

Cyclohexanone Conversion Catalyzed by Pt/ γ -Al₂O₃: Evidence of Oxygen Removal and Coupling Reactions

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Abstract The conversion of cyclohexanone, often identified as an intermediate in the conversion of lignin-derived compounds, was catalyzed by Pt/ γ -Al₂O₃ in the presence of H₂ at 573 K. Dehydrogenation was a kinetically significant reaction, indicated by a high selectivity for phenol. Oxygen-removal reactions are indicated by products including benzene, cyclohexene, and cyclohexane. Bimolecular reactions involving cyclohexanone and/or products of its conversion led to the formation of bicyclic C₁₂ compounds, with 2-cyclohexylcyclohexan-1-one and 2-phenylphenol being the most abundant. Increasing the H₂ partial pressure led to increased oxygen removal and faster formation of monocyclic and bicyclic hydrocarbons. At temperatures higher than 573 K, dehydrogenation became the dominant reaction class.

Keywords Cyclohexanone · Supported platinum catalyst · Dehydrogenation · Oxygen removal · Coupling reactions

1 Introduction

Lignin fractions, which constitute as much as about 30 wt% of plant biomass, offer excellent potential as feedstocks for renewable fuels and chemicals [1, 2]. Fast pyrolysis of lignin yields oxygen-rich bio-oils, which

prominently include compounds such as phenols, guaiacols, and syringols [3–5]. Bio-oils upgrading reactions with H₂ catalyzed by supported metals [6–8] can be used to remove oxygen from these compounds to minimize the instability and corrosivity of the liquids.

In investigations of the catalytic reactions of compounds representative of lignin bio-oils (such as phenol [9–12], anisole [13], and guaiacol [3, 14, 15]), cyclohexanone was observed to be a common reaction intermediate. Investigations of the catalytic reactions of cyclic ketones (e.g., cyclohexanone [16, 17] and cyclopentanone [18]) indicated the formation of hydrocarbons with higher carbon numbers than the reactant (typically, C₁₀–C₁₂), which could be useful as components for jet and diesel fuels [19]. However, there is limited information characterizing the reaction networks and kinetics of catalytic cyclohexanone transformations. Most of them are focused on the chemical routes to monocyclic compounds.

Our approach was to investigate the broader reaction network for cyclohexanone conversion with a specific goal of elucidating the oxygen-removal reactions catalyzed by a supported metal, Pt/ γ -Al₂O₃; the reactions occurred in the near absence of catalyst deactivation. The data presented here include a statement of the reaction network and evidence of the influence of changes in the temperature and H₂ partial pressure.

2 Experimental

Powders of Pt/ γ -Al₂O₃ catalyst (1 wt% Pt, Sigma-Aldrich; BET surface area, 206 ± 1 m²/g, Pt dispersion, 0.25) were pre-treated in a flowing stream of H₂/N₂ as the catalyst was heated at a rate of 5 K/min to the desired reaction temperature and then held for 30 min prior to the start of

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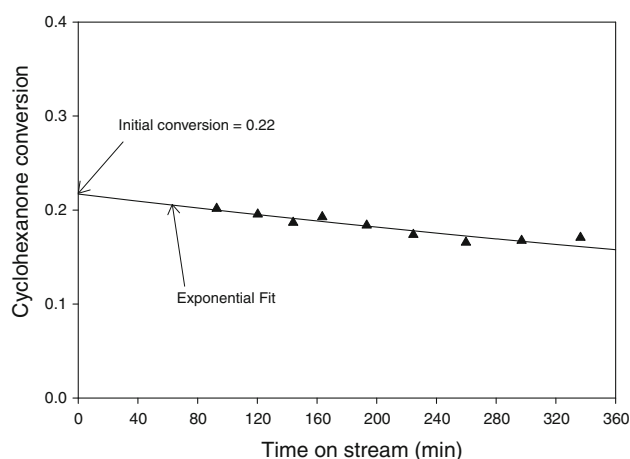


Fig. 1 Change in cyclohexanone conversion catalyzed by Pt/ γ -Al₂O₃ at a WHSV of 56 (g of reactant)/(g of catalyst \times h) at 573 K and 140 kPa. An exponential fit of the data was used to approximate the initial conversion. The fitting equation is as follows and is represented by the line on the figure: $X = 0.22e^{-0.009t}$, where X is cyclohexanone conversion and t is time on stream

reactant flow. Catalytic reactions were performed in a once-through packed-bed tubular reactor under the following conditions, with liquid reactant (99.8 wt% cyclohexanone) vaporized into a flowing gas stream (30% H₂/70% N₂ or H₂): catalyst mass, 0.010–0.100 g (catalyst particles mixed with particles of inert, nonporous α -Al₂O₃); temperature, 523–623 K; pressure, 140 kPa; liquid reactant feed rate, 0.03 mL/min; and gas feed flow rate, 100 mL/min. The downstream product was condensed at 285–288 K. Liquid product samples that were collected periodically and uncondensed gaseous products that were flowing steadily were analyzed by gas chromatography (GC) and gas chromatography/mass spectrometry (GC–MS).

3 Results

More than 15 products of the cyclohexanone conversion catalyzed by Pt/ γ -Al₂O₃ in the presence of H₂ at 573 K were detected. These were identified by GC–MS, using the NIST EI mass spectral database with some compounds being identified with authentic standards. Initial conversions (in the absence of catalyst deactivation) were determined by extrapolating conversion data to zero time on stream (by using an exponential fit, as shown in Fig. 1). Only minimal yields of coke were observed, as the changes in mass of the packed beds containing catalyst and inert α -Al₂O₃ were generally <0.08%. Mass balance closures (Table 1) were typically $96.3 \pm 4.6\%$ (and generally greater than 90%).

The predominant product was phenol; less abundant products were water, cyclohexane, cyclohexene, cyclohexen-1-one, cyclohexanol, and benzene. Several bicyclic (C₁₂) products were detected, including bicyclohexane, cyclohexylbenzene, cyclohexyloxycyclohexane, biphenyl, diphenyl ether, cyclohexyloxybenzene, 2-cyclohexylcyclohexanol, 2-cyclohexylcyclohexan-1-one, dibenzofuran, 2-(1-cyclohexen-1-yl)cyclohexanone, 2-cyclohexylidene-cyclohexan-1-one, 2-phenylphenol, and 2-phenylcyclohexanone. Most of these products were observed at trace levels, except for 2-cyclohexylcyclohexan-1-one and 2-phenylphenol.

Selectivities for formation of the most abundant products formed at an initial cyclohexanone conversion of 0.22 are summarized in Table 2. These data show that dehydrogenation is an important class of reaction observed for the supported metal catalyst, exemplified by the formation of phenol from cyclohexanone. Reactions with H₂ also led to hydrogenation and to oxygen removal as water (i.e., by hydrodeoxygenation (HDO)), exemplified by the formation of benzene from phenol. Dehydration reactions also occurred, leading to removal of oxygen as water without

Table 1 Representative mass balance data characterizing cyclohexanone conversion catalyzed by Pt/ γ -Al₂O₃ in the presence of H₂

Experiment number	Time on stream (min)	Mass of reactant fed ^a (g)	Mass of liquid collected from separator ^a (g)	Mass of product vapor leaving separator ^a (g)	Estimated mass of liquid remaining in separator (g)	Accumulation of solid in catalyst bed ^b (g)	Mass balance closure (%)
1	363	10.30	9.26	0.36	0.5	0.00	98.3
2	350	9.96	8.97	0.34	0.5	0.00	98.5
3	356	10.11	9.29	0.32	0.5	0.00	100.0
4	361	10.23	8.25	0.36	0.5	−0.01	89.1
5	301	8.55	7.73	0.31	0.5	0.00	99.9
6	348	9.92	8.34	0.36	0.5	0.00	92.6
7	326	9.43	8.51	0.33	0.5	−0.01	99.0
8	310	8.62	7.88	0.31	0.5	0.00	100.8

^a Values of the mass of liquid fed, liquid collected from the separator, and reactant leaving the separator in the vapor phase are cumulative for the length of the experiment

^b This term was calculated by subtracting the mass of the packed bed (including quartz wool, inert α -Al₂O₃, and catalyst powder) from the total mass of the solid in this bed recovered at the end of the run

Table 2 Products of conversion of cyclohexanone catalyzed by Pt/ γ -Al₂O₃ (liquid product streams); the cyclohexanone conversion was 0.22

Product	Selectivity to product in reaction catalyzed by Pt/ γ -Al ₂ O ₃ at two H ₂ partial pressures (P_{H_2} , kPa)	
	$P_{H_2} = 39^a$	$P_{H_2} = 131^b$
Cyclohexane	0.006	0.05
Benzene	0.01	0.05
Cyclohexene	0.001	0.002
Cyclohexanol	0.07	0.25
2-Cyclohexen-1-one	0.001	0.0009
Phenol	0.90	0.62
Cyclohexylbenzene	Trace	0.001
Biphenyl	Trace	0.0009
2-Cyclohexylcyclohexan-1-one	0.001	0.004
2-Phenylphenol	0.007	0.009

Data were extrapolated to zero time on stream, and thus represent approximate initial selectivities determined at a weight hourly space velocity of 56 (g of cyclohexanone)/(g of catalyst · h), a pressure of 140 kPa, and a temperature of 573 K. Selectivity is defined as yield [mol product formed/mol of cyclohexanone fed]/conversion [mol of cyclohexanone consumed/mol of cyclohexanone fed]

^a 100 mL/min gas feed rate, 30% H₂/70% N₂; feed molar ratio of H₂ to cyclohexanone was 5

^b 100 mL/min gas feed rate, 100% H₂; feed molar ratio of H₂ to cyclohexanone was 15

the need for H₂, as illustrated by the formation of cyclohexene from cyclohexanol. The bicyclic products were presumably formed in bimolecular reactions (coupling reactions) of (a) two cyclohexanone molecules, (b) cyclohexanone with one of the cyclohexanone conversion products (such as cyclohexene), and (c) two cyclohexanone conversion products.

To determine an approximate reaction network for the conversion of cyclohexanone catalyzed by Pt/ γ -Al₂O₃ in the presence of H₂, selectivity vs. conversion plots (e.g., Fig. 2) were used to identify products as primary or not [20, 21]; a positive intercept indicates a primary product (these designations are empirical, falling short, for example, of providing information about intermediates that were too reactive to be detected).

The selectivity-conversion data (Figs. 2, 3, 4, and 5) indicate that phenol, cyclohexene, 2-cyclohexen-1-one, cyclohexanol, benzene, 2-cyclohexylcyclohexan-1-one, and 2-phenylphenol were primary products, whereas cyclohexane was a non-primary product. Data characterizing the values of the intercepts and the attendant errors are summarized in Table 3.

A semi-logarithmic plot of the fraction of cyclohexanone unconverted as a function of inverse space velocity (Fig. 6) is nearly linear, indicating that the overall

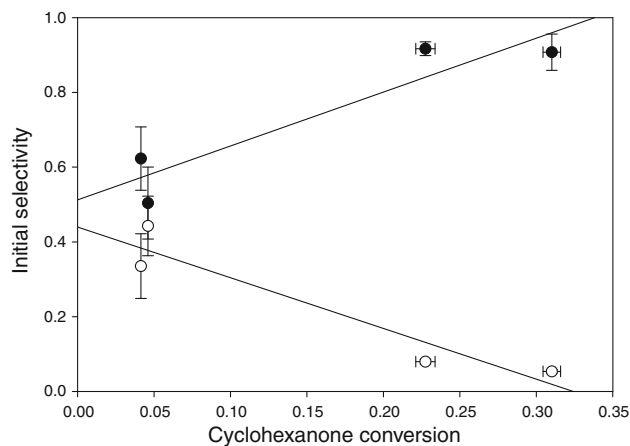


Fig. 2 Selectivity for the formation of phenol (closed circles) and cyclohexanol (open circles) in the conversion of cyclohexanone catalyzed by Pt/ γ -Al₂O₃ in the presence of H₂ at 573 K and 140 kPa. Data for each product were fitted with a straight line and extrapolated to zero conversion; intercepts of regression lines significantly different from zero selectivity at zero conversion (analyzed with 95% confidence limits) indicate primary products, both phenol and cyclohexanol

cyclohexanone conversion is well represented by first-order kinetics over the conversion range investigated. The pseudo first-order rate constant for the disappearance of cyclohexanone was found to be 90 L/(g of catalyst × h).

Presuming that hydrogenation, dehydrogenation, HDO, and coupling reactions are the important reaction classes; by recognizing which compounds were primary and which

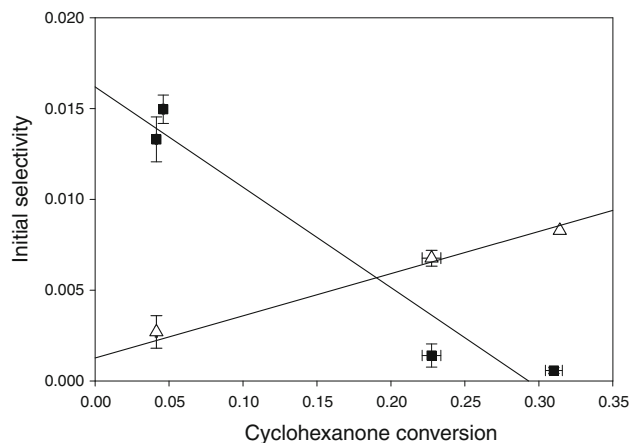


Fig. 3 Selectivity for the formation of 2-cyclohexen-1-one (squares) and cyclohexane (triangles) in the conversion of cyclohexanone catalyzed by Pt/ γ -Al₂O₃; reaction conditions are stated in the text. Data for each product were fitted with a straight line and extrapolated to zero conversion; intercepts of regression lines significantly different from zero selectivity at zero conversion (analyzed with 95% confidence limits) indicate primary products, in this case 2-cyclohexen-1-one, and those not significantly different from zero (analyzed with 95% confidence limits) are considered to be evidence of non-primary products, in this case cyclohexane

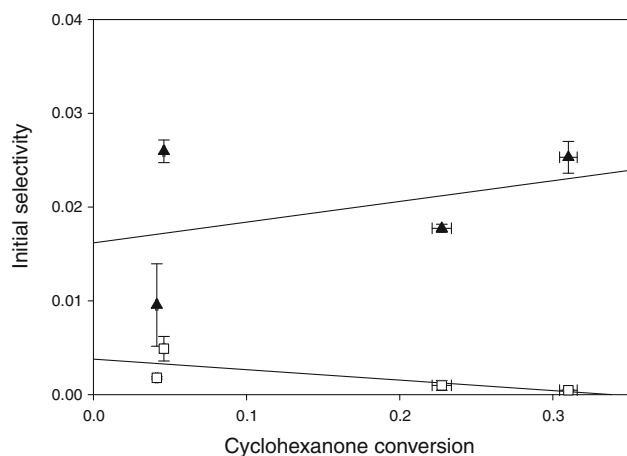


Fig. 4 Selectivity for the formation of benzene (*triangles*) and cyclohexene (*squares*) in the conversion of cyclohexanone catalyzed by Pt/ γ -Al₂O₃; reaction conditions are stated in the text. Data for each product were fitted with a straight line and extrapolated to zero conversion; intercepts of regression lines significantly different from zero selectivity at zero conversion (analyzed with 95% confidence limits) indicate primary products, in this case both benzene and cyclohexene

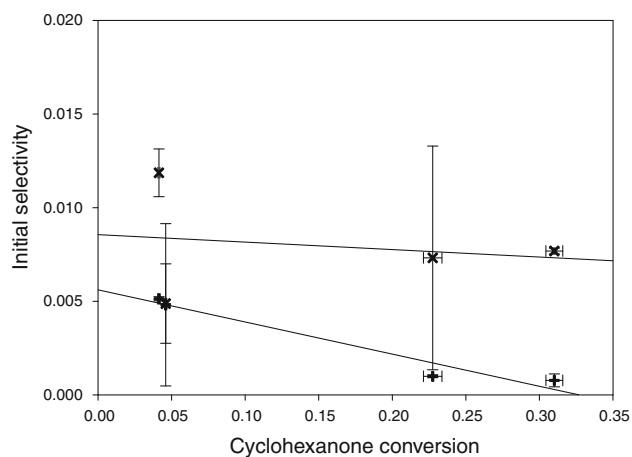


Fig. 5 Selectivity for the formation of 2-phenylphenol (*x*) and 2-cyclohexylcyclohexan-1-one (*+*) in the conversion of cyclohexanone catalyzed by Pt/ γ -Al₂O₃; reaction conditions are stated in the text. Data for each product were fitted with a straight line and extrapolated to zero conversion; intercepts significantly different from zero selectivity at zero conversion (analyzed with 95% confidence limits) indicate primary products, in this case both 2-phenylphenol and 2-cyclohexylcyclohexan-1-one

were non-primary products; and by using our chemical judgment of the most likely classes of reaction for formation of the minor and trace products, we inferred the reaction network of Fig. 7 for cyclohexanone conversion catalyzed by Pt/Al₂O₃ in the presence of H₂.

Our data and the literature broadly show that H₂ plays a crucial role as a co-reactant in several reactions leading to the removal of oxygen from organic compounds in the

Table 3 Summary of initial product selectivities determined from intercept of Figs. 2, 3, 4, and 5

Product	Initial product selectivity at zero cyclohexanone conversion ^a		
	Lower limit	Best value	Upper limit
Cyclohexane	-0.0012	0.0013	0.0038
Benzene	0.0055	0.016	0.027
Cyclohexene	0.0018	0.0038	0.0059
Cyclohexanol	0.33	0.44	0.55
2-Cyclohexen-1-one	0.014	0.016	0.019
Phenol	0.38	0.52	0.65
2-Cyclohexylcyclohexan-1-one	0.0029	0.0056	0.0083
2-Phenylphenol	0.0029	0.0086	0.014

^a The upper-lower limit indicates the interval of values that are not statistically different at 95% confidence level of *p*-test. For example, the data for cyclohexane are characterized by an intercept value that is not statistically different from zero in view of the lower limit of the confidence band; hence it is inferred to be a non-primary product. That is not the case for each of the other products; thus they are inferred to be primary products

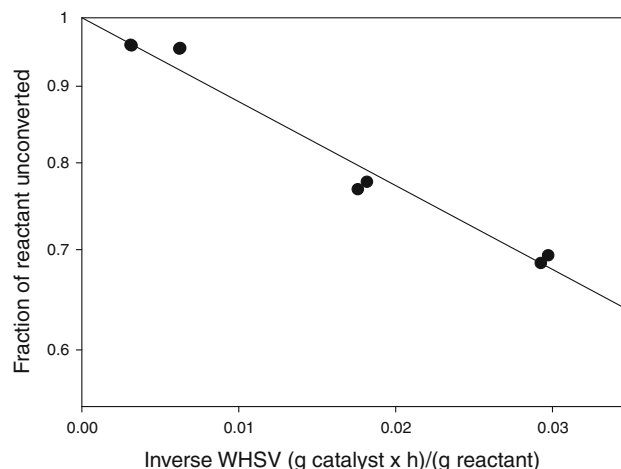


Fig. 6 Demonstration of first-order kinetics of overall conversion of cyclohexanone catalyzed by Pt/ γ -Al₂O₃ in the presence of H₂ at 573 K and 140 kPa. The ordinate scale is logarithmic

presence of supported metal catalysts [6]. To assess the influence of H₂ partial pressure on the cyclohexanone conversion, we performed the reaction experiments at two different H₂ partial pressures. The initial conversion at 573 K was almost unchanged (approximately 0.22) when the reactant gas was switched from 70% N₂/30% H₂ ($P_{N_2} = 92$ kPa, $P_{H_2} = 39$ kPa, $P_{cyclohexanone} = 9$ kPa) to 100% H₂ ($P_{H_2} = 131$ kPa, $P_{cyclohexanone} = 9$ kPa). The comparison of product distributions resulting from this change in reaction conditions is shown in Table 2.

Fig. 7 Reaction network for the conversion of cyclohexanone and H_2 catalyzed by $Pt/\gamma-Al_2O_3$ at 573 K. Reactions are postulated on the basis of the products identified, including trace compounds, and their formation as a result of the likely reaction classes identified in the text. Hydrogenation/dehydrogenation/hydrodeoxygenation reactions are represented by *dashed arrows* and condensation/isomerisation/alkylation/dehydration reactions by *solid arrows*

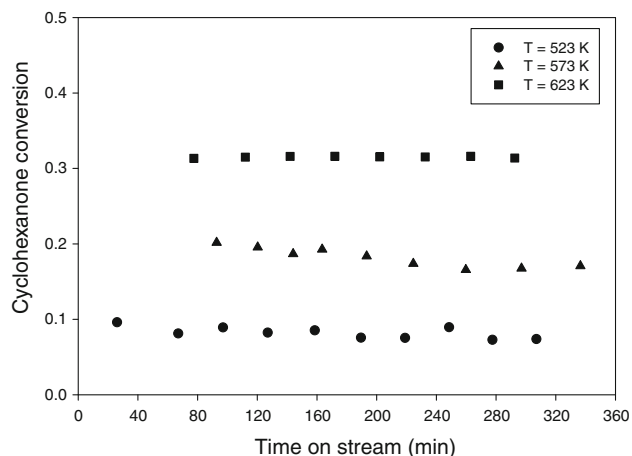
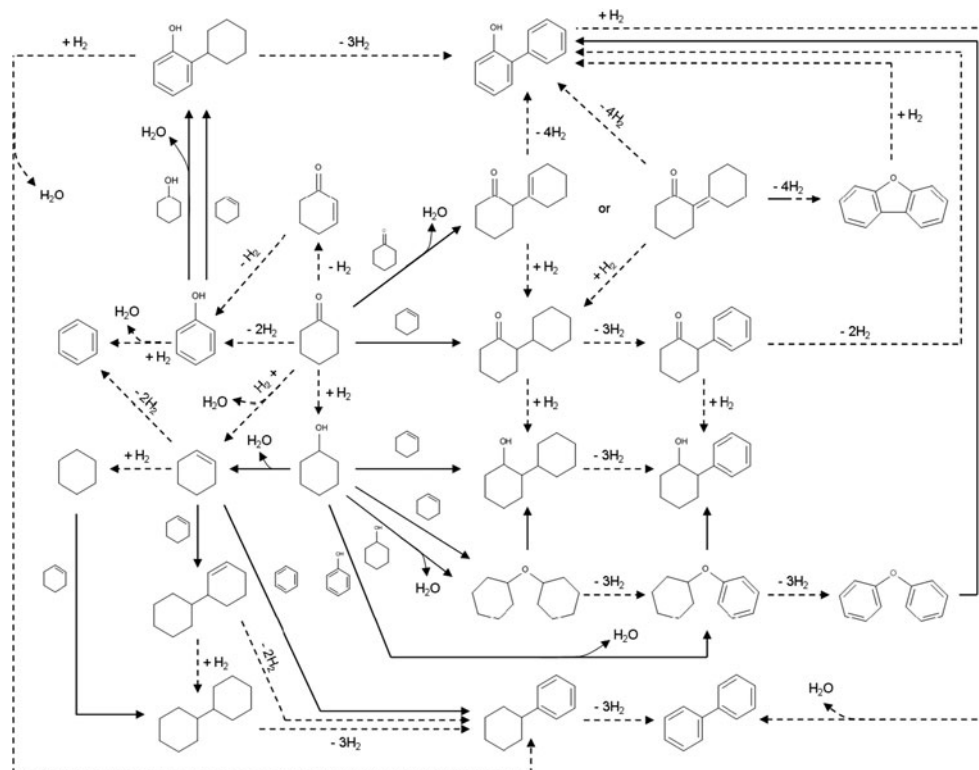


Fig. 8 Change in cyclohexanone conversion catalyzed by $Pt/\gamma-Al_2O_3$ as a function of time on stream in the flow reactor at a WHSV of 56 (g of reactant)/(g of catalyst \times h) at 523 K (circles); at 573 K (triangles), and at 623 K (squares)

Cyclohexanone conversions at a space velocity of 56 (g of cyclohexanone)/(g of catalyst \cdot h) increased as the temperature was raised (0.09 at 523 K, 0.22 at 573 K, and 0.32 at 623 K). Data characterizing the conversion of cyclohexanone as a function of time on stream at various temperatures are shown in Fig. 8. The temperature dependence of the product distributions is summarized in Table 4.

4 Discussion

The reaction network presented in Fig. 7 accounts for major, minor, and trace products in the reactions catalyzed by $Pt/\gamma-Al_2O_3$; it contains more detail than reaction networks reported for the conversion of cyclohexanone in the presence of supported metals and other catalysts. In most of the reported work, only little characterization of reaction networks was presented; the catalysts were sulfided Ni–W [22], Ni/ Al_2O_3 [23], Ni–Mo/ Al_2O_3 [24], Pd/HY zeolite [25], Pt/HZSM-5 [16], and sulfonic acid ion exchange resin [17].

We observed results that are broadly consistent with these reports in terms of the classes of reactions, but we observed different products corresponding to the different catalysts and operating conditions. In the comparable work with the Ni/ Al_2O_3 catalyst [23], cyclohexane was the only major product (formed with a yield of 90%) (the authors did not report the conversion)—in contrast, phenol was our major product, with a selectivity of 90% at a conversion of 0.22 (Table 2). We suggest that the differences are associated with the lower reaction temperature in the reported work (463 K vs. 573 K in our work) and the higher H_2 to cyclohexanone molar feed ratio (\sim 290:1 vs. 5:1 in our work).

Our data show that in the conversion catalyzed by $Pt/\gamma-Al_2O_3$, phenol and 2-cyclohexen-1-one were formed as

Table 4 Products of conversion of cyclohexanone catalyzed by Pt/ γ -Al₂O₃ in the presence of H₂ at various temperatures (liquid product stream). The conversions are stated in the text

Product	Selectivity to product in reaction occurring in presence of H ₂ catalyzed by Pt/ γ -Al ₂ O ₃ ^a at various temperatures (<i>T</i> , K)		
	<i>T</i> = 523	<i>T</i> = 573	<i>T</i> = 623
Cyclohexane	0.008	0.006	0.002
Benzene	0.01	0.01	0.007
Cyclohexene	0.01	0.001	0.0001
Cyclohexanol	0.70	0.07	0.004
2-Cyclohexen-1-one	0.001	0.001	0.0005
Phenol	0.24	0.90	0.98
2-Cyclohexylcyclohexan-1-one	0.004	0.001	0.0004
2-Phenylphenol	0.006	0.007	0.0007

Data were extrapolated to zero time on stream, and thus represent approximate initial selectivities determined at a WHSV of 56 (g of cyclohexanone)/(g of catalyst × h), a pressure of 140 kPa. Selectivity is defined as yield [mol product formed/mol of cyclohexanone fed]/conversion [mol of cyclohexanone consumed/mol cyclohexanone fed]

^a 100 mL/min gas feed rate, 30% H₂/70% N₂; feed molar ratio of H₂ to the organic reactant was 5

primary products, by dehydrogenation of the cyclohexane ring. Hydrogenation of cyclohexanone also occurred simultaneously, as shown by the fact that cyclohexanol was also a primary product. From the selectivity-conversion data, we infer that dehydrogenation was kinetically more favorable than hydrogenation under our reaction conditions as the selectivity for formation of phenol (90%) was significantly higher than the selectivity for formation of cyclohexanol (7%) (Table 2).

These results suggest that cyclohexene was formed as a primary product. We suggest that cyclohexene could be produced along with water by direct HDO of cyclohexanone. In a sequential reaction pathway, dehydration of the primary product cyclohexanol could also have led to formation of cyclohexene [9, 10, 16, 24, 25]. Benzene could be formed either by HDO of phenol or dehydrogenation of cyclohexene. It is unlikely that benzene is produced in a single reaction from cyclohexanone. Thus, we suggest that benzene was not a primary product, although the conversion-selectivity plot (Fig. 4) is consistent with such a designation (although it does not distinguish primary products from higher-order products when the latter are formed via highly reactive, undetectable intermediates). Consequently, we infer that the non-zero selectivity for formation of benzene at zero cyclohexanone conversion implies a relatively high rate of benzene formation relative to phenol and cyclohexene formation.

Several bimolecular reactions are suggested to produce the 12-carbon bicyclic compounds identified in our product stream. We infer that the apparent primary product 2-cyclohexylcyclohexan-1-one was formed by condensation of cyclohexanone and the primary product cyclohexene. Because the intermediate cyclohexene must be formed first, we infer that the alkylation of cyclohexanone with cyclohexene is not a primary reaction and that 2-cyclohexylcyclohexan-1-one is thus not a primary product. The product 2-cyclohexylcyclohexan-1-one could also have been formed by hydrogenation of either 2-(1-cyclohexen-1-yl)cyclohexanone or 2-cyclohexylidenecyclohexan-1-one, which we infer were produced by aldol condensation of cyclohexanone molecules [10, 17]. Dehydrogenation of these two aldol condensation products could also have led to another of the apparent primary products, 2-phenylphenol, consistent with the inference that the dehydrogenation reaction occurred rapidly under current operating conditions.

Similarly, bicyclic C₁₂ compounds were detected in cyclohexanone conversion catalyzed by Pt/HY zeolite [25] and Pt/HZSM-5 [16]; these products include bicyclohexane, cyclohexylcyclohexene, cyclohexylbenzene, 2-(1-cyclohexen-1-yl)cyclohexanone, 2-cyclohexylidenecyclohexan-1-one, 2-cyclohexylcyclohexan-1-one, 2-phenylcyclohexanone, 2-phenylcyclohexanol, 2-cyclohexylphenol, and 2-phenylphenol. These results suggest the occurrence of the same reaction classes that were observed when the catalyst was Pt/ γ -Al₂O₃, Pt/HY zeolite, or Pt/HZSM-5. We infer that cyclohexylcyclohexene and cyclohexylbenzene were formed by alkylation of cyclohexene and benzene with cyclohexene [16]. Bicyclohexane could have been produced by subsequent hydrogenation of cyclohexylcyclohexene. We also infer that dehydration of 2-cyclohexylcyclohexan-1-one could have led to the formation of 2-phenylcyclohexanone. 2-Phenylcyclohexanol could have been formed by pathways including dehydrogenation of 2-cyclohexylcyclohexane and hydrogenation of 2-phenylcyclohexanone. 2-Cyclohexylphenol could have been formed by alkylation of phenol, either with cyclohexanol or cyclohexene [26, 27].

Tricyclic products reported by Alvarez [16] and Silva [25] were not detected in our products, consistent with the presence of weaker acid sites in our catalyst (containing γ -Al₂O₃) than in the catalysts used in the earlier investigations (HY zeolite and HZSM-5). However, we were able to identify other products that were not reported by Alvarez and Silva, including cyclohexyloxycyclohexane, diphenyl ether, and cyclohexyloxybenzene. We infer that these compounds were formed in bimolecular reactions that involve cyclohexanol, which these authors did not observe. It is possible that rapid dehydration of cyclohexanol (to give cyclohexene) occurred more rapidly with HY zeolite and with HZSM-5 than with γ -Al₂O₃, giving cyclohexanol

the opportunity to react to give cyclohexyloxycyclohexane or cyclohexyloxybenzene.

We infer that platinum sites catalyze hydrogenation, dehydrogenation, and HDO and that acidic sites (in HY zeolite, HZSM-5, and γ -Al₂O₃) catalyze dehydration, isomerization, alkylation, and condensation reactions.

When the H₂ partial pressure in the feed was increased approximately threefold, hydrogenation and HDO were significantly favored, as shown by the higher selectivities for cyclohexane, benzene, cyclohexene, and cyclohexanol in this case (Table 2). We infer that dehydrogenation was kinetically less important, as 2-cyclohexen-1-one and phenol were formed with lower selectivities when the H₂ partial pressure was 131 kPa. The higher selectivities for deoxygenated bicyclic C₁₂ compounds (cyclohexylbenzene and biphenyl) bolster the inference that oxygen removal is favored by higher H₂ partial pressures. Thus, the results highlight the importance of H₂ for oxygen removal reactions and point to the possible advantage of high H₂ partial pressures in potential practical processes when oxygen removal is a goal.

The product distribution in the conversion of cyclohexanone is strongly affected by temperature. The data shown in Table 4 show that higher temperatures result in higher selectivities for most products formed by dehydrogenation (especially phenol) and in lower selectivities for products formed by hydrogenation. However, the data do not allow a simple general statement explaining how selectivities for oxygen removal and bimolecular reactions are influenced by temperature because of the occurrence of unresolved parallel and sequential reactions.

5 Conclusions

The catalytic conversion of cyclohexanone catalyzed by Pt/ γ -Al₂O₃ in the presence of H₂ involves several kinetically significant classes of reactions, including hydrogenation, dehydrogenation, HDO, dehydration, isomerization, alkylation, and condensation. Dehydration was found to be kinetically the most significant among the observed reaction classes and was even more favored at the higher temperatures under the conditions of our experiments. Acid-catalyzed alkylation and condensation reactions evidently precede the formation of several bicyclic C₁₂ products. The data suggest that high H₂ partial pressures will be advantageous for selective oxygen removal. The results lead to a better understanding of the catalytic reactions of cyclic oxygen-containing compounds, and they can be incorporated into the reaction networks reported

earlier for the conversion of aromatic oxygen-containing compounds such as guaiacol, anisole, and phenol.

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