

1 Modulating Catalytic Selectivity by Base Addition in Aqueous 2 Reductive Amination of 1,6-Hexanediol Using Ru/C

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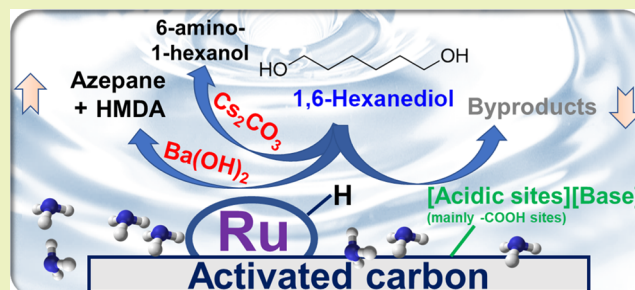
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Supporting Information

5 **ABSTRACT:** Efficient base-modulated product selectivity in the
6 aqueous-phase Ru/C-catalyzed reductive amination of 1,6-
7 hexanediol (HDO) was reported by performing the reaction at
8 mild conditions (463 K, 25 bar H₂). High selectivity of amines
9 could be controlled by the addition of different bases; for example,
10 Cs₂CO₃ addition gave a high yield of 6-amino-1-hexanol (AH,
11 26%). However, the addition of Ba(OH)₂ resulted in the formation
12 of high yield of secondary amination products, hexamethylenedi-
13 amine (HMDA, 34%) and azepane (26%). The hydroxide base,
14 especially Ba(OH)₂, aids in the initial conversion of HDO to AH
15 by significantly decreasing the apparent activation energy from 68
16 to 48 kJ mol⁻¹. A closer analysis of the formation of secondary products (azepane and HMDA) revealed a faster reaction between
17 NH₃ and the carbonyl-containing intermediate by the addition of Ba(OH)₂ into the reaction solution.

18 **KEYWORDS:** amination, 1,6-hexanediol, Ru-supported carbon, base effect, aqueous-phase reaction



1. INTRODUCTION

19 Biomass-derived oxygenates have attracted considerable
20 attention in recent years as renewable raw materials for the
21 green syntheses of value-added chemicals and are readily
22 available from acid hydrolysis, fermentation, catalytic fast
23 pyrolysis, and so forth.^{1–7} For various industrial applications,
24 the catalytic transformation of these oxygenates to amines is
25 considered to be one of the most attractive methods for value
26 addition.^{8–10} Therefore, a lot of research has been performed
27 on the amination of biomass-derived oxygenates (such as
28 alcohols, ketones, aldehydes, carboxylic acids, etc.) to N-
29 containing molecules.^{11–14} For example, industrial methyl-
30 amine production is based on the reaction between methanol
31 and NH₃ in the gas phase usually at high temperatures (623–
32 773 K) and pressure (15–30 bar) over heterogeneous catalysts
33 such as zeolites.¹⁵ Other than zeolites, several catalysts based
34 on Ni, Co, Fe, Cu, and so forth have been employed for the
35 gas-phase amination of alcohols.¹⁶ Due to harsh reaction
36 conditions, mixtures of aminated products (e.g., primary,
37 secondary, and tertiary amines) together with dehydration
38 products are formed.^{17,18} Substantial coke formation leads to
39 catalyst deactivation; thus, the amination at a lower temper-
40 ature using metal-based catalysts has been proposed with the
41 ability to hydrogenate and dehydrogenate alcohols.^{19,20} To
42 achieve high activity of a metal catalyst toward the amination
43 of long-chain alcohols at a lower temperature, reactions are
44 usually performed in inert organic solvents to completely
45 dissolve the long-chain hydrophobic part of the reactant.¹⁸ In

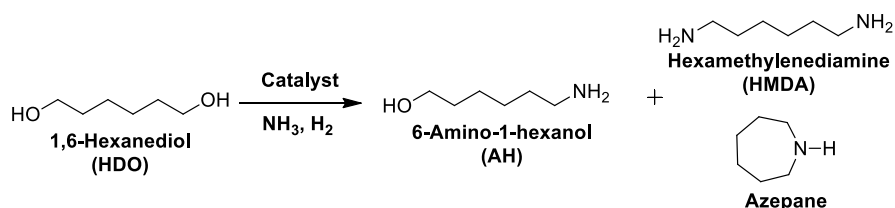
view of applications in the polymer industry, the amination of 46
bifunctional alcohols is of great importance, which can be 47
verified by higher demand and increasing growth of 48
biopolymers.^{21,22} Therefore, significant progress has been 49
made on the amination of biomass-derived diols to molecules 50
containing amine-alcohol, diamines, and/or cyclic amines.^{23,24} 51
Cyclic amination products are chemical intermediates that are 52
used for the synthesis of many industrial reagents, including 53
pharmaceuticals and polymers.^{25–27} Recently, we have 54
reported Ru-supported carbon (Ru/C) as an active and 55
effective catalyst for aqueous-phase sustainable amination of 56
isohexides.^{28,29} Despite great progress in the development of 57
catalysts and sustainable processes, the study of Ru/C- 58
catalyzed reactions is limited to the amination of isosorbides 59
with restricted diamine yields up to 10%.^{28,29} Although it is 60
often acknowledged that base additives have a significant effect 61
on catalytic activity and selectivity during the amination of 62
alcohols,^{30–33} the effect of base additives in the reaction 63
pathways is not well understood, so far. 64

Owing to the high potential of amines, in this 65
communication, we investigated the sustainable conversion of 66

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Table 1. Aqueous-Phase Amination of HDO in the Presence of Heterogeneous Catalysts with External H₂ and NH₃ as a N-Source^a

entries	catalyst	conv./%	amination product yield/%				total amine ^c sel./%	mass balance/%
			AH	azepane	HMDA	others ^b		
1	Pd(OH) ₂ /C	25	2	0	0	<1	7	78
2	Pd/C	25	2	<1	0	<1	8	79
3	Pt/C	36	3	<1	<1	<1	9	70
4	Au/C	27	2	0	1	<1	10	77
5	Ru/C	75, 87 ^d	27, 22 ^d	11, 20 ^d	15, 21 ^d	3, 6 ^d	71, 72 ^d	80, 82 ^d
6 ^e	Ru/C	66	26	3	6	2	53	71
7	Ru/SiO ₂	46	16	2	2	5	42	79
8	Ru/boehmite	47	18	1	2	5	45	79
9	Ru/TiO ₂	50	20	2	2	5	48	79
10	Ru/HT	39	6	<1	0	2	18	70
11	RuO ₂	52	18	2	2	10	42	80
12	Ru/C	62 ^f , 58 ^g	26 ^f , 24 ^g	6 ^f , 4 ^g	8 ^f , 5 ^g	2 ^f , 1 ^g	65 ^f , 56 ^g	80 ^f , 76 ^g
13	C ^h	23	trace	0	0	12	0	89
14	blank	5	trace	0	0	1	0	96

^aReaction conditions: 3.2 mmol HDO, 17.5 mL of 25% aqueous NH₃, 50 mg of catalyst (S/C = 7.8 g g⁻¹), T = 463 K, t = 2 h, and 25 bar H₂.
^bOthers include 1-pentanol, 1-pentylamine, 1-hexanol, and 1-hexylamine. ^cTotal amine selectivity includes the products of AH, azepane, and HMDA. ^dt = 4 h. ^eReaction was conducted in a 40 bar Ar atmosphere. ^fS/C = 15.6 g g⁻¹. ^gS/C = 23.4 g g⁻¹. ^hActivated carbon received from Sigma-Aldrich. Mass balance = 100 × (total amount of products and remaining HDO)/initial amount of HDO.

67 biomass-derived 1,6-hexanediol (HDO) to amines aiming
 68 toward the production of high-performance sustainable
 69 polymers³⁴ and chemicals.³⁵ HDO is one of the key
 70 intermediates and can be obtained in high yield (>70%)
 71 from cellulose via the formation of 5-hydroxymethylfurfural
 72 and/or its derivatives^{36–38} or levoglucosenone³⁹ which is
 73 produced from sugars. Some heterogeneous catalysts, based on
 74 Ni, Ru, and Ce supported on metal oxides, have been
 75 successfully applied for HDO amination in the presence of
 76 NH₃ as an amine source (Table S1).^{16,40,41} However, reductive
 77 amination has so far been exclusively examined in organic
 78 solvents (such as dioxane, toluene, or xylene) at high reaction
 79 temperature (~523–573 K) and high NH₃ pressure, which
 80 significantly hampers practical large-scale HDO amination.
 81 Herein, we propose Ru/C as an efficient catalyst for the one-
 82 pot selective aqueous-phase conversion of HDO into mono-,
 83 di-, and cyclic amines such as AH, HMDA, and azepane,
 84 respectively, under mild conditions at 463 K and 25 bar H₂.
 85 The effect of bases (both carbonate and hydroxide) was
 86 examined to achieve maximum selectivity of amination
 87 products. Based on the kinetic and mechanistic study, the
 88 involvement of the base in the reaction mechanism is
 89 proposed.

2. EXPERIMENTAL SECTION

90 **2.1. Catalysts and Reagents.** Ru supported on activated carbon
 91 (5 wt %), denoted simply as Ru/C, was received from Sigma-Aldrich
 92 (BET surface area 735 m² g⁻¹ and metal dispersion 58–69%) and
 93 used as received (see detailed characterization in the Supporting
 94 Information, Table S2 and Figures S1–S3). For the catalyst screening,
 95 commercial Pd(OH)₂/C (20 wt %, Sigma-Aldrich), Pd/C (10 wt %,
 96 Sigma-Aldrich), and RuO₂ (99.5%, Fisher Scientific) were applied;

however, for the synthesis of catalyst supports such as TiO₂ (99.9%, 97
 Anatase), Catapal B Alumina (boehmite, Sasol), SiO₂ (Aerosil-200, 98
 Degussa), and hydrotalcite (HT, Sigma-Aldrich) were used (see the
 Supporting Information, Section 2.1). 100

HDO (97%) received from Alfa Aesar and AH (97%), azepane 101
 (99%), HMDA (98%), 1-pentanol (99%), pentylamine (99%), 1- 102
 hexanol (99%), and hexylamine (99%) were obtained from Sigma- 103
 Aldrich. Bases, Ba(OH)₂ (>98%), NaOH (>98%), KOH (>98%), 104
 Na₂CO₃ (99.5%), and K₂CO₃ (99.5%) were obtained from Roth; 105
 Cs₂CO₃ (99%), CaCO₃ (99%), SrCO₃ (>98%), and RbOH·H₂O 106
 were procured from Sigma-Aldrich; and Ca(OH)₂ was obtained from 107
 VWR. 25% aqueous NH₃ solution was received from Roth. High- 108
 purity (>99.99%) gases H₂ and Ar were purchased from Air Liquide. 109

2.2. Ru/C-Catalyzed HDO Amination in Aqueous NH₃. Ru/C- 110
 catalyzed HDO amination was typically performed in a 45 mL glass- 111
 lined stainless steel autoclave (Parr) occupied with a magnetic stirring 112
 bar. HDO (3.2 mmol), 50 mg of Ru/C catalyst (S/C = 7.8 g g⁻¹), 113
 17.5 mL of aqueous NH₃ (25%), and 25 bar H₂ were charged to the 114
 autoclave. The autoclave was placed in a heating furnace heated to an 115
 elevated temperature for reaction with a stirring rate of 500 rpm for 116
 0.5–4 h. After completion of the reaction, the autoclave was placed in 117
 an ice bath for fast cooling. The HDO conversion and amination 118
 products in the reaction mixture were analyzed using gas 119
 chromatography (GC; Shimadzu GC-2010 Plus) with a capillary 120
 column (Restek RTX-5 Amine) and *t*-amyl alcohol as an internal 121
 standard. The possibility of in situ CO₂, CO, and H₂ formation during 122
 catalytic reactions was analyzed using GC (Shimadzu GC-2030, TCD 123
 detector) of the gaseous part of the reaction. 124

The base effect was studied by the addition of 10–200 mg of the 125
 base into the reaction mixture containing 3.2 mmol HDO, 50 mg of 126
 Ru/C catalyst (substrate-to-catalyst ratio, S/C = 7.8 g g⁻¹), 17.5 mL 127
 of aqueous NH₃ (25%), and 25 bar H₂. Reactions were performed in 128
 the same way as stated above. 129

For kinetic studies, the amount of the products (AH, azepane, and 130
 HMDA) was monitored at the initial stage of the reaction at 433–473 131

132 K to determine the reaction rates and apparent activation energies.
 133 The rates of product formation at different temperatures were
 134 estimated from the slope of the linear time course at the early stage of
 135 reaction by controlling the conversion by reducing the catalyst
 136 amount from 50 to 10 mg in all cases.

3. RESULTS AND DISCUSSION

137 **3.1. Ru/C-Catalyzed Aqueous-Phase Amination of**
 138 **HDO.** Table 1 lists the catalytic results of HDO amination
 139 using various supported metal catalysts at 463 K for 2 h in
 140 aqueous NH₃ under external H₂ pressure (see the
 141 Experimental Section). The activity of Ru/C was first
 142 examined and compared with other conventional carbon-
 143 supported catalysts such as Au/C, Pt/C, Pd/C, and Pd(OH)₂/
 144 C (Table 1, entries 1–5). A screening of the catalysts clearly
 145 showed the high activity of Ru-based catalysts, and the amines'
 146 selectivity increased in the following order: Pd(OH)₂/C < Pd/
 147 C < Pt/C < Au/C < Ru/C. The Ru/C catalyst afforded a total
 148 amine selectivity of 71% at 75% HDO conversion. A detailed
 149 analysis of all other products showed a total 3% formation of 1-
 150 pentanol, 1-pentylamine, 1-hexanol, and 1-hexylamine due to
 151 decarbonylation and dehydration, where 1-pentylamine was
 152 the major byproduct. Extending the reaction time to 4 h
 153 improved the conversion to 87% without significantly affecting
 154 the selectivity. The yield of byproducts also increased to 6% in
 155 4 h. The total mass balance was 80% due to the formation of
 156 heavy byproducts, which were not detected in the reaction
 157 solution. When the reaction over the Ru/C catalyst was
 158 conducted in an inert atmosphere, the amination products
 159 were still observed due to the borrowing hydrogen mechanism
 160 (BHM) (Table 1, entries 6). In the BHM, the formation of H₂
 161 proceeds by dehydrogenation of alcohol groups, which is
 162 further utilized in imine reduction steps toward the final
 163 amine.⁴² H₂ formation via dehydrogenation, not from other
 164 complex reactions, was verified by gas-phase analysis of the
 165 reaction mixture using GC. The absence of any in situ
 166 generated carbonaceous product confirmed the BHM in inert
 167 conditions, where H₂ produced via dehydrogenation was
 168 reutilized during the reaction (Figure S4). Notably, the rate of
 169 product formation was slow via the BHM, resulted 66%
 170 conversion, and mainly AH (26%) was formed. This suggested
 171 that the combination of metallic sites together with support
 172 and an external H₂ source is apparently required for efficient
 173 aqueous-phase amination of HDO. When non-carbon
 174 materials having different acid–base properties were applied
 175 as a support for Ru metal, the conversion of HDO was
 176 restricted up to 52% (Table 1, entries 7–11). Ru/SiO₂, Ru/
 177 boehmite, Ru/TiO₂, and RuO₂ resulted in moderate selectivity
 178 (42–48%) toward amination products. Surprisingly, selectivity
 179 was dropped to 18% for Ru/HT catalyst. This was tentatively
 180 described by the low stability of the catalyst due to the high
 181 solubility of hydrotalcite in the basic hydrothermal con-
 182 ditions.^{43,44} Among the tested catalysts, the carbon material as
 183 a support was superior in terms of the high amine selectivity
 184 and HDO conversion. Carbon materials are considered
 185 hydrothermally stable and provide a better metal–support
 186 interaction with high dispersity.^{45,46} Further, structural changes
 187 are very common when metal oxides are treated under
 188 hydrothermal conditions;⁴⁶ therefore, Ru/C is considered an
 189 adequate catalyst for aqueous-phase HDO amination. Yields of
 190 other products (4–10%) were significantly higher over Ru-
 191 supported metal oxides or RuO₂ (Table 1, entries 7–11).
 192 Additionally, good results were obtained in the scale-up

conditions for the Ru/C system; at 15.6 and 23.4 substrate-to-
 catalyst (S/C, g g⁻¹) ratios, 56–65% of total amine selectivity
 was obtained on 58–62% conversion (Table 1, entries 12).
 Carbon alone was inactive for catalytic amination; however, it
 favors side product formation due to the presence of surface-
 acidic oxygen functional groups which led to the formation of
 mainly dehydration product, 1-hexanol (Table 1, entry 13).

To better understand the importance of highly dispersed
 Ru/C, the low dispersed Ru on activated Norit carbon (Ru/
 C_{Norit}) was prepared at a reduction temperature of 473 K (see
 the Supporting Information, Section 2.1). Ru/C_{Norit} showed
 only 16.6% dispersity of Ru and resulted in only 18% HDO
 conversion and 10% total amine yields. Furthermore, changing
 the Ru loading from 5 to 1 wt % did not show a significant
 change in the catalytic amination, which could be due to the
 unchanged adsorption and reaction sites (Figure S5).

Three amination products were formed in a consecutive
 step, inducing linear amines such as AH, HMDA, and azepane
 (see time-resolved concentration profiles in Figure 1). At the

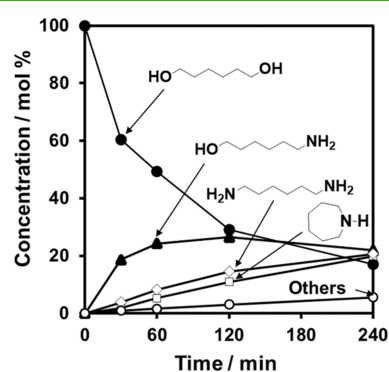


Figure 1. Time course of HDO conversion (●) and amine [AH (▲), azepane (□), HMDA (◇), and others (○)] yields. Reaction conditions: 3.2 mmol HDO, 17.5 mL of 25% aqueous NH₃, 50 mg of Ru/C catalyst (S/C = 7.8 g g⁻¹), T = 463 K, and 25 bar H₂.

initial stages of the reaction, in 1 h high selectivity toward
 monoamination product, AH (yield = 24%) was obtained.
 With increasing reaction time, the conversion increased and
 the selectivity of AH decreased with the formation of
 secondary products, HMDA (21%) and azepane (20%). In
 parallel to the secondary products, other products including
 pentanol, pentylamine, hexanol, and hexylamine were also
 formed by decarbonylation and dehydration reactions.

The Ru/C catalyst was separated from the reaction solution,
 washed with water, and dried overnight under vacuum at 333
 K for further recycling. To see clear changes under recycling
 experiments, the conversion was controlled by decreasing the
 time of experiments to 1 h. Although a drastic decrease in the
 HDO conversion (62 to 41%) and amine yields (50 to 29%)
 was observed after the first cycle, the rate of deactivation was
 lower in successive reuse (Figure 2A). Satisfactory recycling of
 Ru/C catalyst was obtained. The possibility of Ru leaching
 during amination was evaluated by carrying out an interruption
 experiment and analyses of the reaction solution. After carrying
 out an experiment for 0.5 h, the reaction was stopped, the
 catalyst was separated from the reaction solution, and the
 reaction mixture was reacted again for 2 h under analogous
 conditions (Figure S6). Thus, only a slight change in the yields
 was observed after catalyst removal, and XRF of the reaction
 solution showed <1 ppm of Ru leaching during cycles of the

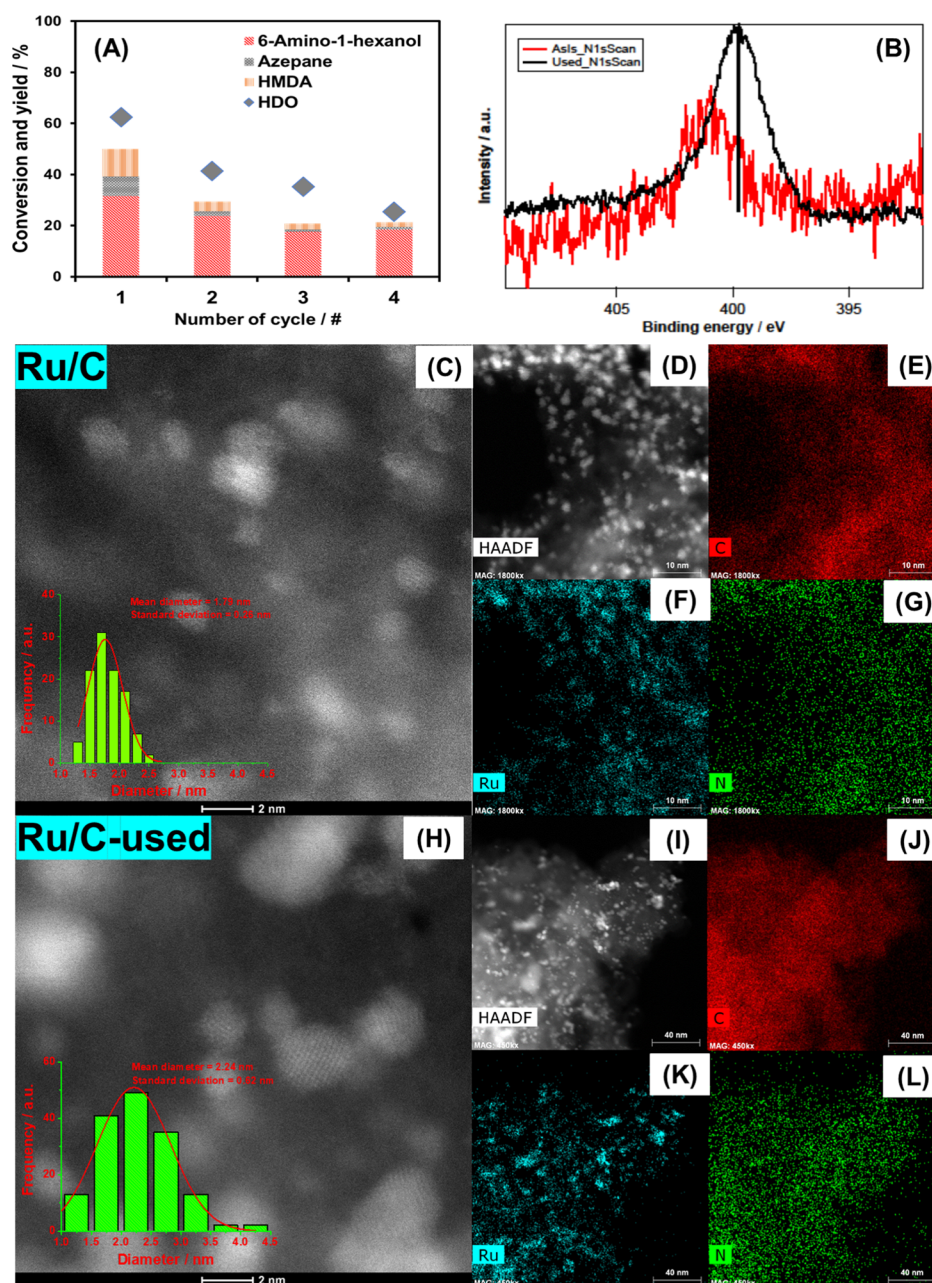


Figure 2. (A) Catalytic activity of fresh and reused Ru/C for amination of HDO at 463 K. Reaction conditions: 3.2 mmol HDO, 17.5 mL of 25% aqueous NH_3 , 50 mg of Ru/C catalyst ($\text{S/C} = 7.8 \text{ g g}^{-1}$), $T = 463 \text{ K}$, $t = 1 \text{ h}$, and 25 bar H_2 . (B) N 1s core-level XPS spectra of Ru/C (red) and used Ru/C (black). (C) TEM and (D) HAADF images and (E–G) EDX screening of fresh and used Ru/C. (H) TEM and (I) HAADF images and (J–L) EDX screening of fresh and used Ru/C.

237 experiment, indicating that Ru was quite stable at the carbon
 238 support. Elemental analysis and X-ray photoelectron spectroscopy (XPS)
 239 measurement of Ru/C-used material showed an increase in N-content,
 240 especially on the surface of the carbon material (XPS as a surface-sensitive
 241 technique evidenced a higher N-content of 4.4 at. % compared to a content
 242 of 2.1 at. % in elemental analysis) (Tables S3 and S4). This gave
 243 evidence to the formation of bulkier N-containing molecules on the spent
 244 Ru/C catalyst, in line with the lower mass balance observed during the
 245 reaction. To understand the surface changes during amination and the
 246 nature of N-containing molecules adsorbed on the used catalyst surface,
 247 high-resolution scans of the Ru 3d, C 1s, O 1s, and N 1s core-level
 248 regions were performed in XPS (Figures 2B and S7). N 1s

251 emission at a binding energy of 400 eV suggests the formation of a
 252 pyrrolic species during amination.⁴⁷ Both C 1s and O 1s spectra
 253 remained unaffected, while a shift of the Ru 3d_{5/2} peaks from 281.55
 254 to 280.0 eV indicated a reduction of Ru to the metallic state, which
 255 was expected as the amination was performed in the presence of H_2 .
 256 Detailed surface analysis was conducted by high-resolution transmission
 257 electron microscopy (TEM) analysis coupled with energy-dispersive X-ray
 258 (EDX) analysis of fresh and used Ru/C catalysts. The fresh catalyst
 259 showed a sharp particle size distribution in the range of 1–3 nm with a
 260 mean diameter of around 1.79 nm, which aligns with the diameter
 261 calculated by the CO chemisorption experiment (Figures 2C and S7
 262 and Table S2). However, in the used catalyst, the particle size
 263 distribution widened, and the 264

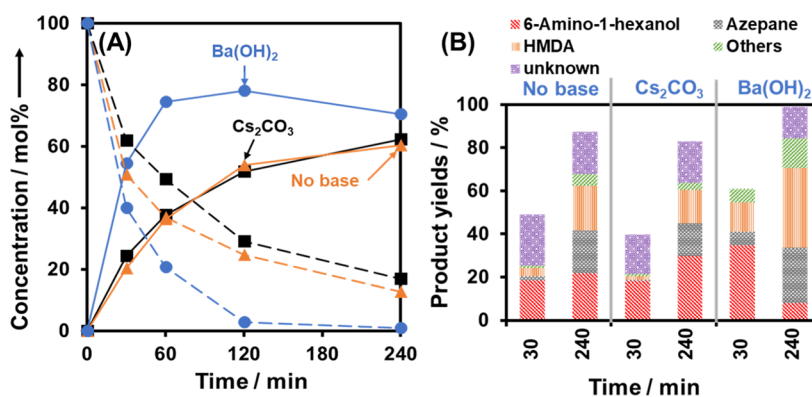


Figure 3. (A) Comparison of total amination product yields (solid line) and corresponding conversions (dashed line) in the presence of Cs₂CO₃ (triangle, ▲), Ba(OH)₂ (dot, ●), and no base (square, ■). (B) Product formation during the different time courses (at 30 and 240 min) under different base additives, see the Supporting Information for the experimental conditions and Figure S10.

265 mean particle size shifted toward larger diameters of around
266 2.24 nm due to particle agglomeration during the reaction
267 (Figure S7). Combining XPS analysis and EDX mapping of the
268 fresh and used catalysts, the formation of large N-containing
269 molecules was observed on the whole carbon surface (Figure
270 2B,I–L).

271 Therefore, the decrease in activity was considered due to the
272 adsorption of large pyrrolic N-containing byproducts over the
273 surface of catalysts, which block the accessibility of pores of the
274 catalysts, confirmed by detailed textural analysis of materials
275 (Table S5). Both specific surface area and pore volume were
276 decreased after the amination, which hinders the accessibility
277 of reactant molecule to reach maximum active sites. Thus, the
278 loss in catalytic activity during the recycling experiments was
279 not only considered due to particle size agglomeration but also
280 the blockage of pore diameter by N-containing heavier
281 products formed during amination.

3.2. Effect of Base Addition in Ru/C-Catalyzed Aqueous-Phase Amination of HDO.

283 To check the effect
284 of base additive, the aqueous-phase Ru/C-catalyzed amination
285 of HDO was carried out in the presence of different alkali or
286 alkaline earth metal carbonates and hydroxides (see the
287 Experimental Section and Table S6). It is interesting to note
288 that base addition under optimum conditions (HDO/base =
289 3.9 g g⁻¹, see Figure S9) showed a significant effect on catalytic
290 HDO conversion as well as on the product's selectivity. By
291 screening various base additives and comparing the reactivity
292 data, Cs₂CO₃ was identified as a suitable additive for yielding
293 the primary amination products, AH and Ba(OH)₂, for the
294 production of secondary amination products, HMDA and
295 azepane (Figure S10). The rates of total amine (AH, HMDA,
296 and azepane) selectivity and conversion were drastically
297 enhanced in the presence of Ba(OH)₂, giving 80% yield in 1
298 h, which is around 2 times higher compared to the reactivity
299 without the base (Figure 3A). By increasing the reaction time,
300 the selectivity toward HMDA enhanced. This confirmed a
301 clear involvement of Ba(OH)₂ in the reaction cycle (Figures
302 3A and S10B). In contrast, the reaction rate of total amination
303 products was unaffected by the addition of Cs₂CO₃ (Figure
304 3A). Nevertheless, the increased selectivity was tentatively
305 described due to the blockage of surface acidic sites by
306 Cs₂CO₃, which were responsible for byproduct formation. A
307 closer look at the reaction time course showed an increase in
308 the rate of AH formation when Cs₂CO₃ was added (Figure
309 S11).

The recyclability of Ru/C in the presence of Ba(OH)₂ was
studied by recovering the solid residue by vacuum filtration,
followed by washing with an excess hot water to remove the
residual base. The activity and product yields decreased after
the first cycle but attended consistent activity in consecutive
cycles. This phenomenon was quite similar to the Ru/C-catalyzed
recycling experiments, which means the intrinsic catalysis is
due to the presence of Ru/C. However, the base participates in
the reaction cycle and improves the amine yields and conversion

3.3. Involvement of Base in the Reaction Mechanism.

The involvement of Ba(OH)₂ in the reaction mechanism was
investigated by kinetic experiments. Figure S13 shows an
Arrhenius plot from the initial amine formation, and Table 2

Table 2. Kinetic Parameters of Ru/C-Catalyzed Aqueous-Phase Amination of HDO under Base (Ba(OH)₂) and Base-Free Conditions^a

catalyst	base	product	E_a^c /kJ mol ⁻¹	TOF ^d /h ⁻¹ at 463 K
Ru/C ^b	none	AH	68	128
		azepane	187	11
		HMDA	129	22
	Ba(OH) ₂	AH	40	130
		azepane	130	23
		HMDA	125	29

^aReaction conditions: 3.2 mmol HDO, 17.5 mL of 25% aqueous NH₃, and 25 bar H₂. ^bCatalyst weight: 10 mg. ^cAll reactions were conducted at 433–473 K. ^dTOF was calculated by dividing the rate of amine product formation by exposed Ru sites calculated by CO chemisorption experiments as shown in the Supporting Information.

summarizes the turnover frequencies (TOFs) derived from the
initial reaction rates at 463 K and apparent activation energies
at 433–473 K (see the Experimental Section). The time course
shows that AH is formed as an intermediate and is converted
further into HMDA and azepane (Figure S10). The rate of the
AH formation was ~1.5 times higher for the reaction with the
base compared to the reaction without the base at 443 K; a
gradual decrease in the slope by increasing temperature could
be observed. As a result, the initial rates (in both Ba(OH)₂ and
base-free conditions) become close at temperature around 463
K and TOF was 128–130 h⁻¹. This was due to the subsequent
reaction and conversion of AH to secondary products, HMDA
and azepane. The observed TOF values in base and base-free
conditions were quite similar at 463 K. Evidently, a lower

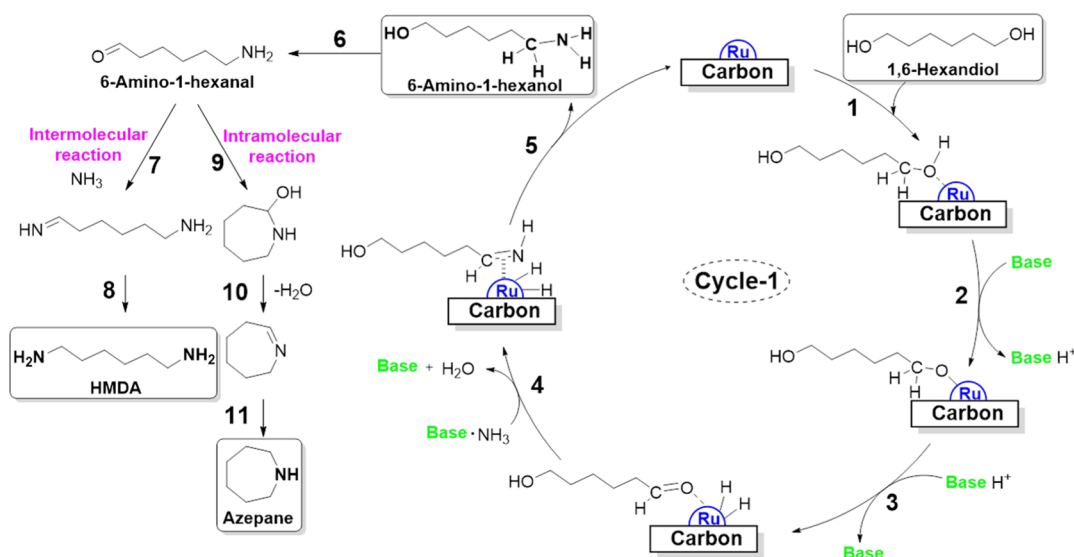


Figure 4. Proposed reaction mechanism and base involvement in Ru/C-catalyzed HDO amination.

338 activation energy (E_a) of 40 kJ mol⁻¹ for AH formation was
 339 estimated in the presence of Ba(OH)₂ from the Arrhenius plot
 340 compared to the reaction in the absence of base (E_a = 68 kJ
 341 mol⁻¹). The TOF for the formation of the cyclic product,
 342 azepane, was about 2 times higher at 463 K than for the base-
 343 free amination. Azepane formation was favored by the addition
 344 of Ba(OH)₂ base and showed a lower E_a of 130 kJ mol⁻¹, while
 345 E_a for base-free conditions was 187 kJ mol⁻¹. Overall, the
 346 apparent activation energies experimentally determined for the
 347 HDO conversion to AH and azepane over Ru/C catalysts
 348 under two different conditions (base and base-free) were
 349 noticeably different. In the presence of a base, the lower
 350 activation energy than the one measured under base-free
 351 conditions indicated the subtle effect of the local environment
 352 of the active sites on the structure and energy of the transition
 353 state. In contrast, the rate of HMDA formation was higher in
 354 the basic solution; however, activation energy was similar to
 355 the non-basic conditions (Figure S13C). This points toward
 356 the fact that by adding a strong base (stronger than NH₃, the
 357 pK_b value of Ba(OH)₂ and NH₃ is 0.15⁴⁸ and 4.75,⁴⁹
 358 respectively), simply more free NH₃ is available for the
 359 reaction. In addition, its higher concentration results in higher
 360 rates rather than lowering of activation energy.

361 **3.4. Proposed Reaction Mechanism for Ru/C-Cata-**
 362 **lyzed HDO Amination.** The results obtained from the
 363 surface analysis and reaction data allowed us to propose the
 364 HDO amination mechanism on Ru/C as shown in Figure 4. In
 365 inert conditions, the Ru/C-catalyzed HDO amination follows
 366 the BHM.⁴² In this mechanism, the hydroxyl group of HDO is
 367 first adsorbed on the Ru sites and favors the dehydrogenation
 368 (abstraction of H₂), which result in the formation of a carbonyl
 369 intermediate and Ru hydride species. Subsequently, the
 370 carbonyl intermediate reacts with NH₃ and results in the
 371 formation of an imine-containing intermediate. The final step
 372 involves the reduction of imine by utilizing hydrogen, which
 373 was abstracted in the form of Ru hydride (in first step), giving
 374 AH and regenerating the Ru sites.

375 In the presence of a base, the adsorption of hydroxyl groups
 376 is favored due to the abstraction of acidic protons of hydroxyl
 377 groups and results in an energetically stable Ru-alkoxy species
 378 and a protonated base (steps 1 and 2).³¹ The protonated base

further releases the proton for the formation of a Ru-hydride 379
 species and an aldehyde (step 3). Together with a base, NH₃ 380
 exists in the molecular form and has a high nucleophilicity for 381
 the reaction with aldehyde and the imine formation (step 4). 382
 The imine is further converted by hydrogenation to AH (step 383
 5). In the presence of external H₂, the rate of step 5 is 384
 enhanced due to the greater number of Ru–H sites available 385
 for the subsequent hydrogenation. This was experimentally 386
 confirmed by varying H₂ pressure during the amination 387
 (Figure S14). The pressure of H₂ clearly showed the influence 388
 in catalysis; the increase in the pressure of H₂ showed the 389
 decrease in AH and the subsequent improvement in the 390
 formation of secondary products without much affecting the 391
 conversion. For the secondary product formation, the hydroxyl 392
 group of AH is adsorbed on the Ru sites, which results in the 393
 formation of a carbonyl intermediate by following steps in the 394
 same manner as shown in steps 1, 2, and 3. The resulted 395
 carbonyl intermediate (6-amino-1-hexanal) comprises alde- 396
 hyde and amine. Once 6-amino-1-hexanal is formed, either 397
 intramolecular amination favors cyclization to azepane or the 398
 reaction with NH₃ results in the formation of a diamine, 399
 HMDA. 400

In the secondary product formation, the base enhances the 401
 reactivity between aldehyde (keto species) and NH₃ by 402
 increasing its nucleophilicity. This was clarified by carefully 403
 analyzing the catalytic results as shown in Figure S15. As stated 404
 earlier, the secondary product formation is favored by inter- or 405
 intra-molecular reaction after the formation of 6-amino-1- 406
 hexanal. Comparing the molar ratio of inter-(HMDA) to intra- 407
 (azepane) molecular products during the reaction course, we 408
 observed a drastic increase in ratio after the addition of 409
 Ba(OH)₂, meaning the reaction between 6-amino-1-hexanal 410
 and NH₃ was highly favored. However, it was unaffected by the 411
 addition of Cs₂CO₃ to the reaction solution. The ratio change 412
 of inter- to intramolecular products was described due to the 413
 different basicity of bases with respect to NH₃. The basicity of 414
 NH₃ (pK_b value = 4.75⁴⁹) was similar to the basicity of CsCO₃ 415
 (pK_b value = 3.27⁵⁰); however, it was much lower than that of 416
 Ba(OH)₂ (pK_b value = 0.15). In the presence of a stronger 417
 base, the equilibrium between NH₃ and NH₃⁺OH⁻ (NH₃ + 418
 H₂O ⇌ NH₄⁺OH⁻) is shifted toward the backward direction, 419

420 and the concentration of free NH_3 is enhanced for the reaction
421 with keto groups.

422 ■ CONCLUSIONS

423 In conclusion, we propose an efficient and green synthesis
424 method for HDO amination catalyzed by recyclable Ru/C in
425 aqueous NH_3 . The addition of a base significantly increased
426 the HDO conversion as well as the formation of amination
427 products. In the presence of Cs_2CO_3 , high selectivity toward
428 AH was achieved by suppressing the side products that
429 occurred on the acidic sites of the carbon support. Contrarily,
430 the addition of $\text{Ba}(\text{OH})_2$ resulted in the fast formation of AH
431 by decreasing the apparent activation energy, which enhanced
432 conversion to the secondary products such as HMDA and
433 azepane. It is proposed that $\text{Ba}(\text{OH})_2$ aids in the initial
434 dehydrogenation step by facilitating better H-abstraction.
435 Additionally, it enables better reactivity between NH_3 and
436 aldehyde-containing intermediates by enhancing the nucleo-
437 philicity of NH_3 .

438 ■ ASSOCIATED CONTENT

439 ■ Supporting Information

440 The Supporting Information is available free of charge at
441 <https://pubs.acs.org/doi/10.1021/acssuschemeng.2c04301>.

442 Literature research; method for catalyst synthesis and
443 characterization; Ru/C characterization result; gas-phase
444 analysis; leaching test; base screening; time course;
445 primary versus secondary products; recycling; Arrhenius
446 plot; and H_2 pressure effect (PDF)

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Notes

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