Chapter 5: 
Reductive Amidation without an External Hydrogen Source Using Rhodium Supported on Carbon Matrix as a Catalyst

In this chapter, a method for reductive amidation was developed using carbon monoxide as the reducing agent with rhodium supported on carbon matrix as catalyst. Rhodium on carbon matrix and other heterogeneous rhodium catalysts that were found active in this study were characterized by BET, TEM, and XPS techniques. It was found that heterogeneous rhodium on carbon works as a precatalyst for homogenous active species due to the leaching of rhodium into the solution.

Part of this chapter has been published:
5.1. Introduction

Amides are an important class of organic compounds because of their wide applications in various fields. Nearly 25% of all pharmaceutical drugs currently on the market contain an amide bond.\textsuperscript{[1]} Peptidomimetics, pseudopeptides, $\beta$-peptidoids comprise an important class of drug molecules.\textsuperscript{[2-4]} Moreover, amide bond coupling is one of the most frequently used transformations in medicinal chemistry.\textsuperscript{[5]} Conventional methods for the synthesis of amides require the usage of stoichiometric amounts of additives which causes low atom efficiency and the formation of stoichiometric amounts of waste. Therefore, the development of new and efficient methods of amide synthesis is of interest for the pharmaceutical chemistry.

For the last decade, there was a growing interest in nonclassical routes for amide synthesis.\textsuperscript{[6-9]} These methods include catalytic amidation of esters, direct condensation of carboxylic acids with amines using boron-based catalysts, oxidative amidation of primary alcohols or aldehydes, and carbonylative amidation of aryl halides. Among them, reductive amidation of carbonyl compounds is a potentially powerful method for the modification of amides because of its high atom efficiency.\textsuperscript{[10-17]} Hydrogen or silanes are typically used as reducing agents for this type of transformation. Since both reducing systems have a hydride source, they can display a poor functional group tolerance. Moreover, there are other disadvantages of these systems such as low step economy (e.g. production of silanes) and disposal of stoichiometric amounts of wastes.

In our group, we demonstrated the unique deoxygenating potential of carbon monoxide.\textsuperscript{[18]} The use of carbon monoxide proved to be effective in reductive alkylation,\textsuperscript{[19,20]} amination,\textsuperscript{[21,22]} and esterification\textsuperscript{[23]} of carbonyl compounds (Figure 22a). The key advantage of this reducing agent is that an external hydrogen source is not present in the system, which leads to high selectivity often surpassing more traditional, hydride-based reducing agents.\textsuperscript{[24]} In addition, carbon monoxide is considered to be a multimillion-ton byproduct of the steel making industry which makes it a highly inexpensive reducing agent.

Previously, our group developed a method for reductive amidation with carbon monoxide as the reducing agent using homogeneous rhodium and ruthenium catalysts (Figure 22b).\textsuperscript{[15,16]} We decided to develop a method of reductive amidation using heterogeneous catalysis which might be more suitable for the potential industrial application of this method. Herein we report reductive amidation on rhodium on carbon matrix (Figure 22b).
Chapter 5

5.2. Results and Discussion

We started with the investigation of the catalytic activity of various commercially available rhodium and ruthenium catalysts on different supports (Table 15). We chose the reaction between \( p \)-anisaldehyde and acetamide as the model reaction due to a clear analysis of its reaction mixture using \(^1\text{H}\) NMR spectroscopy since characteristic signals of the product and starting materials are well-defined and do not overlap. In general, rhodium catalysts demonstrated higher catalytic activity than ruthenium catalysts (Entries 1-5 vs 6-9) and alumina supports are less effective than carbon supports (Entries 1-3 vs 4-5). Rh\( /\text{C}_\text{matrix} \) was the most active catalyst for this transformation (Entry 1) and was used in further optimization.

**Figure 22.** Carbon monoxide as a reducing agent. a. Different nucleophiles for reductive addition reactions. b. Previous catalytic systems developed for the reductive amidation using carbon monoxide as a reducing agent. c. Reductive amidation catalyzed by rhodium supported on carbon matrix.
Table 15. Catalyst screening.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Aldehyde conversion [%]</th>
<th>Yield [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Rh on carbon matrix</td>
<td>97</td>
<td>58</td>
</tr>
<tr>
<td>2</td>
<td>Rh on activated charcoal</td>
<td>48</td>
<td>18</td>
</tr>
<tr>
<td>3</td>
<td>Rh on carbon</td>
<td>43</td>
<td>21</td>
</tr>
<tr>
<td>4</td>
<td>Rh on activated alumina</td>
<td>24</td>
<td>7</td>
</tr>
<tr>
<td>5</td>
<td>Rh on alumina (Degussa-type)</td>
<td>45</td>
<td>7</td>
</tr>
<tr>
<td>6</td>
<td>Ru on activated charcoal</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>Ru on activated carbon (reduced, 50% water)</td>
<td>14</td>
<td>2</td>
</tr>
<tr>
<td>8</td>
<td>Ru on alumina</td>
<td>47</td>
<td>5</td>
</tr>
<tr>
<td>9</td>
<td>Ru on activated alumina</td>
<td>45</td>
<td>7</td>
</tr>
</tbody>
</table>

[a] All supports contain 5 wt% of the metal. 0.2 mmol of acetamide, 1:1 ratio of acetamide and p-anisaldehyde, 1 M. The yield was determined by ^1^H NMR with mesitylene as the internal standard.

Table 16. Solvent screening.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Aldehyde conversion [%]</th>
<th>Yield of 1a [%]</th>
<th>Yield of 2a [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>toluene</td>
<td>&gt;99</td>
<td>70</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>Et₂O</td>
<td>&gt;99</td>
<td>79</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>THF</td>
<td>97</td>
<td>58</td>
<td>17</td>
</tr>
<tr>
<td>4</td>
<td>CH₂Cl₂</td>
<td>43</td>
<td>24</td>
<td>traces</td>
</tr>
<tr>
<td>5</td>
<td>CH₃CN</td>
<td>53</td>
<td>24</td>
<td>8</td>
</tr>
<tr>
<td>6</td>
<td>t-BuOH</td>
<td>&gt;99</td>
<td>77</td>
<td>7</td>
</tr>
<tr>
<td>7</td>
<td>s-PrOH</td>
<td>&gt;99</td>
<td>73</td>
<td>9</td>
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<tr>
<td>8</td>
<td>s-BuOH</td>
<td>&gt;99</td>
<td>73</td>
<td>9</td>
</tr>
<tr>
<td>9</td>
<td>EtOH</td>
<td>&gt;99</td>
<td>35</td>
<td>35</td>
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<tr>
<td>10</td>
<td>MeOH</td>
<td>&gt;99</td>
<td>5</td>
<td>28</td>
</tr>
<tr>
<td>11</td>
<td>H₂O</td>
<td>&gt;99</td>
<td>17</td>
<td>47</td>
</tr>
<tr>
<td>12⁺[b]</td>
<td>Et₂O</td>
<td>&gt;99</td>
<td>93</td>
<td>3</td>
</tr>
</tbody>
</table>

[a] C_{matrix} contains 5 wt% of the metal. 0.2 mmol of acetamide, 1:1 ratio of acetamide and p-anisaldehyde, 1 M. The yield was determined by ^1^H NMR with mesitylene as the internal standard. [b] 0.5 M, catalyst dried in vacuo for 5h and stored in Schlenk tube prior to use.
Solvent screening demonstrated that Et₂O is the optimal solvent for this transformation (Table 16, Entry 2), although toluene (entry 1), tBuOH (entry 6), and iPrOH (entry 7) were also efficient. The main side-product of the reaction is the tertiary amine 2a. The amine 2a could be formed through hydrolysis of acetamide or target amide 1a and consecutive reductive amination. Presence of water or the use of alcohols that are not sterically encumbered results in the increase of product 2a in the reaction mixture.

Further screening of the catalyst loading, concentration, pressure of carbon monoxide, reaction temperature, and drying the catalyst in vacuo allowed us to obtain product 1a in 93% NMR yield (entry 12). We then turned to the analysis of the substrate scope and the limitations of this transformation (Scheme 42). Different aromatic aldehydes can be used in this transformation. Aldehydes bearing electron-donating functional groups show higher activity than aldehydes with electron-withdrawing groups (1a, 1b, 1f, 1g vs. 1h, and 1k vs. 1m).

The system is also sensitive to steric hindrance. The use of aldehydes with ortho substituents led to lower product yields than those with meta and para substituents (1a, 1d vs. 1e). Aliphatic and aromatic amides react similarly. Electron-donating groups in benzamide derivatives increase product yield (1p vs. 1n vs. 1k). Catalytic system demonstrated tolerance to different functional groups such as -OBn (1g, 1i) and -CN (1h) which can be reduced in amidation reactions involving external hydrogen sources such as H₂ or hydrides.

The method has several limitations. Ketones react poorly under these conditions due to their lower electrophilicity and higher sterical hindrance (1q, 1r). Secondary amides also cannot be used as substrates for this reaction. Another limitation of the method is the incompatibility of the method with aliphatic aldehydes. In the reaction conditions, they form complex mixtures of self-aldol condensation products due to high reaction temperature which results in a low yield of target amide (1s). The use of non-enolizable pivaldehyde also results in the low yield of the target amide (1t).
Scheme 42. Substrate scope and limitations. 1 mmol of amide, 1:1 ratio of amide and aldehyde, the yield was determined by ¹H NMR with mesitylene as the internal standard. Isolated yield reported in parenthesis. [a] 2 mol% of Rh/C_matrix was used.

Afterward studying the substrate scope, we conducted a comparative study of the tested catalysts in order to understand the differences in their activity. We measured the surface area of rhodium on the carbon matrix, rhodium on activated charcoal, and rhodium on carbon (Table 17). However, differences in surface area between the catalysts appeared to be insignificant to explain the difference in catalytic activity.
Table 17. Physisorption of samples.

<table>
<thead>
<tr>
<th>Rhodium catalyst</th>
<th>BET surface area, m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh on carbon matrix</td>
<td>1006.8</td>
</tr>
<tr>
<td>Rh on carbon matrix after drying in vacuo</td>
<td>1010.3</td>
</tr>
<tr>
<td>Rh on carbon</td>
<td>951.3</td>
</tr>
<tr>
<td>Rh on activated charcoal</td>
<td>644.9</td>
</tr>
</tbody>
</table>

We then studied the morphology of these three catalysts using TEM (Figure 23). For rhodium on carbon matrix (a and b), regardless of the presence of the catalyst drying step, the mean particle size was about 2.0 nm (approximate size range – 1.5-3.0 nm). The morphology of the support did not depend on the catalyst pretreatment. In the case of rhodium on carbon and rhodium on activated charcoal, the size of the metal particles was somewhat bigger and the agglomeration of the particles was more pronounced (Figures 1c and 1d). The mean size of metal particles was about 3.0 nm (approximate size range – 2.0-4.0 nm) in the case of carbon support and about 2.5 nm (approximate size range – 1.5-3.5 nm) in the case of activated charcoal support. It is important to mention that for all samples under study the spatial distribution of the metal on carbon-based material was non-uniform and particle sizes varied from site to site. Nevertheless, the difference in particle sizes of different catalysts is not significant enough to explain such difference in catalytic activity.

![Image](image.png)

**Figure 23.** TEM images of rhodium on carbon matrix (a), rhodium on carbon matrix after drying in vacuo (b), rhodium on carbon (c), and rhodium on activated charcoal (d).

In order to determine the oxidation states of rhodium on different supports, the catalysts were analyzed with XPS (Figure 24). The Rh $3d_{5/2}$ and Rh $3d_{3/2}$ peaks at 309.8 and 314.7 eV respectively in spectrum (a) can be assigned to Rh$_2$O$_3$•5H$_2$O (309.6 eV).$^{[25]}$ In contrast to the spectrum of Rh/C$_{matrix}$, three states giving Rh $3d_{5/2}$ peaks at 307.5/308.7/309.8 and 307.3/308.7/309.8 eV, which can be assigned to Rh, Rh$_2$O$_3$, and
Reductive Amidation without an External Hydrogen Source Using Rhodium Supported on Carbon Matrix as a Catalyst

$\text{Rh}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$, were deconvoluted in those of rhodium on carbon (b) and rhodium on activated charcoal (c), respectively.

**Figure 24.** Rh 3d photoelectron spectra of rhodium on carbon matrix (a), rhodium on carbon (b), and rhodium on activated charcoal (c).

From this data, it seems that $\text{Rh}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ is responsible for the catalytic activity in reductive amidation since both rhodium on carbon and activated charcoal are only half as active as $\text{Rh/C}_{\text{matrix}}$. To confirm that rhodium (III) can catalyze the reaction, we tested the activity of $\text{RhCl}_3$ in the model reaction (**Scheme 43a**). Indeed, under these conditions, $\text{RhCl}_3$ demonstrated moderate catalytic activity confirming that Rh(III) may serve as a precatalyst for this reaction. We decided to also test Rh(0) complex, namely $\text{Rh}_6(\text{CO})_{16}$ as a catalyst for the reductive amidation (**Scheme 43b**). Interestingly, this complex has shown comparable activity to $\text{Rh/C}_{\text{matrix}}$ giving product 1a in 87% NMR yield.

**Scheme 43.** Testing catalytic activity of homogeneous Rh(III) and Rh(0).
We then investigated catalyst stability and recycling (Table 18). We found that on the second cycle, the activity of the catalyst significantly decreased, and product yield dropped below 30%. Catalyst activity, however, remained the same for the third cycle. These results can be explained by the passivation of active centers or by the leaching of rhodium to solution.

**Table 18.** Catalyst recycling.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Number of cycles</th>
<th>Aldehyde conversion [%]</th>
<th>Yield of 1a [%]</th>
<th>Yield of 2a [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>&gt;99</td>
<td>82</td>
<td>&lt;1</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>&gt;99</td>
<td>28</td>
<td>26</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>90%</td>
<td>25</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

[a] C\text{matrix} contains 5 wt% of the metal. 0.2 mmol of acetamide, 1:1 ratio of acetamide and p-anisaldehyde, 0.5 M. The yield was determined by $^1$H NMR with mesitylene as the internal standard.

We decided to test the catalyst for leaching. First, we packed the catalyst in a piece of filter paper and placed it into an autoclave with starting materials. After one hour of heating, the catalyst was removed and the reaction mixture was heated further for 21 h. Analysis of the reaction mixture after one hour in the presence of catalyst and after 21 h after removal of catalyst showed that leaching occurs since the formation of the product continued for entire reaction time (Scheme 2a). Moreover, the color of the reaction mixture after one hour was deep red which indicates the presence of rhodium complexes. After 21 hours color of the reaction mixture changed to pale yellow. To the catalyst that was removed from reaction a) on Scheme 2 another portion of starting material was added. Target amide was formed in 35% yield (Scheme 2b) which is considerably lower than in standard conditions.
Scheme 44. Testing the catalyst for leaching. a) catalyst was packed in piece of filter paper and placed inside the autoclave. Acetamide, diethyl ether, and aldehyde were added, autoclave was filled with CO and heated. After 1h the catalyst was removed, and the reaction mixture was again filled with CO and heated. b) catalyst that was used for 1h in a) was used again in the second reaction.

After the reaction of reductive amidation in standard condition, Rh/C\text{matrix} was analyzed by TEM (Figure 25). No metal particles or agglomerates can be seen on the sample which further confirms rhodium leaching during the reaction.

Figure 25. TEM image of rhodium on carbon matrix after reaction.

We also compared the catalytic activity of Rh/C\text{matrix} both in carbon monoxide and in hydrogen in identical conditions (Scheme 45). While the usage of carbon monoxide allowed to synthesize the product in a nearly quantitative yield, the use of hydrogen mainly resulted in the reduction of the aldehyde to the corresponding alcohol and further hydrogenolysis to the substituted toluene 3a with some formation of the desired product.
Based on our results herein and our previous studies we propose the following mechanism (Scheme 46). At first rhodium species are leached from carbon matrix into the solution either by coordination with CO or by itself. Then aldehyde is coordinated to the metal center with the formation of complex A. The addition of the amide to the carbonyl group results in the formation of intermediate B.

![Scheme 46. Plausible mechanism for the reductive amidation.](image)

Then intramolecular hydroxylation of CO ligand takes place. Following decarboxylation leads to the formation of the intermediate D. Finally target N-alkylated amide is formed via reductive elimination and next aldehyde and carbon monoxide enter the coordination sphere of the metal.

It appears that Rh/C\text{matrix} serves as a precatalyst of the catalytically active homogeneous species. Therefore, we decided to try to activate the catalytic system with fluoride
additive since in previous chapters of the thesis it was shown that fluoride additive in some cases can significantly increase catalytic activity. However, in this case, the addition of TBAT had a detrimental effect on the yield of the product (Table 19).

**Table 19. Influence of the fluoride additive on catalytic activity**

<table>
<thead>
<tr>
<th>Entry</th>
<th>x%</th>
<th>y%</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0</td>
<td>93%</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>0</td>
<td>59%</td>
</tr>
<tr>
<td>3</td>
<td>0.5</td>
<td>0.5</td>
<td>23%</td>
</tr>
</tbody>
</table>

[a] 0.2 mmol of acetamide, 1:1 ratio of acetamide and p-anisaldehyde, 0.5M, the yield was determined by $^1$H NMR with mesitylene as the internal standard.

### 5.3. Conclusion

We developed a new catalytic system for the reductive amidation of aldehydes using rhodium supported on carbon matrix and carbon monoxide as a reducing agent. Various primary amides and aromatic aldehydes can be used in this transformation. Less active carbonyl compounds such as ketones and enolizable aldehydes poorly undergo this transformation. Catalysts were analyzed with BET, TEM, and XPS techniques, where XPS revealed that Rh/C$_{\text{matrix}}$ mostly consists of Rh(III) species. In addition, it was shown that the catalyst leaches from the carbon matrix which prevents catalyst reuse. As a result, rhodium on carbon matrix serves the role of heterogeneous precursor for homogeneous catalytic species.

### 5.4. Experimental section

#### 5.4.1. General information

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification (THF was distilled over sodium/benzophenone, methanol was distilled over Mg). Carbon monoxide of >98% purity was obtained from NII KM (Moscow, Russia). Isolation of products was performed by preparative TLC (Macherey-Nagel, Silica gel 60 GF254, fluorescence quenching with UV light at 254 nm) or by column chromatography (Acros Organics, silica gel 0.06-0.200 mm). $^1$H and $^{13}$C NMR spectra were recorded on Bruker AV-300, AV-400 and Varian Inova 400 spectrometers at ambient temperature. Chemical shifts $\delta$ are reported in ppm using the solvent resonance signal as an internal standard. NMR yields were calculated with mesitylene as an internal standard (unless otherwise noted). The following
abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad; coupling constants are given in Hertz (Hz). Rhodium on carbon matrix (5% wt. Rh, catalog # 680710), ruthenium on activated charcoal (5% wt. Ru, catalog #84031), rhodium on activated charcoal (5 % wt. Rh, catalog # 83711), ruthenium on alumina (5% wt. Ru, powder, Degussa type H213 R/D, catalog # 381152), rhodium on activated alumina (5% wt. Rh, catalog # 83720), rhodium on alumina (5% wt. Rh, Degussa type G214 RA/D, catalog # 663468) and rhodium on carbon (5% wt. Rh, catalog # 206164) were purchased from Sigma-Aldrich. Ruthenium on activated carbon (5% wt. Rh, reduced, wet paste, 50% water catalog # AB155795) was purchased from ABCR.

5.4.2. General procedure

Rh on carbon matrix (1 mol %), amide (1 equiv.), and aldehyde (1 equiv.) were charged into a glass vial in a 10 mL stainless autoclave. Diethyl ether was added (0.5 M), and the autoclave was sealed, flushed three times with 3 bar of CO, and then charged with 40 bar CO. The reactor was placed into an oil bath preheated to 160 °C. After 22 h of heating, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred into a flask and the autoclave was washed with CH₂Cl₂; in order to get rid of the catalyst reaction mixture was centrifuged; combined solvents were removed under reduced pressure. The reaction mixture was analyzed using ¹H NMR. The NMR yield was determined using mesitylene as an internal standard. The residue was purified by column chromatography.

5.4.3. Spectroscopic and analytical data of isolated compounds

N-(4-Methoxybenzyl)acetamide (1a)

Following the general procedure using Rh on carbon matrix (7 mg, 3.4 µmol, 1 mol %), acetamide (20 mg, 0.34 mmol, 1 equiv.) and 4-methoxybenzaldehyde (41 µl, 0.34 mmol, 1 equiv.) product 1a was obtained in 93% NMR yield. The residue was purified by column chromatography (eluent: hexane/ethyl acetate (1:1); Rf = 0.13) to afford 51 mg (84%) of the product as white crystals.

m.p. 89-91°C.

¹H NMR (300 MHz, Chloroform-d) δ 7.16 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 8.4 Hz, 2H), 6.45-6.10 (br s, 1H), 4.28 (d, J = 5.6 Hz, 2H), 3.75 (s, 3H), 1.94 (s, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 170.1, 158.9, 130.5, 129.2, 114.0, 55.3, 43.1, 23.2. NMR spectra are in agreement with the literature data.[16]
N-(4-Methylbenzyl)acetamide (1b)

Following the general procedure using Rh on carbon matrix (12.4 mg, 6.0 µmol, 1 mol %), acetamide (35.4 mg, 0.6 mmol, 1 equiv.) and 4- methylbenzaldehyde (71 µl, 0.6 mmol, 1 equiv.) product 1b was obtained in 86% NMR yield. The residue was purified by column chromatography (eluent: toluene/ethyl acetate/Et3N (5:1:0.1); Rf = 0.21) to afford 70.8 mg (72%) of the product as white crystals.

m.p. 105-107°C.

1H NMR (300 MHz, Chloroform-d) δ 7.12 (s, 4H), 6.55-6.16 (br s, 1H), 4.30 (d, J = 5.6 Hz, 2H), 2.31 (s, 3H), 1.94 (s, 3H).

13C NMR (101 MHz, Chloroform-d) δ 170.1, 137.1, 135.3, 129.3, 127.8, 43.4, 23.2, 21.1.

NMR spectra are in agreement with the literature data.[16]

N-(4-Fluorobenzyl)acetamide (1c)

Following the general procedure using Rh on carbon matrix (5 mg, 2.4 µmol, 1 mol %), acetamide (14 mg, 0.24 mmol, 1 equiv.) and 4- fluorobenzaldehyde (26 µl, 0.24 mmol, 1 equiv.) product 1c was obtained in 82% NMR yield. The residue was purified by thin-layer preparative chromatography (eluent: hexane/ethyl acetate (2:1); Rf = 0.26) to afford 40 mg (71%) of the product as a white solid.

m.p. 97-99°C.

1H NMR (400 MHz, Chloroform-d) δ 7.21 (dd, J = 8.4, 5.5 Hz, 2H), 6.98 (dd appears as t, J = 8.4 Hz, 2H), 6.22-5.95 (br s, 1H), 4.34 (d, J = 5.8 Hz, 2H), 1.97 (s, 3H).

13C NMR (101 MHz, Chloroform-d) δ 163.5, 161.1, 134.2, 129.6 (d, J = 8.1 Hz), 115.6 (d, J = 21.5 Hz), 43.0, 23.3.

NMR spectra are in agreement with the literature data.[15]

N-(3-Methoxybenzyl)acetamide (1d)

Following the general procedure using Rh on carbon matrix (7 mg, 3.4 µmol, 1 mol %), acetamide (20 mg, 0.34 mmol, 1 equiv.) and 3-methoxybenzaldehyde (41 µl, 0.34 mmol, 1 equiv.) product 1d was obtained in 80% NMR yield. The residue was purified by thin-layer preparative chromatography (eluent: hexane/ethyl acetate (1:1); Rf = 0.15) to afford 43 mg (76%) of the product as a yellow oil.

1H NMR (400 MHz, Chloroform-d) δ 7.30 – 7.14 (m, 2H), 6.88 – 6.73 (m, 2H), 6.32-6.01 (br s, 1H), 4.35 (d, J = 5.7 Hz, 2H), 3.77 (s, 3H), 1.98 (s, 3H).
\(^{13}\text{C NMR}\) (101 MHz, Chloroform-d) \(\delta\) 170.1, 159.9, 139.9, 129.8, 120.1, 113.5, 112.9, 55.3, 43.7, 23.3.

NMR spectra are in agreement with the literature data. \(^{[16]}\)

\textbf{N-(2-Methoxybenzyl)acetamide (1e)}

\begin{center}
\includegraphics[width=0.2\textwidth]{1e.png}
\end{center}

Following the general procedure using Rh on carbon matrix (10 mg, 4.9 \(\mu\text{mol}\), 1 mol %), acetamide (29 mg, 0.49 mmol, 1 equiv.) and 2-methoxybenzaldehyde (66 mg, 0.49 mmol, 1 equiv.) product 1e was obtained in 51\% NMR yield. The residue was purified by thin-layer preparative chromatography (eluent: hexane/ethyl acetate (1:1); \(R_f = 0.26\)) to afford 33 mg (38\%) of the product as a yellow oil.

\textbf{\(^1\text{H NMR}\) (300 MHz, Chloroform-d)} \(\delta\) 7.30-7.23 (m, 2H), 6.94-6.84 (m, 2H), 6.13-5.91 (br s, 1H), 4.42 (d, \(J = 5.8\text{ Hz}\), 2H), 3.85 (s, 3H), 1.97 (s, 3H).

\textbf{\(^{13}\text{C NMR}\) (101 MHz, Chloroform-d)} \(\delta\) 169.8, 157.6, 129.9, 129.0, 126.4, 120.8, 110.4, 55.4, 39.5, 23.5.

NMR spectra are in agreement with the literature data.\(^{[15]}\)

\textbf{N-(4-(Heptyloxy)benzyl)acetamide (1f)}

\begin{center}
\includegraphics[width=0.2\textwidth]{1f.png}
\end{center}

Following the general procedure using Rh on carbon matrix (6 mg, 2.9 \(\mu\text{mol}\), 1 mol %), acetamide (17 mg, 0.29 mmol, 1 equiv.) and 4-heptyloxybenzaldehyde (63 \(\mu\text{l}\), 0.29 mmol, 1 equiv.) product 1f was obtained in 76\% NMR yield. The residue was purified on the InterChim PuriFlash flash chromatograph (eluent: hexane/ethyl acetate (1:1); \(R_f=0.18\)) to afford 57 mg (74\%) of the product as a white solid. \(R_f\) (hexane/ethyl acetate 1:1) = 0.18.

\textbf{m.p.} 93-95°C.

\textbf{\(^1\text{H NMR}\) (400 MHz, Chloroform-d)} \(\delta\) 7.16 (d, \(J = 8.2\text{ Hz}\), 2H), 6.82 (d, \(J = 8.2\text{ Hz}\), 2H), 6.17-5.95 (br s, 1H), 4.30 (d, \(J = 5.0\text{ Hz}\), 2H), 3.91 (t, \(J = 6.6\text{ Hz}\), 2H), 1.96 (s, 3H), 1.75 (p, \(J = 6.6\text{ Hz}\), 2H), 1.45 – 1.38 (m, 2H), 1.39 – 1.22 (m, 6H), 0.88 (t, \(J = 6.6\text{ Hz}\), 3H).

\textbf{\(^{13}\text{C NMR}\) (101 MHz, Chloroform-d)} \(\delta\) 170.0, 158.6, 130.2, 129.2, 114.7, 68.1, 43.3, 31.9, 29.3, 29.1, 26.1, 23.3, 22.7, 14.2.
N-(4-(Benzyloxy)benzyl)acetamide (1g)

Following the general procedure using Rh on carbon matrix (14.4 mg, 7.0 µmol, 1 mol %), acetamide (41.4 mg, 0.7 mmol, 1 equiv.) and 4-benzyloxybenzaldehyde (148.6 mg, 0.7 mmol, 1 equiv.) product 1g was obtained in 72% NMR yield. The residue was purified by column chromatography (eluent: toluene/ethyl acetate/Et₃N (5:1:0.1); Rₛ = 0.25) to afford 127 mg (71%) of the product as white crystals.

m.p. 144-146°C.

¹H NMR (300 MHz, Chloroform-d) δ 7.46 – 7.28 (m, 5H), 7.20 (d, J = 8.3 Hz, 2H), 6.93 (d, J = 8.3 Hz, 2H), 5.95-5.73 (br s, 1H), 5.05 (s, 2H), 4.35 (d, J = 5.5 Hz, 2H), 1.99 (s, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 169.9, 158.2, 136.9, 130.6, 129.3, 128.6, 128.0, 127.5, 115.1, 70.0, 43.2, 23.3.

NMR spectra are in agreement with the literature data.[16]

N-(4-(Benzyloxy)benzyl)acetamide (1h)

Following the general procedure using Rh on carbon matrix (30 mg, 7.0 µmol, 2 mol %), acetamide (43 mg, 0.73 mmol, 1 equiv.) and 4-cyanobenzaldehyde (95 mg, 0.73 mmol, 1 equiv.) product 1h was obtained in 50% NMR yield. The residue was purified on the InterChim PuriFlash flash chromatograph (eluent: ethyl acetate/methanol (10:1); Rₛ = 0.46) to afford 52 mg (41%) of the product as a white solid.

m.p. 142-144°C.

¹H NMR (300 MHz, Chloroform-d) δ 7.60 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 6.30-6.03 (br s, 1H), 4.47 (d, J = 6.1 Hz, 2H), 2.04 (s, 3H).

¹³C NMR (101 MHz, Chloroform-d) δ 170.5, 144.1, 132.5, 128.2, 118.8, 111.2, 43.1, 23.2

NMR spectra are in agreement with the literature data.[26]

N-(4-(Benzyloxy)benzyl)acetamide (1h)

Following the general procedure using Rh on carbon matrix (30 mg, 7.0 µmol, 2 mol %), acetamide (43 mg, 0.73 mmol, 1 equiv.) and 4-cyanobenzaldehyde (95 mg, 0.73 mmol, 1 equiv.) product 1h was obtained in 50% NMR yield. The residue was purified on the InterChim PuriFlash flash chromatograph (eluent: ethyl acetate/methanol (10:1); Rₛ = 0.46) to afford 52 mg (41%) of the product as a white solid.

m.p. 142-144°C.
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$^1$H NMR (300 MHz, Chloroform-d) δ 7.60 (d, $J = 8.0$ Hz, 2H), 7.37 (d, $J = 8.0$ Hz, 2H), 6.30-6.03 (br s, 1H), 4.47 (d, $J = 6.1$ Hz, 2H), 2.04 (s, 3H).

$^{13}$C NMR (101 MHz, Chloroform-d) δ 170.5, 144.1, 132.5, 128.2, 118.8, 111.2, 43.1, 23.2

NMR spectra are in agreement with the literature data. [26]

**N-(4-(Benzyloxy)benzyl)-3-methylbutanamide (1i)**

![N-(4-(Benzyloxy)benzyl)-3-methylbutanamide (1i)](image)

Following the general procedure using Rh on carbon matrix (7 mg, 3.4 µmol, 1 mol %), 3-methylbutanamide (34 mg, 0.34 mmol, 1 equiv.) and 4-benzyloxybenzaldehyde (72 mg, 0.34 mmol, 1 equiv.) product **1i** was obtained in 88% NMR yield. The residue was purified by preparative thin-layer chromatography (eluent: hexane/ethyl acetate (1:1); $R_f = 0.44$) to afford 80 mg (79%) of the product as a white solid.

**m.p.** 104-106°C.

$^1$H NMR (400 MHz, Chloroform-d) δ 7.43-7.31 (m, 5H), 7.19 (d, $J = 8.4$ Hz, 2H), 6.92 (d, $J = 8.4$ Hz, 2H), 6.08-5.87 (br s, 1H), 4.34 (d, $J = 5.6$ Hz, 2H), 2.18-2.08 (m, 1H), 2.04 (d, $J = 7.1$ Hz, 2H), 0.95 (d, $J = 6.5$ Hz, 6H).

$^{13}$C NMR (101 MHz, Chloroform-d) δ 172.4, 158.2, 136.9, 131.0, 129.2, 128.7, 128.0, 127.5, 115.0, 70.0, 46.1, 43.0, 26.2, 22.6.

NMR spectra are in agreement with the literature data. [16]

**N-(4-Methoxybenzyl)-3-methylbutanamide (1j)**

![N-(4-Methoxybenzyl)-3-methylbutanamide (1j)](image)

Following the general procedure using Rh on carbon matrix (4 mg, 1.9 µmol, 1 mol %), 3-methylbutanamide (20 mg, 0.19 mmol, 1 equiv.) and 4-methoxybenzaldehyde (24 µl, 0.34 mmol, 1 equiv.) product **1j** was obtained in 87% NMR yield. The residue was purified by preparative thin-layer chromatography (eluent: hexane/ethyl acetate (1:1); $R_f = 0.54$) to afford 34 mg (80%) of the product as a white solid.

**m.p.** 86-88°C.

$^1$H NMR (400 MHz, Chloroform-d) δ 7.18 (d, $J = 8.4$ Hz, 2H), 6.83 (d, $J = 8.4$ Hz, 2H), 5.97-5.73 (br s, 1H), 4.34 (d, $J = 5.6$ Hz, 2H), 3.77 (s, 3H), 2.14 – 2.07 (m, 1H), 2.03 (d, $J = 7.0$ Hz, 2H), 0.93 (d, $J = 6.4$ Hz, 6H).

$^{13}$C NMR (101 MHz, Chloroform-d) δ 172.4, 159.0, 130.7, 129.2, 114.1, 55.4, 46.2, 43.0, 26.3, 22.6.

NMR spectra are in agreement with the literature data. [16]
N-(4-Methoxybenzyl)benzamide (1k)

Following the general procedure using Rh on carbon matrix (5 mg, 2.4 μmol, 1 mol %), benzamide (29 mg, 0.24 mmol, 1 equiv.) and 4-methoxybenzaldehyde (29 μl, 0.24 mmol, 1 equiv.) product 1k was obtained in 85% NMR yield. The residue was purified by preparative thin-layer chromatography (eluent: hexane/ethyl acetate (1:1); Rf = 0.50) to afford 55 mg (76%) of the product as a white solid.

m.p. 92-94°C.

$^1$H NMR (400 MHz, Chloroform-d) δ 7.78 (d, J = 7.4 Hz, 2H), 7.49 (dd appears as t, J = 7.4 Hz, 1H), 7.40 (dd appears as t, J = 7.4 Hz, 2H), 7.27 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 6.61-6.44 (br s, 1H), 4.56 (d, J = 5.6 Hz, 2H), 3.79 (s, 3H).

$^{13}$C NMR (101 MHz, Chloroform-d) δ 167.4, 159.2, 134.5, 131.6, 130.4, 129.4, 128.6, 127.1, 114.2, 55.4, 43.7.

NMR spectra are in agreement with the literature data.[15]

N-(4-Fluorobenzyl)benzamide (1l)

Following the general procedure using Rh on carbon matrix (5 mg, 2.4 μmol, 1 mol %), benzamide (29 mg, 0.24 mmol, 1 equiv.) and 4-methoxybenzaldehyde (26 μl, 0.24 mmol, 1 equiv.) product 1l was obtained in 78% NMR yield. The residue was purified by preparative thin-layer chromatography (eluent: hexane/ethyl acetate (1:1); Rf = 0.59) to afford 39 mg (70%) of the product as a white solid.

m.p. 111-113°C.

$^1$H NMR (400 MHz, Chloroform-d) δ 7.78 (d, J = 7.4 Hz, 2H), 7.51-7.47 (m, 1H), 7.42-7.38 (m, 2H), 7.30-7.27 (m, 2H), 7.02-6.98 (m, 2H), 6.87-6.52 (br s, 1H), 4.56 (d, J = 5.8 Hz, 2H).

$^{13}$C NMR (101 MHz, Chloroform-d) δ 167.5, 162.3 (d, J = 245.6 Hz), 134.3, 134.2 (d, J = 2.8 Hz), 131.7, 129.6 (d, J = 8.1 Hz), 128.7, 127.1, 115.6 (d, J = 21.4 Hz), 43.4.

NMR spectra are in agreement with the literature data.[27]

N-(4-(trifluoromethyl)benzyl)benzamide (1m)

Following the general procedure using Rh on carbon matrix (7 mg, 3.4 μmol, 2 mol %), benzamide (21 mg, 0.17 mmol, 1 equiv.) and 4-trifluoromethylbenzaldehyde (23 μl, 0.17 mmol, 1 equiv.) product 1m was obtained in 76% NMR
yield. The residue was purified by preparative thin-layer chromatography (eluent: hexane/ethyl acetate (1:1); Rf = 0.68) to afford 33 mg (69%) of the product as a white solid.

**m.p.** 138-140°C.

**1H NMR** (400 MHz, Chloroform-d) δ 7.79 (d, J = 7.5 Hz, 2H), 7.57 (d, J = 7.5 Hz, 2H), 7.53-7.40 (m, 5H), 6.86-6.70 (br s, 1H), 4.67 (d, J = 5.8 Hz, 2H).

**13C NMR** (101 MHz, Chloroform-d) δ 167.6, 142.5, 134.2, 132.0, 130.0 (d, J = 32.6 Hz), 128.9, 128.2, 127.1, 125.9 (d, J = 3.8 Hz), 124.2 (q, J = 272.3 Hz), 43.6.

NMR spectra are in agreement with the literature data.[28]

3,4,5-Trimethoxy-N-(4-methoxybenzyl)benzamide (1n)

Following the general procedure using Rh on carbon matrix (5 mg, 2.4 µmol, 1 mol %), 3,4,5-trimethoxybenzamide (51 mg, 0.24 mmol, 1 equiv.) and 4-methoxybenzaldehyde (29 µl, 0.24 mmol, 1 equiv.) product 1n was obtained in 83% NMR yield. The residue was purified by preparative thin-layer chromatography (eluent: hexane/ethyl acetate (1:1); Rf = 0.30) to afford 49 mg (64%) of the product as a white solid.

**m.p.** 130-132°C.

**1H NMR** (400 MHz, Chloroform-d) δ 7.23 (d, J = 8.4 Hz, 2H), 7.02 (s, 2H), 6.83 (d, J = 8.4 Hz, 2H), 6.81-6.67 (br s, 1H), 4.50 (d, J = 5.5 Hz, 2H), 3.84 (s, 3H), 3.81 (s, 6H), 3.76 (s, 3H).

**13C NMR** (101 MHz, Chloroform-d) δ 167.1, 159.2, 153.3, 141.0, 130.4, 130.0, 129.5, 114.2, 104.5, 61.0, 56.4, 55.4, 43.8.

3,4,5-Trimethoxy-N-(4-methylbenzyl)benzamide (1o)

Following the general procedure using Rh on carbon matrix (5 mg, 2.4 µmol, 1 mol %), 3,4,5-trimethoxybenzamide (51 mg, 0.24 mmol, 1 equiv.) and 4-methylbenzaldehyde (29 µl, 0.24 mmol, 1 equiv.) product 1o was obtained in 85% NMR yield. The residue was purified on the InterChim PuriFlash flash chromatograph (eluent: hexane/CH2Cl2/PrOH (10:2:1); Rf = 0.40) to afford 61 mg (79%) of the product as a white solid.

**m.p.** 145-147°C.
Reductive Amidation without an External Hydrogen Source Using Rhodium Supported on Carbon Matrix as a Catalyst

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.25 (d, $J = 7.8$ Hz, 2H), 7.17 (d, $J = 7.8$ Hz, 2H), 7.01 (s, 2H), 6.39-6.27 (br s, 1H), 4.59 (d, $J = 5.6$ Hz, 2H), 3.88 (s, 6H), 3.87 (s, 3H), 2.35 (s, 3H).

$^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 153.3, 137.6, 135.3, 130.0, 129.6, 128.1, 104.5, 61.1, 56.5, 44.2, 21.3.

4-Methoxy-N-(4-methoxybenzyl)benzamide (1p)

Following the general procedure using Rh on carbon matrix (5 mg, 2.4 µmol, 1 mol %), 4-methoxybenzamide (37 mg, 0.24 mmol, 1 equiv.) and 4-methoxybenzaldehyde (29 µl, 0.24 mmol, 1 equiv.) product 1p was obtained in 99% NMR yield. The product was obtained as a white solid and has not required additional purification.

m.p. 128-129°C.

$^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.76 (d, $J = 8.6$ Hz, 2H), 7.26 (d, $J = 8.6$ Hz, 2H), 6.96 – 6.78 (m, 4H), 6.61-6.49 (br s, 1H), 4.54 (d, $J = 5.5$ Hz, 2H), 3.83 (s, 3H), 3.79 (s, 3H).

$^{13}$C NMR (101 MHz, Chloroform-d) $\delta$ 166.9, 162.2, 159.1, 130.6, 129.3, 128.9, 126.8, 114.1, 113.8, 55.4, 43.57.

NMR spectra are in agreement with the literature data. $^{[16]}$

5.4.3. Analysis of catalysts

BET

Nitrogen physisorption at 77 K was measured by an ASAP Micromeritics 2020 instrument. The samples were outgassed at 250 °C under a vacuum prior to analysis.

TEM

Target-oriented approach was utilized for the optimization of the analytic measurements. $^{[29]}$ Before measurements, the samples were deposited on the 3 mm carbon-coated copper grids from isopropanol suspension. Samples morphology was studied using Hitachi HT7700 transmission electron microscope. Images were acquired in bright-field TEM mode at 100 kV accelerating voltage.

XPS

The X-ray photoelectron spectra were acquired with an ESCA unit of the NanoPES synchrotron station (Kurchatov synchrotron radiation source, National Research Center Kurchatov Institute) using a hemispherical analyzer (SPECS Phoibos 150) at room temperature. Photoelectrons were excited with a monochromatic Al Kα source with a photon energy of 1486.61 eV at a base pressure in the analytical chamber below
10⁻⁹ mbar. Survey and high-resolution spectra of appropriate core levels were recorded at pass energies of 120 and 40 eV and with step sizes of 1 and 0.1 eV, respectively. The powdered samples were pressed into a two-sided carbon conductive tape and attached to the sample holder. The energy scale of the spectrometer was calibrated to provide the following values for reference samples (i.e., metal surfaces freshly cleaned by ion bombardment): Au 4f½—83.96 eV, Cu 2p½—932.62 eV, Ag 3d½—368.21 eV. Sample charging was corrected by referencing to the sp² state deconvoluted in the C 1s spectrum (284.44 eV). After charge referencing, a Shirley-type background with inelastic losses was subtracted from the high-resolution spectra. The photoelectron spectra were fitted with Gauss functions, while the sp² states in the C 1s spectra were approximated with a related spectrum of HOPG. Quantification was performed using atomic sensitivity factors included in the software of the spectrometer.

The oxidation states of Rh were analyzed with XPS. Identification of oxidation states of Rh was based on reference data compiled in Table 20. On the spectrum of sample (a) (Figure 24), Rh 3d₅/₂ and Rh 3d₃/₂ at 309.8 and 314.7 eV can be assigned to Rh₂O₃•5H₂O (309.6 eV).[25]

Table 20. Reference data of oxidation states of Rh.

<table>
<thead>
<tr>
<th>Oxidation State</th>
<th>Rh 3d₅/₂, eV</th>
<th>Rh 3d₃/₂, eV</th>
<th>Charge reference, eV</th>
<th>Assignment</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh⁰</td>
<td>307.2</td>
<td>311.94</td>
<td>Au 4f½=83.98</td>
<td>Rh⁰</td>
<td>[30]</td>
</tr>
<tr>
<td>Rh/C</td>
<td>309.3</td>
<td>313.0</td>
<td>-</td>
<td>Rh³⁺</td>
<td>[32]</td>
</tr>
<tr>
<td>Rh/Ir/C</td>
<td>307.4</td>
<td>312.2</td>
<td>-</td>
<td>Rh⁰</td>
<td>[32]</td>
</tr>
<tr>
<td>Rh₃Ir/C</td>
<td>309.4</td>
<td>313.5</td>
<td>-</td>
<td>Rh³⁺</td>
<td>[32]</td>
</tr>
<tr>
<td>RhO₃</td>
<td>307.3</td>
<td></td>
<td>Au 4f½=84.0</td>
<td>Rh⁰</td>
<td>[33]</td>
</tr>
<tr>
<td>RhO₃/C</td>
<td>308.2</td>
<td></td>
<td>Cu 2p½=932.7</td>
<td>Rh³⁺</td>
<td>[33]</td>
</tr>
<tr>
<td>RhO₃/C</td>
<td>309.9</td>
<td></td>
<td>Cu 2p½=932.7</td>
<td>satellite</td>
<td>[33]</td>
</tr>
<tr>
<td>RhO₃/C</td>
<td>311.5</td>
<td></td>
<td>Cu 2p½=932.7</td>
<td>satellite</td>
<td>[33]</td>
</tr>
<tr>
<td>Rh/γ-Al₂O₃</td>
<td>307.6</td>
<td>321.7</td>
<td>C 1s=284.8</td>
<td>Rh⁰</td>
<td>[34]</td>
</tr>
<tr>
<td>Rh/γ-Al₂O₃</td>
<td>309.1</td>
<td>313.6</td>
<td>C 1s=284.8</td>
<td>Rh³⁺</td>
<td>[34]</td>
</tr>
<tr>
<td>Rh₂O₃</td>
<td>308.2-309.4</td>
<td></td>
<td>C 1s=284.8</td>
<td>Rh³⁺</td>
<td>[25]</td>
</tr>
<tr>
<td>Rh₂O₃</td>
<td>308.2</td>
<td></td>
<td>C 1s=284.8</td>
<td>Rh³⁺</td>
<td>[31]</td>
</tr>
<tr>
<td>Rh₂O₃</td>
<td>308.8</td>
<td></td>
<td>C 1s=284.8</td>
<td>Rh³⁺</td>
<td>[31]</td>
</tr>
<tr>
<td>Rh₂O₃•5H₂O</td>
<td>309.6</td>
<td>310.2</td>
<td>C 1s=284.8</td>
<td>[25]</td>
<td></td>
</tr>
<tr>
<td>Rh₂O₃•2H₂O</td>
<td>309.3</td>
<td></td>
<td>C 1s=284.8</td>
<td>[25]</td>
<td></td>
</tr>
</tbody>
</table>
A close value of 310.2 eV for Rh₂O₃•5H₂O is given, however, there are no data on surface charge reference. Similarly to Kibis et al., we exclude the presence of Rh(OH)₃, since states with binding energies of 533.4 eV, which correspond to hydrated water, are deconvoluted in the O 1s spectra. The binding energies of 309.9 and 311.5 eV presented in Table 1 were assigned to satellites. However, in our case, the peak at 309.8 is the main peak, while there is a signal at 311.5 eV which can be assigned to the satellite.

In contrast to the spectrum of rhodium on carbon matrix, three states at 307.5/308.7/309.8 and 307.3/308.7/309.8 eV were deconvoluted in those of rhodium on carbon (b) (Figure 24), and rhodium on activated charcoal (c) (Figure 24), which can be assigned to Rh, Rh₂O₃ and Rh₂O₃•5H₂O, respectively. Their corresponding intensity ratios are 0.44/0.37/0.19 and 0.43/0.45/0.12. A comparison of Rh 3d line shapes and peak widths for the difference spectra of rhodium on carbon (b) and rhodium on activated charcoal (c) after subtracting the Rh⁰ state from those of sample (a) showed that they could not be described by a single state. Therefore, the spectra were fitted with three states. The Rh 3d₅/₂ peak of rhodium on carbon demonstrated a 0.2 eV shift to higher binding energy in comparison with that of rhodium on activated charcoal. This shift can be related to the size effect in photoelectron spectra. In other words, the size of Rh nanoparticles in rhodium on carbon is larger than that of rhodium on activated charcoal.

5.5. References

Chapter 5


