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# Enhanced Selectivity in the Hydrogenation of Anilines to Cycloaliphatic Primary Amines over Lithium-Modified Ru/CNT Catalysts

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Abstract: The hydrogenation of aromatic amines to the corresponding cycloaliphatic primary amines is an important industrial reaction. However, secondary amine formation and other side reactions are frequently observed resulting in reduced selectivity. The side-products are formed mostly on the support, yet support effects are little understood at present. This study describes the facile modification of Ru/CNT catalysts with LiOH, by this means significantly improving catalyst selectivity in toluidine hydrogenation without decreasing the activity of the catalysts. The effect is explained by LiOH diminishing acidic sites on the catalyst support and enhancing the adsorption of the aromatic ring on the metallic ruthenium nanoparticles. With the LiOH modified Ru/CNT catalyst also other substrates, such as methylnitrobenzenes, are converted efficiently. This study, thus, describes an improved catalyst for the preparation of cyclohexylamines and provides guidelines for future catalyst design.

# prominent of which are condensation reactions and hydrogenolysis of the C-N bond. With most catalysts, the formation of the corresponding diamine predominates as side reaction in the hydrogenation of anilines. In a recent study, we investigated the effect of nitrate additives on the hydrogenation of toluidines.<sup>[7a, 10]</sup> In the presence of nitrates catalyst activity and the selectivity toward the primary amine were increased significantly. This is attributed to the nitrates being co-adsorbed on the catalyst surface, thus facilitating the planar adsorption of the aromatic ring of toluidine on the catalyst surface.



#### Introduction

Cyclohexylamines are significant as intermediates for largescale production in the chemical industry. The parent cyclohexylamine is applied as an intermediate for producing sulfenamide vulcanization accelerators and corrosion inhibitors.<sup>[1]</sup> Substituted derivatives, are utilized in the manufacture of pharmaceuticals<sup>[2]</sup> and as the amine component for aliphatic polyurethanes.<sup>[3]</sup> An example is the use of fully hydrogenated methylene dianiline (H12-MDA) in the manufacture of white polyurethane foams. Cyclohexylamines are commonly produced by hydrogenating the corresponding aniline derivative.<sup>[1]</sup> The reaction is catalyzed by iridium,<sup>[4]</sup> nickel,<sup>[5]</sup> rhodium<sup>[6]</sup> and ruthenium<sup>[7]</sup> compounds. Alternative synthesis strategies comprise the hydroamination of alkenes<sup>[8]</sup> and the reductive amination of phenols to substituted cyclohexylamines.[9] Another strategy to synthesize cyclohexylamines is the selective hydrogenation of nitrobenzene by using carbon nanotube (CNT)-supported ruthenium and mixed Pt/CNT - Ru/CNT catalysts.<sup>[7b, 10]</sup>

The hydrogenation of anilines and nitroaromatics is marked by a considerable number of side reactions, the most

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**Scheme 1.** Reaction sequence of aniline hydrogenation to cyclohexylamine as the target product and generally established main route to the formation dicyclohexylamine as most prominent side-product.

So far, the role of the support has not been thoroughly investigated. For related reactions, such as the reductive amination of carbonyl compounds,<sup>[11]</sup> the dynamic kinetic resolution of amines<sup>[12]</sup> and nitrile hydrogenation,<sup>[11, 13]</sup> significantly reduced secondary amine formation has been reported when basic supports are used.<sup>[14]</sup> A common feature is that the reaction involves an imine as key intermediate (Scheme 1).<sup>[10] [11, 15]</sup> The formation of aminals from the imine intermediates and subsequent elimination of ammonia is acid-catalyzed (Scheme 2). In aniline hydrogenation, this reaction sequence results in the formation of dicyclohexylamine. In analogy to related reactions, we anticipated that the formation of condensation products is suppressed through the use of a basic support. Upon using basic inorganic supports, the high dispersion of the active metal often cannot be preserved.<sup>[16]</sup>. For carbon materials doping with nitrogen promotes high dispersion of supported nanoparticles.<sup>[17]</sup> However, deactivating of acidic groups present in carbon materials has been given little attention.[18]

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 $\ensuremath{\textbf{Scheme}}$  2. Likely mechanism for the acid-promoted formation of secondary amines.

The main objective of this current work is, thus, to provide a facile method for counteracting the effect of acidity present on carbon nanotube supported metal catalysts by base modification. With the size of supported metal nanoparticles remaining unchanged differences in reactivity ought to be effected mostly by introducing basicity into the catalyst. A parallel objective is to explore the sequence, in which cyclohexane diastereomers occur in the product mixture during the hydrogenation of substituted anilines, so as to gain fresh insights into the reaction pathways. Controlling diastereoselectivity in the same manner as chemoselectivity is particularly relevant, when cycloaliphatic di-amines are synthesized. During later conversion to the corresponding di-isocyanates for producing polyurethanes, for example, proximal amine groups can react to urea moieties.[19] As this lowers the average functionality of the di-isocyanates, diastereoselectivity control is crucial.

#### **Results and Discussion**

#### Catalyst synthesis and characterization

The authors envisioned ruthenium and rhodium to be the most suitable metals for the hydrogenation of aromatic amines, based on the successful use of these two metals in related hydrogenation reactions.<sup>[7a, 20]</sup> Carbon nanotubes (CNT) were chosen as the support, as they are generally inert materials and specific modification, such as directed oxidation of surface groups, results in well-defined and predictable functional groups.<sup>[7a, 21]</sup> Moreover, the latter act as suitable anchoring sites for metal nanoparticles.<sup>[10]</sup> Multiwall carbon nanotubes obtained in a fluidized bed reactor were used as support.<sup>[22]</sup> The material consisted of approximately spherical beads of 0.1 mm diameter. Closer inspection with scanning electron microscopy revealed the internal morphology of the beads. Multi-walled carbon nanotubes formed loose bundles with a discernible pore system between the nanotubes. The pore size distribution determined by nitrogen adsorption according to Barrett, Jovner, and Halenda (BJH) revealed a broad distribution of mesopores. These mesopores ought to enable rapid diffusion of the substrates to the surface of the CNT.



Figure 1. Representative transmission electron microscopy (TEM) image and particle -size distribution (insert) of Ru/CNT (left) and Rh/CNT (right).

The Ru/CNT and Rh/CNT pre-catalysts were prepared with a deposition-precipitation method (DPM).<sup>[10]</sup> For this, multi-walled carbon nanotubes were oxidized first in refluxing nitric acid to generate the anchoring sites. The metal precursor was then introduced by suspending the carbon nanotubes in an aqueous solution of the metal precursor. Subsequently, the pH-value of the suspension was gradually increased through decomposing dissolved urea to ammonia. For preparing the Ru/CNT precatalyst, the oxidized carbon nanotubes were suspended in an aqueous solution of  $[Ru(NO)(NO_3)_x(OH)_y]$ . During DPM, ruthenium-hydroxide precipitated on the surface of the carbon nanotubes. The pre-catalyst was isolated by filtration and dried in a gentle flow of argon. Thereafter, the pre-catalyst was reduced at 200 °C in a flow of hydrogen to yield the final Ru/CNT catalyst. The Rh/CNT catalyst was prepared accordingly using Rh(NO<sub>3</sub>)<sub>3</sub> as metal precursor.

The shape of the carbon nanotube beads did not change visibly throughout the sequence of pre-treatment with nitric acid, DPM and reduction of the pre-catalyst. After reduction, the Ru/CNT and Rh/CNT catalysts had a metal loading of 3.6 wt% ruthenium and 2.3 wt% rhodium, respectively. The surface area (~185 m<sup>2</sup>·g<sup>-1</sup>) was identical throughout all preparation steps, indicating that there was no pronounced pore blockage (see SI). Energy dispersive X-ray spectroscopy (EDX) showed that the metals, Ru and Rh, were evenly distributed in the respective catalysts (see SI).

Closer inspection of Ru/CNT and Rh/CNT by electron microscopy showed the presence of small metal nanoparticles that were evenly distributed over the surface of the carbon nano-tubes (Figure 1). The nanoparticles were located on the outer surface of the nanotubes; accumulation of metal nanoparticles inside the nanotubes was not detected. Thorough analysis of the nanoparticle size revealed a narrow size-distribution with mean particle diameter of 1.5 nm for Ru/CNT and 1.2 nm for Rh/CNT (Figure 1, inserts). Such small particles provide a high proportion of surface metal atoms in edges and vertices that ought to provide high activity.<sup>[23]</sup> The slightly larger particle diameter of the metal nanoparticles in Ru/CNT compared with Rh/CNT reflects the somewhat higher metal loading.



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Scheme 3. Hydrogenation of toluidines as model reaction for the hydrogenation of multi-functional aromatic amines with more intricate substituents.

The hydrogenation of toluidines served as a model for more complex substrates. The idea here is that the methyl-group is chemically rather inert under the reaction conditions and is an apt replacement for more intricate substituents. Despite being the smallest alkyl substituent, the methyl group has a pronounced steric effect. Thus, the authors believed it would be a good model to identify trends for the hydrogenation of disubstituted anilines. The hydrogenation products are methylcyclohexylamines, which can be formed as trans- or cisdiastereomer (Scheme 3). Each of the three toluidine regioisomers gives rise to two methylcyclohexylamine diastereomers. For o- and p-toluidine, the corresponding hydrogenated trans-methylcyclohexylamines with both substituents in equatorial position are most stable.<sup>[24]</sup> For mtoluidine the cis-product with both substituents in equatorial position is the most stable diastereomer. The methyl group has a stronger impact on the energy difference compared to the amino group. Thus, the energy difference between the rotamers of methylcyclohexane has been determined to be  $1.80 \pm 0.02$ kcal mol-1.[24d] The energy difference between the rotamers of cyclohexylamine has been calculated to be 0.70 kcal mol<sup>-1.[24c]</sup>

# Performance of Ru/CNT and Rh/CNT as benchmark catalysts

In a first step, the activity and selectivity of the parent Ru/CNT and Rh/CNT catalysts was explored for p-toluidine. Using 1 mol% catalyst, p-toluidine was hydrogenated at 110 °C and 100 bar pressure in THF. The reaction was monitored over time. In the case of Ru/CNT (Figure 2), the reaction commenced after an initiation period of approximately 10 min. The concentration of *p*-toluidine decreased rapidly at а rate of -5 mol<sub>p-toluidine</sub> min<sup>-1</sup> mol<sub>Ru</sub><sup>-1</sup> (Table 1) with close to zero-order kinetics. After 30 min the reaction slowed down and 99 % of p-toluidine had been converted after 80 min. The reduced rate after 30 min may be related to the different self-association constants of toluidine and methyl cyclohexyl amine.<sup>[25]</sup> Likewise,



Figure 2. Molar fractions against time for the hydrogenation of *p*-toluidine using Ru/CNT as catalyst.

the formation of the more basic secondary amine may lead to increased catalyst inhibition and a reduced rate in the final phase of the reaction.

Analysis of the product distribution after 3 h reaction time showed the primary amine 4-methylcyclohexylamine to be the main product with 92.1% selectivity. The only side-product that formed in significant amounts was the secondary amine di(4methyl cyclohexylamine), which was obtained in a yield of 7.9 %. To gain closer insight into the reaction sequence, the ratio of 4methyl cyclohexylamine to di(4-methyl cyclohexylamine) was plotted against time. The first 30 min were characterized by a steep decrease in the ratio of primary to secondary amine (Figure S7). Thereafter the ratio remained nearly constant. Inspection of the reaction profile shows that the first 30 min are marked by the presence of *p*-toluidine in the reaction mixture. This implies that secondary amine formation may commence by condensation of the primary amine with p-toluidine. This is analogous to the mechanism proposed for the formation of secondary amines during the hydrogenation of aniline<sup>[26]</sup> and for the deep hydrogenation of nitrobenzene.<sup>[10]</sup>

<b>Table 1.</b> Kinetic data and selectivity toward MeCy-NH2 for the hydrogenation of <i>p</i> -toluidine using CNT-supported Ru and Rh catalysts.								
Catalyst	r <sub>ini</sub> ∕ mol∙min <sup>-1</sup> ∙mol <sub>M</sub> <sup>-1</sup>	t <sub>50%</sub> /min	t <sub>99%</sub> /min/	S(MeCy-NH <sub>2</sub> ) /% <sup>[a]</sup>				
Ru/CNT	-5.01 ± 0.22	18	80	92.1				
Ru/CNT (LiOH)	-5.55 ± 0.05	18	47	>99.8				
Rh/CNT	-11.29 ± 0.27	10	67	93.8				
Rh/CNT (LiOH)	-7.9 ± 1.2	9	>120	83.0				

[a] Selectivity toward MeCy-NH<sub>2</sub> after 180 min, for Rh/CNT (LiOH) after 120 min.

The two diastereomers were obtained in a 3:2 trans: cis molar ratio. A plot of the diastereomer ratio against time revealed a constant ratio, showing that the two diastereomers were formed in parallel. There is no evidence for isomerization. Note that for formation of the thermodynamically more stable trans-product, the hydrogen atoms have to approach the aromatic ring from one as well as the opposite side. To allow for this, the imine formed as intermediate, or another partially hydrogenated intermediate, has to flip over, while being adsorbed on the catalyst surface, or desorb and re-adsorb with the opposite face.<sup>[7a]</sup> The *cis*-product, on the other hand, is formed when all hydrogen atoms approach the aromatic ring from the same side. Preferential formation of the trans-product is consistent with moderate adsorption strength of the intermediates resulting in the necessary mobility of the intermediate for the hydrogen atoms to approach from different sides of the aromatic ring.



Figure 3. Molar fractions against time for the hydrogenation of *p*-toluidine using Rh/CNT as catalyst.

For Rh/CNT, the reaction profile was analogous. The reaction commenced after a short initiation phase of 5 min at a rate of -11.3 mol<sub>p-toluidine</sub>·min<sup>-1</sup>·mol<sub>Ru</sub><sup>-1</sup> (Table 1). In comparison, the rate was twice as high as that for Ru/CNT. A conversion of 99 % was obtained after 67 min, slightly faster than for Ru/CNT. The selectivity toward primary cycloaliphatic amines (93.8 %) was slightly higher for Rh/CNT than for Ru/CNT (91.9 %). Dimethyl cyclohexylamine was formed to a lower extent, with a yield of 6.1 %. Also in this case, analysis of the product distribution with time revealed that the secondary amine was formed as a consecutive product (Figure S8). Likewise, trans-4-methyl cyclohexylamine was obtained as the major diastereomer with a yield of 63.6 % after 3 h time of reaction, while the corresponding cis-isomer was formed in 30.2 % yield. This suggests similar mobility of the partially hydrogenated intermediates on Rh/C compared to Ru/CNT.

Ru/CNT and Rh/CNT have thus been shown to be suitable catalysts for the hydrogenation of *p*-toluidine towards the corresponding 4-methylcyclohexylamine. In comparison, Rh/CNT is more active and provides a higher selectivity toward methylcyclohexylamine. The secondary amine, however, is formed in significant amounts as side-product.

#### LiOH modification of the catalysts

Inspired by work on related reactions, such as the hydrogenation of nitriles<sup>[27]</sup> and the racemization of amines,<sup>[14]</sup> we considered identifying a method to further reduce the amount of secondary amines formed without decreasing the high activity of the catalyst. We envisioned that this might be achieved by concealing acidic groups on the catalyst surface. Thus, we turned to base treatment of the Ru/CNT and Rh/CNT catalysts to eliminate acidic sites, while maintaining the size of the metal nanoparticles. LiOH has a pK<sub>b</sub> value of -0.4.<sup>[28]</sup> Weakly acidic phenolic moieties on oxidized CNTs have a pK<sub>a</sub> value of approx. 10.<sup>[29]</sup> Other acidic moieties have a lower pK<sub>a</sub> value. Consequently, all acidic groups should be removed by treatment of the parent catalysts with LiOH. In the hydrogenation of toluidines over Ru/C, however, the use of LiOH as an additive was reported to improve the selectivity only slightly compared to the reaction in the absence of LiOH.<sup>[7a]</sup> In that case, isopropanol had been used as solvent. We reasoned that a more defined support with tailored surface-oxygenated groups<sup>[30]</sup> combined with the use of tetrahydrofuran as aprotic solvent ought to result in enhanced suppression of condensation reactions.

For preparation of LiOH modified catalysts, the parent M/CNT catalysts were suspended for 10 min in an aqueous solution of LiOH. Subsequently, the M/CNT (LiOH) catalysts were separated by filtration and carefully dried. For Ru/CNT, this treatment resulted in a lithium content of 0.67 wt% (0.87 mmol·g<sup>-1</sup>cat). As LiOH had been employed in excess and in view of the large difference in pKa value of the LiOH base and the acidic groups on the support, most acid sites ought to have been neutralized. Assuming that one Li<sup>+</sup>-ion is adsorbed per acid site a surface concentration of 3 acid sites per nm<sup>2</sup> catalyst is calculated. At the characteristic nanometer length scale of the CNT surface, significant interaction of substrates that are converted on the metal nanoparticles with lithium ions associated with neighboring acid sites can be expected. Note that also multinuclear Li-clusters may have formed.<sup>[31]</sup> Therefore, the lithium content represents an upper limit of the number of accessible acidic sites on the catalyst.

# Performance of the LiOH modified Ru/CNT and Rh/CNT catalysts

The LiOH-doped catalysts were tested for the hydrogenation of *p*-toluidine. Using Ru/CNT (LiOH) (Figure 4), *p*-toluidine was converted at a slightly higher rate of -5.5 mol<sub>*p*-toluidine</sub>·min<sup>-1</sup>·mol<sub>Ru</sub><sup>-1</sup> (Table 1) compared to the parent Ru/CNT catalyst. The time to 50 % conversion remained equal at 18 min, while the time to 99 % conversion decreased from 80 min to 47 min after LiOH treatment of the catalyst. Noteworthy is also that the selectivity toward primary amines increased remarkably to >99 %. No

secondary amine was detected in the reaction mixture by GC analysis. This suggests that acidic sites play indeed a key role for the formation of secondary amines. By means of LiOH treatment, these acidic sites are removed. Most likely, partially hydrogenated intermediates (imines) are at the base for the formation of the secondary amines.<sup>[10]</sup> Adsorption of the imine intermediate at the acidic sites on the catalyst facilitates the nucleophilic attack of the aliphatic amine through the strong electron withdrawing effect of the resulting iminium group. Likewise noteworthy is the substantial reaction rate at the later stage of the reaction. Reduced poisoning of the catalyst in the absence of quite basic secondary amines may provide a more active catalyst, the *trans*-isomer was formed preferentially. This suggests that the reaction pathway did not change significantly.



Figure 4. Molar fractions against time for the hydrogenation of *p*-toluidine using LiOH modified Ru/CNT as catalyst.

LiOH-modified Rh/CNT was also tested in the hydrogenation of p-toluidine (Figure 5). Unexpectedly, the reaction proceeded only sluggishly after an initially fast conversion of toluidine. After a two-hour reaction time, merely 85 % conversion had been obtained. The rate of toluidine consumption of -7.9 mol<sub>p-toluidine</sub> min<sup>-1</sup> mol<sub>Rh</sub><sup>-1</sup> was lower compared to the parent Rh/CNT catalyst (Table 1). Also the selectivity toward primary amines decreased noticeably to 83 %. Closer analysis of the side-products revealed that the formation of secondary amines was indeed suppressed thereby supporting the hypothesis drawn for Ru/CNT that removal of the acidic sites reduces condensation reactions. Instead, unidentified sideproducts were obtained. We speculate that the side reactions are triggered by a change in the nature of the rhodium nanoparticles on which the hydrogenation takes place upon interaction with LiOH.

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Figure 5 Molar fractions against time for the hydrogenation of *p*-toluidine over Rh/CNT (LiOH).

# Diastereoselectivity of toluidine hydrogenation over Ru/CNT (LiOH)

To investigate the influence of the substitution pattern, the *ortho*and *meta*- toluidine isomers were hydrogenated using Ru/CNT (LiOH) as catalyst (Table 2). *o*-Toluidine was converted at a rate of -5.96 mol<sub>o-toluidine</sub>·min<sup>-1</sup>·mol<sub>Ru</sub><sup>-1</sup>. This rate is almost identical to that of *p*-toluidine *m*-Toluidine reacted at a slightly higher rate of -7.62 mol<sub>*m*-toluidine</sub>·min<sup>-1</sup>·mol<sub>Ru</sub><sup>-1</sup> compared to that of *p*-toluidine. In both cases very high selectivities (>99.8 %) towards the cycloaliphatic primary amine were obtained. For o-toluidine, the *trans*-isomer was the preferential isomer, albeit it was formed with a slightly higher diastereoselectivity (75 %). In the case of *m*-toluidine, the *cis*-isomer was formed as the preferential isomer with a diastereoselectivity of 78 %.

Table 2. Kinetic data and selectivity toward MeCy-NH<sub>2</sub> for different toluidine hydrogenations using 1 mol% Ru/CNT (LiOH) at 110 °C. The reactions were carried out for 180 min.

Substrate	r <sub>ini</sub> / mol∙min <sup>-1</sup> ∙mol <sub>M</sub>	Selectivity toward MeCy-NH <sub>2</sub> /% [a]		
		total	trans	cis
o-Toluidine	-5.96 ± 0.28	> 99	75.4	24.6
<i>m</i> -Toluidine	-7.62 ± 1.2	> 99	22.0	78.0
<i>p</i> -Toluidine	-5.55 ±0.05	> 99	59.8	40.2

[a] Selectivity toward MeCy-NH<sub>2</sub> after 180 min.

Thus, hydrogenation of the three toluidines under our reaction conditions preferentially yields the regioisomer with the methyland amine substituent in axial position. This implies that each hydrogenation step is micro reversible allowing for the reaction

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to proceed under thermodynamic control. Adequately high rate of desorption and re-adsorption of intermediates and products allows for a pathway where the hydrogen atoms approach the aromatic ring from different sides resulting in the formation of the trans-product. An alternative explanation for the observed diastereomer distribution may be found in the steric requirements of the corresponding adsorbed imine intermediates.<sup>[7a]</sup> Steric interference by the methyl group with the catalyst surface enhances the mobility of the adsorbed imine molecule in the case of o- and p- toluidine hydrogenation. Consequently, the intermediate can flip over more readily, resulting in the formation of the trans-isomer (Scheme 4). For mtoluidine, the adsorbed intermediate is sterically not hindered by the methyl group. Consequently, the reaction pathway, where all hydrogen atoms approach the molecule from the same side, is preferred. Thus, thermodynamic as well as kinetic factors may contribute to the observed diastereomer distribution in the product.



 $\label{eq:Scheme 4. Model for the hydrogenation of toluidines over lithium modified M/CNT catalysts.$ 

The drastically improved chemoselectivity with the LiOH modified Ru/CNT catalyst is most likely related to specific coordination geometry of unsaturated reaction intermediates. For the toluidine substrate, the aromatic ring must undoubtedly coordinate to the ruthenium nanoparticle to be hydrogenated. Due to the proximity, it is likely that the amine groups coordinate to neighboring lithium cations and thus assist in directing the substrate on the catalyst surface. Such a binding mode may result in higher rates for hydrogenation of the aromatic ring. The effect may be particularly relevant at higher conversions where the inhibiting effect of the amine group is more pronounced. Coordination of unsaturated intermediates in the same manner will likewise result in faster hydrogenation. This prevents the intermediates from entering parallel reaction pathways leading to condensation products. The absence of acidic sites further reduces the rate of the acid catalyzed formation of secondary amines resulting in a lower concentration of secondary amines that inhibit the hydrogenation reaction. Note that the above described binding mode results in the formation of a hydrophobic pocket around the ruthenium nanoparticles, which lessens product inhibition by aliphatic amines.

As Ru/CNT (LiOH) has been shown to be an excellent catalyst for the hydrogenation of the three toluidine derivatives, we explored extending the concept to nitroarenes. The direct reduction of nitroarenes to cycloaliphatic amines [4, 10] omits the stage of reducing the nitrobenzene to aniline, resulting in higher economy. Being interested in the diastereoselectivity, we explored the hydrogenation of the three different nitrotoluene regioisomers towards the corresponding cycloaliphatic amine (Table 3). In all cases, the nitrotoluene was converted first to the corresponding toluidine intermediate. In a consecutive reaction step, the toluidine was hydrogenated to give the cycloaliphatic primary amines with >99 % chemoselectivity. This reflects a higher reactivity of the nitro group under our reaction conditions compared to the aromatic ring. The diastereoselectivities were almost identical to that of toluidine hydrogenation. This is consistent with the reaction proceeding via the toluidine intermediate. One major difference between the hydrogenation of toluidines and nitrotoluenes is the formation of water as byproduct <sup>[32]</sup> during nitrotoluene hydrogenation. Under our conditions, the Ru/CNT (LiOH) nevertheless showed excellent activity: the formation of phenols was not observed. This implies that the potentially inhibiting competitive adsorption of water is insignificant and that the acidic sites of the catalyst are not restored in the presence of small amounts of water.

Table 2. Selectivities towards the two primary amine MeCy-NH<sub>2</sub> diastereomers in the hydrogenation of nitrotoluenes over Ru/CNT (LiOH).

Substrate	Selectivity toward MeCy-NH <sub>2</sub> /%		
×	total	cis	trans
o-Nitrotoluene	> 99	24.4	75.2
<i>m</i> -Nitrotoluene	> 99	78.9	20.9
<i>p</i> -Nitrotoluene	> 99	40.4	59.0

[a] Selectivity toward MeCy-NH<sub>2</sub> after 180 min.

A prospective application of the hydrogenation of aromatic amines is the hydrogenation of aromatic diamines, such as toluene diamine (TDA), which are used in large scale for the production of polyurethanes.<sup>[33]</sup> Consequently, we examined the performance of Ru/CNT (LiOH) in the hydrogenation of aromatic diamines (Table 3). The reaction temperature was increased to 130 °C as these substrates turned out to be considerably less reactive. Even at this temperature, the hydrogenation of ophenylene diamine provided relatively low conversion of 11 % at good selectivity toward the corresponding cycloaliphatic diamine (89 %). The hydrogenation of 2,4-toluene diamine resulted in 83 % yield at 47 % selectivity. 2,6-Toluene diamine gave full conversion at 54 % selectivity. The low conversions suggest that the use of diamines as substrate leads to pronounced catalyst inhibition. Closer analysis, however, reveals that conversion may be related indirectly to the propensity of the aromatic diamine to

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coordinate with both amino groups to the metal centers on the catalyst surface. o-Phenylene diamine having neighboring amino groups binds most readily in a chelating fashion. In 2,4-toluene diamine ,the amino groups are separated by an aromatic C-H moiety; thus  $\eta^2$  coordination is less favorable. By introducing a methyl group in between the two amino groups, as in 2,6toluene diamine,  $\eta^2$  coordination is hindered significantly. The observed inhibition effect appears to be a consequence of competitive adsorption of amino groups and aromatic rings on ruthenium. Stronger adsorption of the amine reduces the number of aromatic rings bound to the active sites. The lower selectivity in the case of the toluene diamines is attributed to the propensity of the substrate to lose one of the amino groups upon hydrogenation.<sup>[7a, 10, 34]</sup> When hydrogenating 2,4-dinitrotoluene instead of 2,4-toluene diamine, full conversion was obtained even though the reaction proceeded through the aromatic diamine as intermediate (Table 3). This reflects the pronounced promoting effect of nitro compounds on the conversion of aromatic amines.<sup>[7a, 10, 19, 35]</sup>

Table 3. Conversion and selectivity toward the primary diamine in the hydrogenation of aromatic diamines and 2,4-dinitrotoluene over Ru/CNT (LiOH).



[a] Selectivity toward primary diamine after 180 min.

### Conclusions

Ru/CNT and Rh/CNT showed remarkable activity in the hydrogenation of toluidines. Upon LiOH modification of the Ru/CNT catalyst, a substantial increase in selectivity for the formation of the corresponding primary amines was obtained. Over Ru/CNT (LiOH) the primary amines were obtained in excellent selectivity with >99 % yield. Insights into the reaction

pathways were obtained by comparing the hydrogenation of the three different toluidine isomers. The *ortho-* and *para-*isomers showed similar reactivity; the *trans-*substituted diastereomer was formed preferentially. In contrast, the *meta-*isomer showed slightly higher reactivity; the *cis-*diastereomer was formed preferentially. The authors believe that the excellent performance of the Ru/CNT (LiOH) catalyst is related to concurrent binding of the substrate with the aromatic ring on the ruthenium nanoparticles and the amine group to lithium cations in proximity. Preferred formation of the *trans* diastereomer ought to be related with a moderate adsorption strength and high mobility of the intermediates on the catalyst surface.

The LiOH-modified catalyst Ru/CNT (LiOH) is also an excellent catalyst for the hydrogenation of the corresponding nitrotoluenes. The primary amines were obtained in excellent selectivity in >99 % yield. Also 2,4-dinitrotoluene was hydrogenated readily, reflecting a pronounced promoting effect of nitro groups on the conversion of aromatic amines. The reaction proceeds in a consecutive reaction sequence *via* the corresponding aromatic amine. Implemented as a one-pot reaction in a reactor with plug-flow characteristics, the hydrogenation of aromatic amines constitutes an economical access to cycloaliphatic primary amines.

In conclusion, LiOH treatment of ruthenium-based CNT catalysts is a ready method for increasing the selectivity for the hydrogenation of aromatic amines. The insights described here can be transferred to related reactions, such as amine racemization or nitrile hydrogenation.

## **Experimental Section**

#### Catalyst synthesis

**Pre-treatment of the CNT.** Carbon nanotubes (Baytubes 150P,<sup>[22]</sup> 20 g) were suspended in concentrated nitric acid (68 wt%, 150 mL). The mixture was refluxed for 2 h. After being gradually cooled to room temperature, the suspension was filtered and the filter cake washed with deionized water until the pH-value of the filtrate was neutral. Subsequently the oxidized CNT were dried in ambient air overnight, followed by drying at 140 °C.

**Ru/CNT.** A mixture of the pre-treated CNT (10.05 g), a solution of  $[Ru^{III}(NO)(NO_3)_x(OH)_y]$  (Aldrich, ~1.5 wt% Ru, 33.43 g, 4.96 mmol), urea (1.46 g, 24.3 mmol) and 300 mL deionized water was heated overnight under argon at 90 °C. The reaction mixture was filtered, the filter cake washed and dried overnight in ambient air. Subsequently, the CNT were dried in a stream of argon (100 mL/min) at 120 °C followed by reduction in a stream of hydrogen (100 mL/min) at 200 °C.

**Rh/CNT.** Rh/CNT was prepared in the same way as Ru/CNT, but using a Rh(NO<sub>3</sub>)<sub>3</sub> solution (~10 wt% Rh, 2.645 g, 2.57 mmol) instead of [Ru<sup>III</sup>(NO)(NO<sub>3</sub>)<sub>x</sub>(OH)<sub>y</sub>] and smaller amounts of the pretreated CNT (5.03 g), urea (0.43 g, 7.15 mmol) and deionized water (200 mL).

**Base treatment.** A sample of the catalyst was suspended in an aqueous solution of LiOH (3 wt% LiOH with respect to catalyst, 2 g CNT in ~20 mL water) for 10 min. The basic pH-value of the supernatant (pH > 9) suggests the successful neutralization of the acidic sites in the catalyst.

**Evaluation of the catalysts.** Hydrogenation reactions were carried out in a 200 mL stainless steel reactor equipped with gas entrainment stirrer, heating mantel, and sampling valve. The reactor was charged with substrate (58.8 mmol), THF (140 °C), catalyst (1 mol% metal with respect to substrate) and internal standard (hexadecane). The mixture was heated to 110 °C, and the reaction initiated by pressurizing the autoclave with hydrogen to 100 bar. Samples of the liquid phase were taken during the reaction for analysis by gas chromatography. Molar fractions are given as the concentration of the particular substance  $c_i$  normalized to the initial concentration of the substrate ( $c_i/c_{substrate,t=0} \times 100$  mol %). For further experimental details, please refer to the supporting information.

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