Novel improved ruthenium catalysts for the generation of hydrogen from alcohols

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The dehydrogenation reaction of alcohols to generate hydrogen at ambient conditions has been studied, it is shown for the first time that ruthenium in the presence of easily available amine ligands constitutes an active catalysts for this reaction: high turnover frequencies (TOF) up to 519 h⁻¹ (after 2 h) and catalyst stability (>250 h) were achieved for the dehydrogenation of isopropanol with a combination of [RuCl₂(*p*-cymene)]₂/TMEDA.

The use of alternative feedstocks for energy generation is one of the central challenges of this century. Due to the progressive depletion of fossil fuel reserves and the continuously increasing energy demands, hydrogen is becoming an increasingly attractive feedstock for energy generation.¹ An obvious advantage of a hydrogen economy is the significant reduction of the emission of green house gases.

Apart from the ultimate solution, which is water cleavage,² renewable resources such as biomass or its fermentation products, *e.g.* alcohols are a promising basis for the on-time production of hydrogen for stationary devices. However, efficient hydrogen production from renewable resources remains difficult and improved chemical and engineering technologies for generating hydrogen at higher reaction rates and under milder conditions are required. In this respect the development of more efficient catalysts and their understanding will be a key issue. With regard to catalysts, improvements have been made in the past mainly in the field of heterogeneous catalysis.³ Consequently, the use of soluble transition metal complexes for hydrogen generation has been largely neglected.⁴

$$\searrow -OH \xrightarrow{[RuCl_2(p-cymene)]_2/ \text{ ligand}}_{6 \text{ h, }90^\circ\text{C}} \longrightarrow (1)$$

To date, only few molecularly defined catalysts have been developed towards the production of hydrogen.^{5–7} Among these reports the work of Cole-Hamilton *et al.* who used catalysts of the type [Ru(H₂)(X₂)(PPh₃)₃] (X₂ = N₂, H₂) is especially noteworthy.⁶ Here, turnover frequencies (TOF) of 150 h⁻¹ for ethanol, 330 h⁻¹ for isopropanol and up to >500 h⁻¹ for glycol and *n*-butanol were achieved at 150 °C in the presence of NaOH. More recently, we have demonstrated that the dehydrogenation of isopropanol also proceeds at a comparably lower temperature (90 °C) in the

presence of RuCl₃·xH₂O and adamantylphosphines or biarylphosphines.⁸ The best results were observed applying 2-di-*tert*-butylphosphinyl-1-phenyl-1H-pyrrole as the ligand.⁹

From a catalyst development point of view it is also interesting to note that recently various research groups, *e.g.* Milstein,¹⁰ Williams,¹¹ Park,¹² Hulshof¹³ and Hartwig¹⁴ investigated the related oxidations of alcohols in the presence of ruthenium phosphine catalysts. Here, hydrogen is produced as a side-product. However, the catalyst efficiency with respect to hydrogen production is in general low.

Clearly, for future applications in this area it is crucial to improve the catalysts with respect to economy, stability, and easy availability. Here, we report an important step towards this direction. For the first time convenient catalysts consisting of ruthenium and easily available amines are shown to be active in the generation of hydrogen under mild conditions (isopropanol: TOF >500 h⁻¹; 90 °C).

As a starting point and model system the dehydrogenation of isopropanol to hydrogen and acetone in a 1 : 1 molar ratio was chosen (Fig. 1) due to easy product analysis, availability and handling. Hydrogen production was measured both by volumetric methods and at the same time by a gas sensor. In addition, gas-chromatographic measurements of the produced gas have been made. In all cases only hydrogen and argon (from the inert gas atmosphere) were detected as gaseous products.¹⁵ In the liquid phase, hydrogen and acetone, but also minor amounts (1–15%) of the aldol condensation, partly followed by hydrogenation (Guerbet reaction^{16,17}), products could be detected. Hence, it is important to note that a small part of the evolved hydrogen is consumed by this side-reaction.

Typically, catalyst tests were performed at 90 °C in the presence of sodium isopropylate (0.8 mol L^{-1} ; 6.7–6.9 mol%). In our previous work we have demonstrated that without base, hydrogen generation is very slow.⁹

In order to develop more economical and less sensitive ruthenium catalysts we turned our attention to nitrogen ligands instead of phosphines (Fig. 1). Comparison of different ruthenium precursors, *e.g.* RuCl₃·*x*H₂O and [RuCl₂(*p*-cymene)]₂ without any ligand present revealed that the latter system already displayed significant activity (TOF after 2 and 6 h: 192 and 120 h⁻¹, respectively) (Fig. 2, entry 1). Therefore a broad screening of various mono-, bi-, and tridentate nitrogen ligands has been done in the presence of 16 ppm of this ruthenium source (Ru : N = 1 : 2 for bidentate, 1 : 3 for tridentate ligands) (Fig. 2). Almost all of the tested amines showed some dehydrogenation activity in the model reaction. However, the addition of trialkylamines gave much better results compared to secondary and primary amines (Fig. 1,

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Fig. 1 Selected nitrogen ligands applied in the catalyst screening.



Fig. 2 Screening of several nitrogen containing ligands.[†]

compare reactions with tetramethylethylenediamine (TMEDA), with dimethylethylenediamine 6 and ethylenediamine 7). To our surprise, often applied coordinating ligands such as terpyridine and

Table 1 Variation of catalyst to substrate ratio

2-aminomethylpyridine showed a significant inhibition of the reaction (TOF after 2 h: $<60 \text{ h}^{-1}$). On the other hand, simple aliphatic amines, *e.g.* triethylamine and *n*-butyldimethylamine increased the catalyst activity (TOF after 2 h: $>250 \text{ h}^{-1}$). This can not be explained by a simple base effect because *N*,*N*-dimethylamiline gave even better results and the amount of the respective ligand is small in solution (64 ppm).

Best results were observed in the presence of TMEDA, the N, N, N', N'-tetramethyl-1,3-diamine **1**, the tridentate TMEDA derivative 5,2-dimethylaminoethanol and N, N-dimethylamiline (TOF after 2 h: >300 h⁻¹). At this point it is also interesting to compare the described activity with the previous results obtained by Cole-Hamilton's catalyst [Ru(H₄)(PPh₃)₃],⁶ which still belongs to the most active catalysts published for the dehydrogenation of alcohols in the absence of a hydrogen acceptor. Previously, a catalyst turnover frequency of about 50 h⁻¹ was obtained at 90 °C after 2 h.⁹

On the basis of the promising results, we studied the ruthenium-TMEDA and ruthenium-9 in situ catalysts in more detail (Table 1). Decreasing the $[RuCl_2(p-cymene)]_2$ concentration from 80 ppm to only 4 ppm increased the catalyst activity, which might be explained by the higher dilution of deactivating aldol condensation products (mesityloxide and water) (Table 1, entries 1-3). At this low ruthenium concentration it is beneficial to increase the amount of the nitrogen ligand. Applying a Ru : N ratio of 1 : 20 led to a turnover frequency of 519 h^{-1} (Table 1, entry 5). To the best of our knowledge this is the highest catalyst activity reported below 100 °C for alcohol dehydrogenations. In general, the TOF values decreased slightly for all catalytic systems after 6 and 24 h, respectively. This deactivation seems to correlate with the formation of aldol by-products and water, which are both generated by self-condensation of acetone. In agreement with this finding, the addition of mesityloxide and water decreased the rate of hydrogen formation. Nevertheless, the catalyst system is stable for several days. Exemplarily, it has been shown that the combination of [RuCl₂(p-cymene)]₂ and 10 equiv. TMEDA is still active after 11 days! Within this time 71 mmol hydrogen have been produced, which corresponds to a total turnover number (TON) of 17215 and a potential electric energy of 4.8 Wh.¹⁸

Finally, the dehydrogenation of 1-phenylethanol and ethanol were studied under modified reaction conditions (Table 2).

In the presence of $[\text{RuCl}_2(p\text{-cymene})]_2-9$ both alcohols generate hydrogen below 100 °C. However, the reactivity is almost one order of magnitude lower compared to isopropanol. Besides hydrogen acetophenone or acetaldehyde are formed. The latter is mainly converted into higher alcohols by the Guerbet reaction, C₄, C₆ and C₈-alcohols could be detected by GC/MS. In the case of

	Ru-Precursor	Catalyst amount/ppm	Ligand	Ligand : Ru Ratio	V _{H2} ^a / mL2 h	$TOF^{b}/h^{-1}2 h$	V _{H2} ^a / mL6 h	$TOF^{b}/h^{-1}6$ h	V _{H2} ^a / mL24 h	$TOF^{b}/h^{-1}24 h$
1^c	[RuCl ₂ (<i>p</i> -cymene)] ₂	80	TMEDA	1	166	161	270	87		
2^c	[RuCl ₂ (p-cymene)] ₂	16	TMEDA	1	64	309	116	190		
3^d	[RuCl ₂ (p-cymene)] ₂	4.0	TMEDA	1	90	439	177	288		
4^d	[RuCl ₂ (<i>p</i> -cymene)] ₂	4.0	TMEDA	3	104	505	194	315		
$5^{d,e}$	[RuCl ₂ (p-cymene)] ₂	4.0	TMEDA	10	107	519	195	317	466	189
6 ^{<i>d</i>}	$[RuCl_2(p-cymene)]_2$	4.0	9	10	64	313	144	233	337	137
^{<i>a</i>} Mea 4.0 m	asured by gas burette. L ISTD. ^e after 268 h:	^b Calculated con V _{H2} 1756 mL, TO	cerning to va $OF 64 h^{-1}$.	lues measured b	oy gas bure	ette. ^c 10 m	L <i>i</i> -PrOH,	1.0 mL IS	TD. ^d 40 m	L <i>i</i> -PrOH,

Table 2 Dehydrogenation of various alcohols (5.0 mL) with20.5 mmol $[RuCl_2(p-cymene)]_2-9$ at 90 °C

	v	Va/	TOF^{b}	Va/	TOF ^b /	
Entry	Substrate	mL2 h	$h^{-1}2$ h	mL6 h	$h^{-1}6$ h	
1)—он	134	66	208	34	
2		15	7.6	25	4.1	
3	ОН	6.0	3.0	11	1.8	

^{*a*} Gas burette. ^{*b*} Calculated concerning to values measured by gas burette.

ethanol also traces of methane as a second gaseous product could be detected.

In conclusion, we have shown for the first time, that it is possible to generate significant amount of hydrogen from alcohols in the presence of *in situ* generated ruthenium–amine complexes. Compared to previously known catalysts the presented complexes are more easily available, more stable, and show improved turnover frequencies for the dehydrogenation of isopropanol below 100 °C. Interestingly, the catalyst systems are active for more than 11 days, which has so far never achieved for such reactions.

In addition, our catalyst systems might be also of interest for transfer-hydrogenation reactions and the dynamic kinetic resolution processes of chiral alcohols.¹⁹ Work towards the further improvement of the catalyst is in progress in our laboratories.

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Notes and references

 \dagger For ligand 6 values are not reproducible; in 5 experiments turnover frequencies from 74 to 387 h^{-1} after 2 h and 56 to 210 h^{-1} after 6 h have been obtained.

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