [9] M.H.S.A. Hamid, P.A. Slatford, J.M.J. Williams, *Adv. Synth. Catal.* 349 (2007) 1555–1575.
- [10] J.W. Kim, K. Yamaguchi, N. Mizuno, *J. Catal.* 263 (2009) 205–208.
- [11] K. Yamaguchi, J.L. He, T. Oishi, N. Mizuno, *Chem. Eur. J.* 16 (2010) 7199–7207.
- [12] J.L. He, J.W. Kim, K. Yamaguchi, N. Mizuno, *Angew. Chem. Int. Ed.* 48 (2009) 9888–9891.
- [13] K. Yamaguchi, K. Mori, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc.* 122 (2000) 7144–7145.
- [14] C. Mondelli, D. Ferri, A. Baiker, *J. Catal.* 258 (2008) 170–176.
- [15] K. Mori, S. Kanai, T. Hara, T. Mizugaki, K. Ebitani, K. Jitsukawa, K. Kaneda, *Chem. Mater.* 19 (2007) 1249–1256.
- [16] Z. Opre, J.D. Grunwaldt, T. Mallat, A. Baiker, *J. Mol. Catal. A: Chem.* 242 (2005) 224–232.
- [17] Z. Opre, D. Ferri, F. Krumeich, T. Mallat, A. Baiker, *J. Catal.* 241 (2006) 287–295.
- [18] Z. Opre, D. Ferri, F. Krumeich, T. Mallat, A. Baiker, *J. Catal.* 251 (2007) 48–58.
- [19] S. Fukahori, M. Morikawa, J. Ninomiya, *J. Mater. Sci.* 44 (2009) 374–378.
- [20] K. Mori, K. Yamaguchi, T. Mizugaki, K. Ebitani, K. Kaneda, *Chem. Commun.* (2001) 461–462.
- [21] K. Mori, T. Hara, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc.* 125 (2003) 11460–11461.
- [22] S. Wuyts, D.E. De Vos, F. Verpoort, D. Depla, R. De Gryse, P.A. Jacobs, *J. Catal.* 219 (2003) 417–424.
- [23] K. Tanabe, T. Yamaguchi, *J. Res. Inst. Catal. (Hokkaido University)* 11 (1964) 179–184.
- [24] K. Tanabe, M. Misono, Y. Ono, H. Hattori, *New solid acids and bases*, in: *Studies in Surface Science and Catalysis*, Elsevier, Amsterdam, 1989.
- [25] S. Koutsopoulos, *J. Biomed. Mater. Res.* 62 (2002) 600–612.
- [26] C.M. Ho, W.Y. Yu, C.M. Che, *Angew. Chem. Int. Ed.* 43 (2004) 3303–3307.
- [27] Z. Opre, J.D. Grunwaldt, M. Maciejewski, D. Ferri, T. Mallat, A. Baiker, *J. Catal.* 230 (2005) 406–419.
- [28] A. Tillack, D. Hollmann, K. Mevius, D. Michalik, S. Baehn, M. Beller, *Eur. J. Org. Chem.* (2008) 4745–4750.
- [29] C.W. Jung, J.D. Fellmann, P.E. Garrou, *Organometallics* 2 (1983) 1042–1044.
- [30] D. Hollmann, S. Baehn, A. Tillack, M. Beller, *Angew. Chem. Int. Ed.* 46 (2007) 8291–8294.