

## Short Communication

## Mechanism study on Raney nickel-catalyzed amination of resorcinol



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## ABSTRACT

Amination of resorcinol catalyzed by Raney nickel has been examined with good yield. Using the first principle density functional theory, some detailed mechanism of the amination of resorcinol on the Ni(111) surface is explored. The resorcinol is adsorbed on the Ni surface at the hollow site to form ketone by isomerization. The isomerization has a barrier of 122.1 kJ/mol. Ketone can couple with secondary amine mediated by resorcinol to afford hemiaminal. For the formation of hemiaminal, the steric effect of the alkyl group of secondary amine is obvious. Hemiaminal undergoes dehydration to get final product, which occurs by the preferred adsorption in the bridge site, cleavage of C–O bond initially, followed by subsequent cleavage of C–H bond.

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## 1. Introduction

3-(*N,N*-dialkylamino)phenol is the key intermediate that has a wide application in pharmaceuticals and dyes. 3-(*N,N*-dimethylamino)phenol is used to synthesize *neostigmine bromide*, which has a reversible cholinesterase inhibition and is a useful drug in the treatment of myasthenia gravis [1]. *Astrazon Blue BG* (Basic Blue 3) that synthesized by 3-(*N,N*-diethylamino)phenol, is one of the dyes most commonly used in nylon and acrylic textiles [2].

The alkylation of alkyl halides with 3-aminophenol is a classical procedure [3]. However, it needs a large number of acid-binding agents and the atom economy of this route is poor. With the rise of green chemistry, the atom efficiency has become important. In the synthesis of 3-(*N,N*-dimethylamino)phenol, there are only two methods with the high atom economy. One of them is the reduction amination of 3-aminophenol with aldehyde [4], which proceeds addition of 3-aminophenol with aldehyde, dehydration and reduction by metal-catalyzed hydrogenation [5] or reducing agent [6]. The other attractive protocol is the amination of resorcinol with secondary amines. It is reported that phosphorous acid [7] and metaphosphoric acid [8] can catalyze this reaction and the byproduct is only water. The amination of resorcinol is also a relatively green method, but the catalysts such as phosphorous acid and metaphosphoric acid could pollute environment and its yield has room for improvement.

In this paper, we explored Raney Ni-catalyzed amination of resorcinol with secondary amines and described a detailed investigation on mechanism studies on the Ni surface.

## 2. Experimental section

General procedure for the amination of resorcinol with secondary amine catalyzed by Raney Ni. Resorcinol (2.2 g, 20 mmol), secondary amine (30 mmol) and Raney Ni (110 mg) were added to water (50 ml) in a 100 ml autoclave. The autoclave was purged with hydrogen gas three times, then maintained 0.05 Mpa pressure. The mixture was heated to 200 °C rapidly. Then stirring was maintained for 3 h. The reaction mixture was cooled to room temperature, and then extracted with *N*-butyl acetate. The organic layer was dried ( $\text{MgSO}_4$ ), filtered and concentrated to give the crude product. The pure product was got through flash column chromatography on silica gel (petroleum ether/acetylacetic ester (3/1, v/v)).

## 3. Computational details

DFT calculations were performed with the program package CASTEP in Materials Studio of Accelrys Inc. [9–11]. Plane wave basis functions with spin polarization and the Perdew, Burke, Erzenhof gradient corrected functional (GGA-PBE) were used [12–15]. The transition state search was performed with the linear and quadratic synchronous transit (LST/QST) complete search [16]. Ultrasoftpseudopotential (USP) was used to perform simulation of core electron. Energy cut-off of 400.0 eV was used to improve computational performance [17].

Ni(111) surface was modeled using three-layer periodicslab model with a (6 × 6) super cell including 10 Å vacuum slab, within which the adsorption and reaction occurs. The reciprocal space of the (6 × 6) super cell was sampled with the *k*-points set of (3 × 3 × 2). Larger *k*-points sets are needed if more accurate energy value wanted. Study in this work focused on the relative results of different systems, so the *k*-points set of (3 × 3 × 2) should be enough. Geometry optimization was performed for all the relevant adsorbates with Ni atoms

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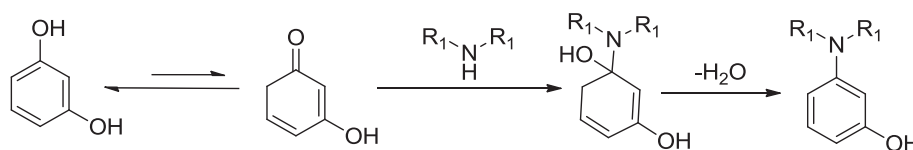
**Table 1**  
Amination of resorcinol with secondary amines.<sup>a</sup>

$\text{R}_1 = \text{alkyl}$

Entry	R <sub>1</sub>	Catalyst (wt.%)	Time/h	Yield/% <sup>b</sup>
1	CH <sub>3</sub>	H <sub>3</sub> PO <sub>4</sub> (5)	3	76
2	CH <sub>3</sub> CH <sub>2</sub>	H <sub>3</sub> PO <sub>4</sub> (5)	6	5
3	CH <sub>3</sub> CH <sub>2</sub>	Raney Ni (5)	3	68
4	CH <sub>3</sub> CH <sub>2</sub>	Raney Ni (2)	6	47
6	CH <sub>3</sub> CH <sub>2</sub>	Raney Ni (10)	3	67
7	CH <sub>3</sub>	Raney Ni (5)	3	93

<sup>a</sup> Temperature is 200 °C. Raney-catalyzed amination is under hydrogen gas atmosphere. General procedure of H<sub>3</sub>PO<sub>4</sub>-catalyzed amination see supporting information.

<sup>b</sup> Isolated yield.



**Fig. 1.** The proposed mechanism of amination of resorcinol with secondary amines.

constrained except the uppermost layer. The convergence tolerances of energy and displacement were  $2 \times 10^{-5}$  eV/atom and  $2 \times 10^{-3}$  Å, respectively, and the SCF tolerance was  $2 \times 10^{-6}$  eV/atom.

Chemisorption energies were calculated using the equation

$$\Delta E_{\text{ads}} = E_{\text{adsorbate-Ni}} - E_{\text{adsorbate}} - E_{\text{Ni}}$$

where  $\Delta E_{\text{ads}}$  represents the adsorption energy of the adsorbate on Ni(111) surface,  $E_{\text{adsorbate}}$  is the energy of free adsorbate,  $E_{\text{Ni}}$  is the energy of clean slab and  $E_{\text{adsorbate-Ni}}$  is the energy of adsorbate–Ni adsorption system.

For a reaction, which can be represented as:  $A + B \rightarrow C + D$ , the energy barrier was calculated as follows:

$$\Delta E_{\text{React}} = E_{\text{TS}} - E_{A+B-Ni}$$

where  $E_{\text{TS}}$  is the energy of the transition state and  $E_{A+B-Ni}$  is the energy of  $A + B - Ni$  adsorption system.

## 4. Results and discussion

Initially, we attempt H<sub>3</sub>PO<sub>4</sub> to catalyze the amination of resorcinol with dimethylamine (DMA), which affords 76% yield (entry 1, Table 1). It is consistent with previous reported [7]. However, it failed to catalyze diethylamine (DEA) with 5% yield (entry 2, Table 1). Fortunately, we examine that the commercially Raney Ni can catalyze the reaction of resorcinol with DEA and attempt to optimize the reaction by varying other parameters systemically. As expected, lower catalyst loading (2 wt.%) incurs a significant decrease in chemical yield and prolonged reaction time (entry 4, Table 1). Thus, the appropriate catalyst loading is 5 wt.% (entries 3, 5, Table 1). With the presence of 5 wt.% Raney Ni at 200 °C in water, the product is got in 68% yield. Then the effects of DMA are examined with 93% yield (entry 6, Table 1).

The proposed pathway in Fig. 1 is preceded through three stages: the formation of ketone, the addition reaction of ketone with secondary amine and dehydration. It is slightly different from the *N*-alkylation of alcohol and amine that ketone is formed by the isomerization of resorcinol with Raney Ni as catalyst. We tried to find the suitable mechanism by the computational study.

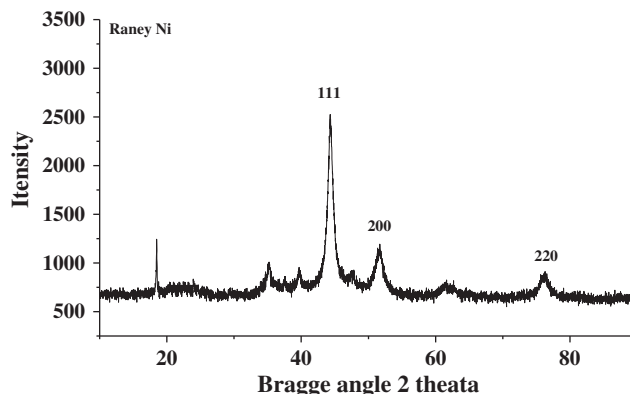
The structure parameters of the Raney Ni were characterized by XRD, which was showed in Fig. 2.

The Raney Ni catalyst showed three diffraction peaks of Ni(111), Ni(200) and Ni(220). Ni(111) is the main diffraction peak of Raney Ni catalyst. Surface science studies have been performed on well-defined Ni(111) for the chemisorption and hydrogenation of benzene [18–23] and phenol [23,24]. The aromatic ring oriented parallel to the Ni(111) surface is adsorbed via the  $\pi$  orbitals [23]. Resorcinol is a benzene and phenol like molecule. At the same time, due to the fact that is a well understood system, Ni(111) represents a convenient model substrate. Thus herein Ni(111) model is applied for the investigation on the adsorption and reaction of resorcinol, in order to illuminate the mechanism.

### 4.1. Adsorption of resorcinol on Ni(111)

For resorcinol in gas phase, the calculations predicted bond lengths and angles are 1.397–1.404 Å (1.39 Å) for the distance between the carbon atoms, 1.391 Å (1.36 Å) for C1–O7, 1.389 Å (1.37 Å) for C3–O8, 123.53° (123°) for C6–C1–O7 and 117.193° (117.6°) for C4–C3–O8, respectively, which is consistent with the experimental results [25,26].

Resorcinol can adsorb at different high-symmetry sites of the (111) surface. It is similar to the benzene adsorbed Ni(111) surface [21]. After the adsorption on the Ni surface, the hollow(0) site (Fig. 3) was found to be the preferred adsorption site, with calculated adsorption enthalpy of –88.8 kJ/mol (Supporting information). Adsorption at the hollow-hcp



**Fig. 2.** X-ray diffraction patterns of Raney Ni catalyst.

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