

# The Direct Conversion of Phenol to Cyclohexylamines – a New and Sustainable Pathway to Aliphatic Polyurethanes?

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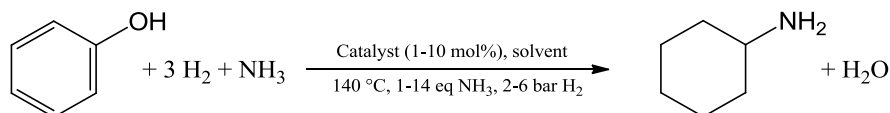
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**Abstract:** Cyclohexylamines are important intermediates for chemical industry are used for various applications and are currently synthesized by hydrogenation of anilines. However, the direct synthesis from bio-derived phenol using ammonia is an interesting alternative. We herein present the high-yield synthesis of cyclohexylamines using Rh/C, in contrast to Pd-based catalysts, which are the state-of-the-art materials for the formation of N-alkylated cyclohexylamines and resulted in poor yields for the reaction with ammonia. The hydrogen bonding of isopropanol as solvent allowed for excellent activity. These results will broaden the catalyst landscape for the direct amination of phenol and give new incentives to fellow researchers.

**Keywords:** Phenol, amination, cyclohexylamine.

## 1. Introduction

Cyclohexylamines have many applications. However, one of the most important examples is the fully hydrogenated 4,4'-methylenedianiline-derivative (H<sub>12</sub>-MDA). Currently this is synthesized by the reduction of methylenedianiline. With a potential change in feedstock from fossil sources to lignin-derived phenolics the traditional route is barely possible. Recently there were several reports describing the conversion of phenol to N-alkylated anilines using Pd/C.<sup>1,2</sup> In this reaction, a reductant is used to initially convert phenol to cyclohexanone, which then reacts with an amine to form an N-alkylated cyclohexylamine which is then hydrogenated towards the corresponding cyclohexylamine in one pot. However, the use of ammonia, although highly relevant, was not reported and has the additional complexity, that the formation of secondary amines has to be avoided. We herein pioneer the direct amination of phenol to cyclohexylamine using Rh/C as catalyst, as the Pd/C catalyst reported for related reactions was not selective.



## 2. Experimental (or Theoretical)

Reactions were carried out in home-made 11 mL autoclaves. Catalyst (usually 2 mol%), hexadecane (10 μL), phenol (0.1 mmol), solvent (1 mL) and ammonia dissolved in methanol (0.4 mL) are added to the autoclave and it was charged with the designated hydrogen pressure (mostly 6 bar) after purging with nitrogen. Reactions were carried out by stirring the reaction at the desired temperature (usually 140 °C) in a thermostated copper block.

## 3. Results and discussion

Initially the reaction has been carried out using Pd/C as catalyst at a pressure of 2 bar hydrogen at 140 °C to allow for fast conversion of phenol (Table 1). Already after 30 min the conversion was rather high (86 %), while the selectivity towards cyclohexylamine was limited (59%). To overcome the low selectivity, a series of other carbon supported catalysts, namely Pt/C, Rh/C and Ru/C were tested in the reaction (Table 1). The activity of these catalysts was lower with conversions of 38 % and 26 % for Pt/C and Rh/C, respectively, whereas Ru/C was inactive. Surprisingly, the selectivities of Pt/C and Rh/C were considerable higher than those obtained using Pd/C with values 79 % and 99 %. To date, only palladium based catalysts are known for this and related reactions, thus these results encouraged us to investigate these two catalysts more in detail. When increasing the hydrogen pressure to 6 bar, it was possible to increase the conversion to 64 % and 98 %, respectively. The selectivity of platinum decreased to a similar level to that of Pd/C (63 %). However, when

using Rh/C an excellent selectivity of 98 % was maintained. In a next step, the substrate to catalyst ratio was lowered, while increasing the reaction time to 6 h.

Using 1 mol% Rh/C resulted in a conversion of 57 % at 98 % selectivity, 2 mol% gave 90 % conversion at 97 % selectivity and 5 mol% gave 99 % conversion at 94 % selectivity. This shows that rather high conversions are already possible at low catalyst loadings. With 5 mol% Rh/C the selectivity slightly decreased. This can be caused by rather high concentrations of cyclohexylamine being exposed to the catalyst for extended times. The ammonia concentration plays a crucial role in this conversion (Figure 1). At low ammonia concentrations (0.9 eq), phenol was not fully converted, cyclohexanone was present in high concentrations (35 mmol%) and dicyclohexylamine was the only nitrogen containing product. With increasing ammonia concentrations, phenol conversion became excellent and the cyclohexanone and dicyclohexylamine concentrations decreased, while cyclohexylamine was formed in high yields up to 94 %.

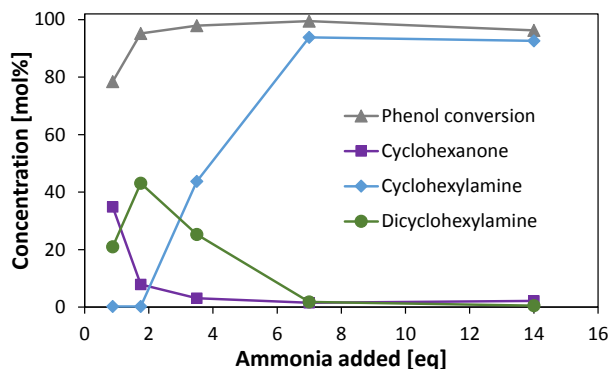
At ammonia concentrations >7 eq the reaction outcome barely changed. Using 2-propanol, the cyclohexylamine yield was further increased to excellent 97 %. Excellent selectivities were achieved for different substituted phenols, such as the bio-derived 4-n-propyl phenol or guaiacol. The hydrogenation of bisphenol F resulted in up to 68 % H<sub>12</sub>-MDA, with 31 % of the intermediate in which only one of the two rings reacted still remaining.

#### 4. Conclusions

The here presented results give an unprecedented access to cyclohexylamines from phenols. Excellent yields of 97 % were reached using Rh/C as catalyst, in contrast to Pd/C which is used for related chemistry and resulted in poor selectivity in this case. Ammonia concentration plays a key role, as insufficient ammonia results in incomplete amination and cyclohexanone and dicyclohexylamine as major byproduct. These results will open routes for new catalysts in the field of phenol amination and might give industry a sustainable alternative for the production of cyclic polyamines.

#### References

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**Figure 1.** Ammonia concentration dependence for the amination of phenol towards cyclohexylamine after 6 h reaction in toluene at 2 bar hydrogen using 5 mol% Rh/C.