In-depth experimental and theoretical investigations on Co-SAC catalyzed transfer hydrogenation of azo compounds using methanol and ethanol

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Abstract:

Transfer hydrogenation of non-polar bond using methanol or ethanol such hydrogen source is of great challenge, and development of efficient catalyst for performing such challenging reactions always an exciting area to explore. Herein, using Co-SAC various azo bonds were very efficiently hydrogenated to the corresponding amines, including commercially used dyes. A number of kinetics study and Hammett studies were to investigate the plausible mechanism and electronic effects. Further, a detailed DFT-calculation was performed to get a deeper insight about the mechanism.

Introduction:

Transfer hydrogenation (TH) is considered as an attractive alternative to the direct hydrogenation using molecular H\textsubscript{2}, as it doesn’t require flammable H\textsubscript{2} gas or specialized reaction set-up\textsuperscript{1, 2}. The TH of C=O, N=C, C≡N bonds is well studied in literature using various hydrogen donors\textsuperscript{3-7}. However, TH of challenging azo -N≡N- bonds is relatively less explored compared to other unsaturated bonds due to inferior reactivity and the lower bond polarity. To overcome this challenge more reactive hydrogen source such as NH\textsubscript{3}BH\textsubscript{3} and NH\textsubscript{2}NH\textsubscript{2} are commonly employed\textsuperscript{8-14}. Still, in all these cases, the semi-hydrogenated product (-NH-NH-) was the major product, which suggested that -NH-NH- bond cleavage in hydrazine derivatives (R\textsubscript{1}NH-NHR\textsubscript{2}) is relatively more uphill than partial reduction of the -N≡N- bond. Thus, more efficient catalytic system is required for the complete transfer hydrogenation of -N≡N- bond in azo compounds to the corresponding amines.

Moreover, hydrogenation of azo compounds to the corresponding amine is highly relevant in the context of the dinitrogen (N\textsubscript{2}) activation towards the synthesis of NH\textsubscript{3}\textsuperscript{15-18}. On the other hand, azo compounds are extensively used as dyes in various textile and leather industries\textsuperscript{19}. Inevitably, the residual colours in the untreated waste-water released from these industries cause immense pollution to the sea and other water bodies\textsuperscript{20, 21}. Hence, sustainable transformation of such massively generated unwanted wastes into value added products is highly desirable. In this regard, several transition-metal based catalytic systems were reported for direct hydrogenation of azo compounds; however, most of them suffered from longer reaction time (up to 48 h) as well as high H\textsubscript{2}-pressure (up to 50 bar)\textsuperscript{22-29}. 

The employment of alcohols especially, methanol and ethanol as hydrogen source has spurred considerable interest as a potential feedstock due to their abundance, sustainability, and environmentally benign nature.\textsuperscript{30, 31} Nevertheless, the main challenge associated with the employment of these alcohols is their comparatively higher energy of dehydrogenation (\(\Delta H^0_{\text{MeOH}} = +84 \text{ KJ mol}^{-1}, \Delta H^0_{\text{EtOH}} = +68 \text{ KJ mol}^{-1}\)) than other long chain alcohols.\textsuperscript{32-34} In literature, few precious transition metal-based systems are reported for the TH of polar unsaturated bonds using methanol or ethanol.\textsuperscript{35-41} Notably, among the reported protocols, transfer hydrogenation of nonpolar bond is rare, even till now there is no report with 3d-metal based catalyst. Remarkably, Huang group reported a (NCP)Ir(I)-complex catalyzed transfer hydrogenation of unactivated alkenes and alkynes employing ethanol.\textsuperscript{30, 42, 43} During preparation of this manuscript, Xu and coworkers demonstrated protocol for transfer hydrogenation azoarenes using ethanol, catalyzed by a (NC)Ru(II)-complex; however, this catalytic system was incapable for complete hydrogenation of \(-\text{N}=\text{N}-\) bond, produced the hydroazoarenes as the major product.\textsuperscript{44}

Nowadays, 3d-metal-based single atomic catalysts (SAC) are becoming a promising candidate for developing more efficient catalytic systems for various organic transformations because of their improved atom-utilization efficiency.\textsuperscript{45-52} Moreover, the unique electronic structure of the single metal centre on the surface and labile coordination environment around the active site play a vital role in its unique catalytic activity compared to their nanoparticle or nanocluster counterparts.\textsuperscript{53, 54} Recently, several cobalt-based SACs were developed for hydrogenation/dehydrogenation related chemistry, which showed excellent catalytic activities in diverse range of organic transformations.\textsuperscript{55-59}

Considering the importance and challenges associated with nonpolar bond transfer hydrogenation and utilization of methanol and ethanol as hydrogen source, herein employing Co-SAC catalyst, transfer hydrogenation of azo compounds to amines using ethanol and methanol is disclosed (Scheme 1).

**Scheme 1**: Transfer hydrogenation of azo compounds.

**Results and Discussions:**
This study commenced with the synthesis of Co-SAC, where the Co(Phen) species were impregnated on the carbon support through pyrolysis at various temperature followed by acid wash furnished the desired catalysts (see SI for details). The catalysts were represented as Co-Phen/T, where T is the pyrolyzing temperature. Later, the catalytic activities of these catalysts were investigated for the transfer hydrogenation of -N=N- bonds using both ethanol and methanol.

Optimization of the reaction conditions:

To achieve the optimized condition for the transfer hydrogenation using ethanol, azobenzene (1a) was selected as the benchmark substrate. At first, 1a (0.15 mmol), Cs$_2$CO$_3$ (0.75 equiv.), and Co-Phen/800 (1.3 mol%) was taken in ethanol (1 mL) and was refluxed at 150 °C (oil bath temperature) for 15 h, which furnished the aniline (2a) in >99% (Table 1, entry 1). Next, various cobalt catalysts, synthesized at different pyrolysis temperatures, were screened; where Co-Phen/800 was found to be the most active one for this transformation (Table 1; entries 2-5). Afterward, several weak and strong bases was explored among them Cs$_2$CO$_3$ exhibited the highest yield of 2a (Table S2; entries 1-9). Later, with the lowering of the oil-bath temperature to 110 °C, the yield of 2a was decreased considerably; notably, at 130 °C moderate yield of 2a was observed, thus the further optimizations were performed at 130 °C. Next, upon extending the reaction time and increasing the catalyst amount the yield of 2a was improved significantly (Table 1, entries 10-11). Further, the base amount was optimized to 0.25 equiv. (Table 1, entries 12-14). However, formation of aniline was not detected in the absence of Co-Phen/800 and Cs$_2$CO$_3$ (Table 1, entries 15-16). Finally, 2.2 mol% Co-Phen/800, 0.25 equiv. Cs$_2$CO$_3$ at 130 °C in 24 h furnished 88% of 2a, which was taken as the optimized condition (Table 1, entry 13).

**Table 1**: Optimization of transfer hydrogenation of azobenzene using ethanol.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (mol%; Co)</th>
<th>Base (equiv.)</th>
<th>Time (h)</th>
<th>Temperature (°C)</th>
<th>Yield of 2a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Co-Phen/800 (1.3)</td>
<td>Cs$_2$CO$_3$ (0.75)</td>
<td>15</td>
<td>150</td>
<td>&gt;99</td>
</tr>
<tr>
<td>2</td>
<td>Co-Phen/600 (1.3)</td>
<td>Cs$_2$CO$_3$ (0.75)</td>
<td>15</td>
<td>150</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>Co-Phen/700 (1.3)</td>
<td>Cs$_2$CO$_3$ (0.75)</td>
<td>15</td>
<td>150</td>
<td>44</td>
</tr>
<tr>
<td>4</td>
<td>Co-Phen/900 (1.3)</td>
<td>Cs$_2$CO$_3$ (0.75)</td>
<td>15</td>
<td>150</td>
<td>61</td>
</tr>
<tr>
<td>5</td>
<td>Co-Phen/1000 (1.3)</td>
<td>Cs$_2$CO$_3$ (0.75)</td>
<td>15</td>
<td>150</td>
<td>40</td>
</tr>
<tr>
<td>6</td>
<td>Co-Phen/800 (1.3)</td>
<td>Cs$_2$CO$_3$ (0.75)</td>
<td>15</td>
<td>140</td>
<td>87</td>
</tr>
<tr>
<td>7</td>
<td>Co-Phen/800 (1.3)</td>
<td>Cs$_2$CO$_3$ (0.75)</td>
<td>15</td>
<td>130</td>
<td>66</td>
</tr>
<tr>
<td>8</td>
<td>Co-Phen/800 (1.3)</td>
<td>Cs$_2$CO$_3$ (0.75)</td>
<td>15</td>
<td>120</td>
<td>45</td>
</tr>
<tr>
<td>9</td>
<td>Co-Phen/800 (1.3)</td>
<td>Cs$_2$CO$_3$ (0.75)</td>
<td>15</td>
<td>110</td>
<td>24</td>
</tr>
<tr>
<td>10</td>
<td>Co-Phen/800 (1.3)</td>
<td>Cs$_2$CO$_3$ (0.75)</td>
<td>24</td>
<td>130</td>
<td>73</td>
</tr>
<tr>
<td>11</td>
<td>Co-Phen/800 (2.2)</td>
<td>Cs$_2$CO$_3$ (0.75)</td>
<td>24</td>
<td>130</td>
<td>99</td>
</tr>
<tr>
<td>12</td>
<td>Co-Phen/800 (2.2)</td>
<td>Cs$_2$CO$_3$ (0.50)</td>
<td>24</td>
<td>130</td>
<td>98</td>
</tr>
<tr>
<td>13</td>
<td>Co-Phen/800 (2.2)</td>
<td>Cs$_2$CO$_3$ (0.25)</td>
<td>24</td>
<td>130</td>
<td>88</td>
</tr>
<tr>
<td>14</td>
<td>Co-Phen/800 (2.2)</td>
<td>Cs$_2$CO$_3$ (0.10)</td>
<td>24</td>
<td>130</td>
<td>24</td>
</tr>
</tbody>
</table>
Table 2: Optimization of transfer hydrogenation of azobenzene using methanol

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (mol%)</th>
<th>Base (equiv.)</th>
<th>Yield of 2a (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Co-Phen/800 (2.2)</td>
<td>Cs₂CO₃ (0.25)</td>
<td>26</td>
</tr>
<tr>
<td>2</td>
<td>Co-Phen/800 (3)</td>
<td>Cs₂CO₃ (0.25)</td>
<td>32</td>
</tr>
<tr>
<td>3</td>
<td>Co-Phen/800 (6)</td>
<td>Cs₂CO₃ (0.25)</td>
<td>44</td>
</tr>
<tr>
<td>4</td>
<td>Co-Phen/800 (7.5)</td>
<td>Cs₂CO₃ (0.25)</td>
<td>50</td>
</tr>
<tr>
<td>5</td>
<td>Co-Phen/800 (8)</td>
<td>Cs₂CO₃ (0.25)</td>
<td>62</td>
</tr>
<tr>
<td>6</td>
<td>Co-Phen/800 (8)</td>
<td>Cs₂CO₃ (0.75)</td>
<td>75</td>
</tr>
<tr>
<td>7</td>
<td>Co-Phen/800 (8)</td>
<td>Cs₂CO₃ (0.75)</td>
<td>86</td>
</tr>
<tr>
<td>8</td>
<td>-</td>
<td>Cs₂CO₃ (0.75)</td>
<td>N.D.</td>
</tr>
<tr>
<td>9</td>
<td>Co-Phen/800 (8)</td>
<td>-</td>
<td>N.D.</td>
</tr>
</tbody>
</table>

*Reaction condition: 1a (0.15 mmol), base (y mmol), MeOH (1 mL) for 24 h at 130 °C; yields were calculated through GC-analysis using mesitylene as the internal standard.

**Characterization of Co-800-SAC catalyst:**

After observing promising activity for the transfer hydrogenation of the azo benzene using ethanol and methanol, Co-Phen/T (600 °C - 1000 °C) were characterized through several spectroscopic techniques to understand the structural features (see SI). In present discussion, characterization of the most effective catalyst, Co-Phen/800 is included.

The PXRD pattern of Co-Phen/800 did not show any peaks assignable to cobalt metal or its compounds, only the peaks corresponded to (002) and (100) graphitic planes were observed, which indicated the Co species in the sample were either highly dispersed or amorphous (Figure 1a). Later, HRTEM was employed to examine the dispersed Co-species. However, no cobalt-containing nanoparticles were observed, only graphitic layers were revealed which was
in accordance with the PXRD pattern (Figure 1b). This implied that the cobalt species must be highly dispersed as tiny clusters or single atoms that are undetectable or invisible by PXRD, TEM techniques.

Later, in order to get information at atomic scale, sub-Ångström-resolution HAADF-STEM technique was used to examine the Co-Phen/800. Interestingly, a large number of uniformly dispersed Co single atoms were observed (Figure 1c). Additionally, the EDX analysis also demonstrated homogeneous distribution of the Co-SACs on the carbon support (Figure 1d-h).

Next, XPS analysis was performed to gain the information about the electronic states of the elements present in the surface. The high resolution deconvoluted Co2p$_{3/2}$ spectra revealed Co(II)-CoNx was present as the major Co-species (Figure 1i). Later the oxidation state of cobalt as Co(II) was further confirmed by XNAES analysis where the adsorption K-edges of Co-Phen/800 were more-or-less overlayed the cobalt phthalocyanine and the CoO edge (Figure SI). This indicated the Co(II) oxidation state of Co-Phen/800. In the N1s XPS spectra, two peaks were observed at 399.02 eV and 400.7 eV, the lower energy peak corresponded to pyridinic nitrogen whereas the higher energy peak represented the overlap of CoNx and pyrrolic nitrogen (Figure 1h).

The textural properties of Co-Phen/800 catalysts were investigated through N$_2$-adsorption desorption studies. The Co-Phen/800 presented a type-II isotherm. BET surface area and pore volume of the catalyst were found to be 64.96 m$^2$/g, 0.398 cc/g, respectively. Further, the pore size distribution was derived using BJH method, and two peaks were observed at 23.2 Å and 36.3 Å, which signified the meso-porous nature of the catalyst (see SI).

![Figure 1](image)

Figure 1: a) PXRD pattern; b) HRTEM; c) AC-HAADF image; d-h) EDX analysis i) High-resolution Co2p$_{3/2}$ h) N1s XPS spectra of Co-Phen/800.

Substrate scope:
After achieving the details about the characteristic features of the material, the scope of this present methodology was evaluated for the transfer hydrogenation of various symmetric azo compounds under the optimized conditions, using both ethanol and methanol (Table 2). The para-, meta-, and ortho-substituted azo compounds worked well under this protocol (1a-11a). Notably, for both ethanol and methanol the transfer hydrogenation of azo compounds was more favourable with substrates bearing electron-donating groups than the electron-withdrawing one. Afterward, several di and tri substituted azo compounds were tested, which furnished the corresponding amines in good to excellent yields (12a-14a); however, the tri-substituted azoarenes displayed comparatively lower reactivity, possibly due to steric reason.

Table 3: Substrate scope for the transfer hydrogenation of symmetric azo compounds

<table>
<thead>
<tr>
<th>Reaction Condition 1</th>
<th>Reaction Condition 2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Condition 1</strong>: Co-Phe of 900 (2.2 mol%)</td>
<td><strong>Condition 2</strong>: Co-Phe of 900 (8 mol%)</td>
</tr>
<tr>
<td><strong>Co-cat</strong> (2.2 mol%)</td>
<td><strong>Co-cat</strong> (5 mol%)</td>
</tr>
<tr>
<td><strong>EOH, 150 °C, 36 h</strong></td>
<td><strong>MEOH, 150 °C, 24 h</strong></td>
</tr>
</tbody>
</table>

Table 3: Substrate scope for the transfer hydrogenation of symmetric azo compounds

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Yield</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a-11a</td>
<td>81%</td>
<td>82%</td>
</tr>
<tr>
<td>12a-14a</td>
<td>90%</td>
<td>88%</td>
</tr>
</tbody>
</table>

**Table 3**: Substrate scope for the transfer hydrogenation of symmetric azo compounds
mmol), $^{24}\text{Co}$-cat (8 mol%), 36 h, 150 °C; $^{24}\text{Co}$-cat (8 mol%), 36 h, 150 °C; $^{24}\text{Co}$-cat (8 mol%), 24 h, 140 °C; isolated yields; isolated yields; $^E$ NMR yield.

Next, various reducible functional group containing azo compounds were tested, where the -CO$_2$H, -CO$_2$Et, -CN groups remained unaltered whereas ketone and alkene functionalities were hydrogenated (Table 2, 15a–19a). Notably, under this protocol heterocycle containing azo compounds also efficiently transformed to their corresponding amines in good to excellent yields (20a–22a). Moreover, challenging aliphatic azo compounds exhibited satisfactory reactivity under this protocol (23a–24a). Next, the substrate scope was further extended with different unsymmetric azo compounds to assess the versatility of current protocol. Employing this methodology, various azo compounds with two different functionalities were successfully transformed to their corresponding amines (25a–36a). Particularly, few commercially used dyes (methyl red, methyl orange, Sudan I, and Sudan II) were transfer hydrogenated efficiently using both ethanol and methanol, demonstrating the environmental aspects of this protocol (37a–40a).

**Kinetic and control experiments:**

Next, a number control and kinetic experiments were performed, to get clear mechanistic insight. At first, the time-course of the TH of azobenzene using ethanol was studied under the optimized conditions (Figure 2a). Throughout the course of the reaction, the aniline concentration was found to increase with the expense of azobenzene. However, the intermediate hydrazobenzene was not detected.
Figure 2. a) Time-dependent study; Hammett plot using different $p$-substituted azobenzene by b) EtOH and c) MeOH and d) KIE study for the transfer hydrogenation of azobenzene.

Next, when $S1$ was exposed to the optimized condition, significantly higher yield of $p$-CH$_3$ aniline (68%) was observed compared to the $p$-CF$_3$ aniline (N.D.) (Scheme 2A). Notably, in the case of the $p$-CF$_3$ azobenzene, the corresponding hydrazobenzene was the major product. In transfer hydrogenation of $S2$, $p$-CH$_3$ hydrazobenzene and $p$-CF$_3$ hydrazobenzene presented 100% and 15% conversion, respectively. This suggested that the electron-withdrawing substituents may stabilized the hydrazobenzene in greater extent compared to electron-donating groups. Moreover, both the hydrazobenzenes were disproportionated into their corresponding amines and azo; for the $p$-CH$_3$, one the amount of aniline was higher than the azo, on the contrary for $p$-CF$_3$, the azobenzene concentration was higher than the amine, which indicated in the presence of electron-withdrawing substituents, H$_2$-elimination was more feasible than -NH-NH- bond breakage. These two control experiments suggested that the transfer hydrogenation of azobenzene to aniline was facilitated by the electron-donating substituent. Afterwards, in order to investigate the counter-cation effect, the transfer hydrogenation using ethanol was studied in presence and absence of cation scavenger (crown ether). Interestingly, in the presence of crown-ether there was drastic decease in the yield of 2a, which indicated that the counter-cation of the base had a significant role in this transformation (Scheme 2C). Next, to investigate the fate of the in situ generated formaldehyde, the crude reaction mixture was analysed through $^1$H-NMR, where HCO$_2^-$ (C-H at $\delta = 8.26$ ppm) was detected (Scheme 2D). However, the possibility of further dehydrogenation to CO$_2$, couldn’t be ruled out.

Scheme 2: Control experiments.

In the Hammett study, transfer hydrogenation of a series of $para$-substituted azobenzenes to their corresponding amines using both ethanol and methanol were investigated, which showed
that substitution variation on the azobenzene had a significant impact on the reaction rate (Figures 2b and 2c). In both cases, decent linear relation was observed between the relative rates (log(k_X/k_H)) and the substituent constants (σ) with the ρ values of -1.74 and -1.72, respectively. The negative ρ values for this transformation suggested that there was a build-up of positive charge in the transition state of the slowest step and the electron-donating substituents on the azobenzene will favour the hydrogenation of the -N=N- bonds, which was in accordance with Tables 3.

Moreover, kinetic isotope study on the transfer hydrogenation of the azobenzene using CH₃OH and CD₃OD separately under the optimized condition, showed k_H/k_D = 2.3 (Figure 2d). This result suggested that the breaking of the C-H bond of alcohol was one of the slow steps in this transformation.

Easy catalyst separation and recyclization of the catalysts are the primary advantages of heterogeneous catalysis. To examine this aspect, recyclability test was performed for the transfer hydrogenation of azobenzene using ethanol under the optimized condition, which disclosed that the catalysts could be recycled up to 5th times without significant loss in the catalytic activity (Figure 3).

![Figure 3. Recyclability test.](image)

**Theoretical investigation of the plausible mechanism**

Further, a detailed DFT calculation was performed to get more clear insight about the mechanism. The plausible mechanistic pathways for the Co-Phen/800 catalyzed transfer hydrogenation of azobenzene using ethanol are shown in Scheme 3. Based on previous reports exploring Co-SACs, species A was considered as the single cobalt site for this study where the Co-N bond lengths (1.90 - 1.91 Å) were well matched with reported systems (1.89 - 1.92 Å). In this study, the reaction was divided into two parts: dehydrogenation of ethanol and hydrogenation of azobenzene to aniline. For alcohol dehydrogenation, two mechanistic pathways were investigated; one path started with alkoxide (1) followed by β-hydride elimination to generate the Co-H (2), whereas, in the other path, the dehydrogenation of
ethanol was considered through a metal-ligand cooperative manner, where one of the nitrogen atoms of the support participated in the alcohol activation and subsequently 9 was generated. Next, for the hydrogenation step, three different mechanistic pathways might be possible. Among three pathways, two could be initiated from the Co-H (2) and proceeded differently: a) direct insertion of -N=N- or -NH-NH- bond into Co-H bond to furnish the desired product aniline, and b) the hydride of Co-H (2) shifted to any one of the adjacent support nitrogens, followed by, insertion of -N=N- or -NH-NH- bond into support N-H bond. These two processes were designated as Co-H insertion and spill-over pathways, respectively. Moreover, in the third pathway, intermediate 9 could hydrogenate the -N=N- and -NH-NH- bond in metal-ligand cooperative manner, which named as MLC pathway.

Scheme 3: Plausible mechanistic pathways for the transfer hydrogenation of azobenzene.

a) Dehydrogenation of ethanol and generation of Co-H

PES (potential energy surface) and optimized structures of the transition state for ethanol dehydrogenation were revealed in Figure 4. The β-hydride elimination pathway was initiated with the cobalt-ethoxide (I1p-H) species, where the cobalt atom resided in a distorted square pyramidal geometry. Afterward, the ethanol was dehydrogenated through a four-membered transition state (TS1p-H) with an activation barrier of 40.07 kcal/mol to furnish the Co-H species (I3p-H). On the other hand, the MLC pathway was constituted of two consecutive steps; initially, one ethanol molecule came into the vicinity of the catalyst through a hydrogen bonding between hydroxyl proton and ligand nitrogen (I1MLC). Consequently, that proton was transferred to the nitrogen through TS1MLC with an activation barrier of 30.63 kcal/mol, and the intermediate I2MLC was generated. In the next step, the Co-H was transferred to the cobalt centre through TS2MLC (69.14 kcal/mol) and produced the Co-H species, I3MLC. Although, the O-H hydrogen transfer of the MLC pathway (TS1MLC, 30.63 kcal/mol) was kinetically more favourable than β-hydride elimination transition state TS1p-H(40.07 kcal/mol), the Co-H hydrogen transfer step (TS2MLC) of the MLC pathway, required 29.07 kcal/mol more energy to complete the process. Thus, the β-hydride elimination (global activation barrier of 40.07 kcal/mol) was found to be an energetically more favourable pathway compared to the MLC path (global activation barrier of 69.14 kcal/mol) for ethanol dehydrogenation (Table 3).
b) Hydrogenation of azo to hydrazo

After generation of the Co-H (I3_{β-H} or I3_{MLC}), next step was the hydrogenation of azobenzene to hydrazobenzene. The potential energy diagram for the three plausible pathways were shown in Figure 5. In the control experiment, it was observed that the Cs⁺ had a significant role in this catalytic process. During the hydrogenation of azobenzene; on coordination with Cs⁺, the azobenzene was stabilized by 17 kcal/mol. Hence, in this study the azobenzene was considered to be activated through Cs⁺-coordination, except the MLC pathway. In the first path (cyan), the -N=N- bond of a Cs⁺-coordinated azobenzene was directly inserted into the Co-H of I3_{β-H} through a four-membered transition state (TS1_{Hyd1}, 22.18 kcal/mol). Afterward, alcoholysis by an ethanol molecule produced the hydrazobenzene and the Co-ethoxide (I1_{β-H}). Whereas the second path (pink) was initiated with hydrogen transfer from cobalt to support nitrogen via TS1_{Hyd1(spill)} with an activation barrier of 23.73 kcal/mol, followed by insertion of the -N=N- bond into the support N-H through TS2_{Hyd1(spill)}(41.8 kcal/mol). Notably, in these two pathways, the Cs⁺-coordination facilitated the insertion process by increasing the electrophilicity of the -N=N- bond. The third path (green) was the MLC pathway, where initially the nitrogen-bound hydrogen of I1_{MLC} transferred to azobenzene through TS1_{Hyd(MLC)} (48.10 kcal/mol). In the next step, the -N=N- bond was inserted into Co-H via the transition state TS2_{Hyd(MLC)} with an activation barrier of 45.81 kcal/mol. Finally, the hydrazobenzene was released and the catalyst re-entered the alcohol dehydrogenation stage. Overall, the global activation barriers for the Co-H insertion, spill over and MLC pathways were 22.18 kcal/mol, 41.8 kcal/mol and 48.71 kcal/mol respectively, which clearly indicated the Co-H insertion route was the most favourable pathway for azobenzene to hydrazobenzene transformation (Table 3).
Figure 5: PES along with the relevant thermodynamic parameters and structures of the stationary points for the hydrogenation of azobenzene to hydrazo benzene.

Figure 7: The optimized structures of the transition states involved in the azo to hydrazo conversion.

c) Hydrogenation of hydrazo to aniline
Finally, in the last stage of this transformation, transfer hydrogenation of hydrazobenzene to aniline was studied. The PES and optimized structures of the transition states involved in this stage were shown in Figures 7 & 8 respectively. Similar to the previous stage, this hydrogenation was also investigated in three plausible pathways. Before initiation of this stage, one cycle of alcohol dehydrogenation was occurred to generate the Co-H species ($I_1^{Hyd2}$, $I_1^{Hyd2(spill)}$ or $I_1^{Hyd2(MLC)}$). In the first path (cyan), the Co-H directly transferred to the Cs$^+$-coordinated hydrazobenzene with simultaneous rupture of the -N-N- bond through $TS_{1}^{Hyd2}(36.85 \text{ kcal/mol})$. The second path (pink) consisted of three steps; it initiated with hydrogen transfer from cobalt to support nitrogen through $TS_{1}^{Hyd2(spill)} (22.53 \text{ kcal/mol})$, followed by support nitrogen to hydrazo nitrogen hydrogen transfer via $TS_{2}^{Hyd2(spill)} (19.91 \text{ kcal/mol})$. In the last step the -N-N- bond was ruptured to form the aniline with an activation barrier of 40.28 kcal/mol ($TS_{3}^{Hyd2(spill)}$). However, the third pathway (green) was the combination of two steps; in the first step the support nitrogen-bound hydrogen ($I_1^{MLC}$), was transferred to hydrazobenzene through $TS_{1}^{Hyd2(MLC)} (36.62 \text{ kcal/mol})$. In the next step, Co-H hydride transfer and -N-N- bond breakage occurred in concerted manner via $TS_{2}^{Hyd2(MLC)}$, which required 48.71 kcal/mol energy to cross the barrier. Thus, among these three pathways, the Co-H insertion route found to be the most favourable one for the hydrazobenzene to aniline transformation (Table 3).

Figure 7: PES along with the relevant thermodynamic parameters and structures of the stationary points for the hydrogenation of hydrazobenzene to aniline.
Figure 8: The optimized structures of the transition states involved in the hydrazo to aniline.

Table 3: Comparison of Gibb’s free Energy barriers (in kcal mol$^{-1}$) associated with different fragmented steps and overall process in dehydrogenation, first hydrogenation, and second hydrogenation.

<table>
<thead>
<tr>
<th>Pathways</th>
<th>Activation barrier (ΔG$^\ddagger$) (kcal mol$^{-1}$)</th>
<th>Dehydrogenation</th>
<th>First hydrogenation</th>
<th>Second hydrogenation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pathway No.</td>
<td>Alcohol proton transfer to N-atom</td>
<td>Transfer of hydride to Co catalyst</td>
<td>Global Activation Barriers</td>
</tr>
<tr>
<td>Dehydrogenation</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MLC Pathway</td>
<td>Pathway No.</td>
<td>Alcohol proton transfer to N-atom</td>
<td>Transfer of hydride to Co catalyst</td>
<td>Global Activation Barriers</td>
</tr>
<tr>
<td></td>
<td>MLC Pathway</td>
<td>30.63</td>
<td>39.19</td>
<td>69.14</td>
</tr>
<tr>
<td></td>
<td>β-H elimination pathway</td>
<td>-</td>
<td>40.07</td>
<td>40.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>First hydrogenation</td>
<td>Pathway No.</td>
<td>Co to N Hydride transfer</td>
<td>N-N hydride transfer</td>
<td>Co-H insertion</td>
</tr>
<tr>
<td></td>
<td>Spillover Pathway</td>
<td>14.36</td>
<td>9.46</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Co-H Insertion Pathway</td>
<td>-</td>
<td>-</td>
<td>14.07</td>
</tr>
<tr>
<td></td>
<td>MLC Pathway</td>
<td>-</td>
<td>19.61</td>
<td>6.07</td>
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<tr>
<td>Second hydrogenation</td>
<td>Pathway No.</td>
<td>Co to N Hydride transfer</td>
<td>N-N hydride transfer</td>
<td>Co-H insertion</td>
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<td>Spillover Pathway</td>
<td>13.06</td>
<td>2.86</td>
<td>-</td>
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<td></td>
<td>Co-H Insertion Pathway</td>
<td>-</td>
<td>-</td>
<td>31.77</td>
</tr>
<tr>
<td></td>
<td>MLC Pathway</td>
<td>-</td>
<td>8.16</td>
<td>19.66</td>
</tr>
</tbody>
</table>
Conclusion:

In summary, employing a cobalt-based single atomic catalyst (Co-SAC) effective transfer hydrogenation of azo compounds using methanol and ethanol as hydrogen source was established. For this transformation among several heterogeneous Co materials, Co-Phen/800 found to be the most efficient. With the aid of STEM, the presence of Co-SACs was confirmed, further the XPS and XNAES analysis revealed the oxidation state of Co-Phen/800 as Co(II). A wide range functionalized azo compounds including commercially used dyes were successfully transfer hydrogenated to the corresponding amines following this protocol. Control experiments suggested electron-donating substituted azo compounds were hydrogenated in comparatively in faster rate than the electron-withdrawing substituted one, which was further elucidated by Hammett studies using both methanol and ethanol. Importance of counter cation (Cs+) in this transformation was illustrated by control experiments using crown ethers. Notably, a deeper insight of the mechanism was achieved, through a detailed theoretical study, where for the alcohol dehydrogenation, the β-H elimination step was found to be energetically more favourable over the MLC pathway and for both azo and hydrazo benzene hydrogenation the Co-H insertion route was the lowest energy pathway, among MLC and spill-over pathway. This report provided a new approach for transfer hydrogenation of non-polar bonds using ethanol and methanol as the hydrogen source, employing inexpensive cobalt-based heterogeneous catalyst.

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References


