JOURNAL OF CATALYSIS **159,** 253–258 (1996)
ARTICLE NO. 0086

Selective Hydrogenation of Benzene to Cyclohexene on Ru/γ-Al_2O_3

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Received July 5, 1994; revised November 1, 1995; accepted November 28, 1995

Hydrogenation of benzene to cyclohexene has been studied over Ru/Al_2O_3 catalysts in the presence of water. Attention has been paid to the influence of reaction conditions, ruthenium precursors, and catalyst pretreatment. The reaction was carried out under kinetic control and under strong mass transfer limitation. In the presence of water the formation of cyclohexene cannot be simply ascribed to physical effects. Mass transfer limitations are, however, important to obtain high selectivities at high conversion. A pretreatment of the catalyst under hydrogen, in the absence of benzene, increases the selectivity to cyclohexene. No effect has been observed when the pretreatment is carried out under nitrogen. Catalysts prepared from $RuCl_3$ are more selective with respect to samples prepared from chlorine-free precursors.

INTRODUCTION

In recent years, selective hydrogenation of benzene to cyclohexene has been extensively investigated and yields up to 45–50% have been reported (1–9). The results obtained are more interesting if one considers that when applying the traditional catalytic systems only cyclohexane is formed.

A survey of the literature data shows that in order to obtain high yields of cyclohexene, the hydrogenation of benzene has to be carried out over ruthenium catalysts in the presence of an aqueous salt solution.

Notwithstanding the large number of patents and papers which have appeared in the recent past, the chemistry of the catalytic system used and the role of water have not been fully explained. The interpretation of the results is generally complicated by the fact that the reaction is carried out under diffusion constraints and in the presence of contaminants which stem from the reaction vessel. In this paper we report the results of a systematic investigation carried out on Ru/Al_2O_3 catalysts under mild conditions ($T_r = 333$ K) in order to minimize the influence of mass transfer limitations on the cycloolefin formation. A reactor made of Teflon has been used to avoid contamination by metals. Catalysts prepared from different ruthenium precursors and with different metal loading have been investigated to get information on the role of precursor on the catalytic performance.

EXPERIMENTAL

Ru/Al_2O_3 catalysts were prepared by impregnation of the support (γ-Al_2O_3, Rhone Poulenc, particle size 62–125 μm, surface area 220 $m^2\ g^{-1}$) with different Ru precursors. (See Table 1.) The precursors used were an acidic aqueous solution of $RuCl_3$ in HCl (10% wt), an aqueous solution of $Ru(NO)(NO_3)_3$, and a toluene solution of $Ru(acac)_3$. Catalysts ex-$RuCl_3$ and ex-$Ru(NO)(NO_3)_3$ were obtained by the incipient wetness impregnation method. Catalysts ex-$Ru(acac)_3$ were obtained by contacting the Al_2O_3 support with an excess toluene solution of $Ru(acac)_3$ for several hours. The amount of ruthenium on the catalyst was varied from 0.1 to 20 wt%. Catalysts ex-$RuCl_3$ and ex-$Ru(NO)(NO_3)_3$ were dried at 423 K for 1 h and then reduced in flowing H_2 at 673 K for 2 h. Reduction conditions for samples prepared from $Ru(acac)_3$ are reported elsewhere (10).

The dispersion of Ru was determined by H_2 chemisorption at 373 K (10). Metal surface areas and particle size were calculated assuming $H/Ru = 1$ and a Ru surface density of 1.63×10^{19} atoms m^{-2}. Hydrogenation of benzene was carried out in an autoclave (BERGHOF model BAR 1845). The reaction vessel and all the internal parts in contact with the reaction mixture were made of Teflon in order to avoid metal contamination. During each run the reactor was connected to a H_2 cylinder and the pressure was maintained constant throughout the experiment.

Before catalytic activity measurements, catalyst samples (100–200 mg) were treated *in situ* with H_2O (100 cc) and H_2 (3 MPa) at 423 K, unless otherwise specified. After treatment, 25 cc of degassed benzene was introduced into the reaction vessel (containing 100 cc of water) through the gas entrance tube, avoiding any contact of the catalyst with air.

RESULTS AND DISCUSSION

Mass Transfer Limitations

Preliminary runs carried out with several Ru/Al_2O_3 catalysts have shown that hydrogenation of benzene (in the absence of water) leads to the formation of only cyclohexane

0021-9517/96 $18.00

TABLE 1

Chemical Composition, H/Ru, Ratio, and Metal Particle Size, *d* (nm), of Ru/Al_2O_3 Catalysts

Catalyst	Precursor	Ru (wt%)	H/Ru	*d*(nm)	TEM
A	$RuCl_3$	0.1	—	—	
B	$RuCl_3$	0.5	0.19	7.1	
C	$RuCl_3$	1	0.28	4.8	
D	$RuCl_3$	2	0.18	7.4	
E	$RuCl_3$	4	0.16	8.4	
F	$RuCl_3$	10	0.10	13.2	
G	$Ru(acac)_3$	1	0.88	1.6	(1)
H	$Ru(acac)_3$	2.5	0.44	3.0	(2)
I	$Ru(acac)_3$	4	0.25	5.4	(3)
L	$Ru(NO)(NO_3)_3$	1	0.23	5.8	(4)
M	$Ru(NO)(NO_3)_3$	2.5	0.23	5.8	
N	$Ru(NO)(NO_3)_3$	4	0.26	5.2	
O	$Ru(NO)(NO_3)_3$	20	0.17	7.0	

Note. TEM observation from Ref. (13): (1) particles of 0.8–1.5 nm, narrow distribution; (2) bimodal distribution around 1 and 6 nm; (3) particles of 1–10 nm, wide distribution; (4) particles of 1–10 nm, bimodal distribution.

in the whole range of temperatures investigated. No cyclohexene was observed even at conversion as low as 1%. In the presence of liquid water the rate of reaction is slowed down by a factor of about two and cyclohexene is formed together with cyclohexane. In Fig. 1 is reported a typical course of reaction carried out in the presence of water. A decrease of activity of a factor of about three was previously observed by Struijk *et al.* (3) on Ru supported on Al_2O_3 in the presence of water. The positive effect of water on the formation of cyclohexene has been previously reported by several authors (3, 4, 7, 12).

Struijk *et al.* (3, 4), working with unsupported Ru, salt-containing water, and an H_2 pressure of 5 MPa, report that due to the low solubility of hydrogen and of the organic substrate in water, the reaction is diffusionally retarded. Under their conditions, the concentration of hydrogen on the catalytic surface is very low and therefore the rate of hydrogenation of the adsorbed cyclohexene is slowed down, favoring its desorption. Moreover, due to the low solubility of cyclohexene in water, the rate of readsorption is low and therefore its transformation to cyclohexane occurs at longer contact times. The importance of the hydrogen mass transfer limitations on cyclohexene yields has been pointed out also by Odenbrand and Lundin (1).

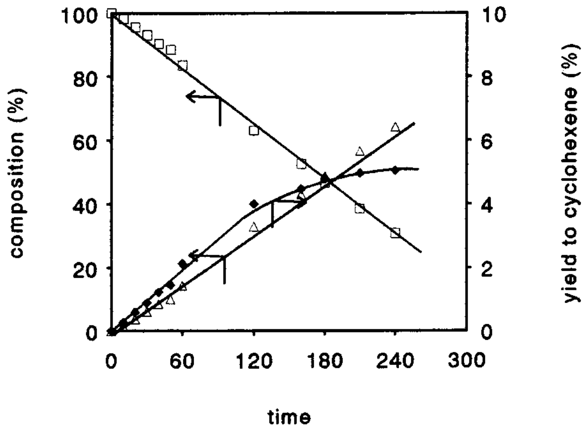

FIG. 1. Hydrogenation of benzene over Ru/Al_2O_3. Reaction conditons: $T_r = 333$ K, $P_{H_2} = 3$ MPa, catalyst D.

To acquire more information on the influence of water outside the region of mass transfer limitations, we have studied the hydrogenation of benzene in aqueous phase, using conditions under which it is possible to minimize, at least in some cases, the diffusion constraints and we have compared the results with data obtained under diffusional limitations.

A reaction temperature of 333 K was used in order to run, at least on one sample, the reaction under kinetic control. The drawback of working at low temperature is that under these conditions cyclohexene yields are low.

Gas–liquid mass transfer limitations can be eliminated by appropriate stirring conditions. This was verified by a series of experiments carried out using different amounts of catalyst (13).

To evaluate the extent of mass transfer limitations related to diffusion from the liquid to the solid phase and within the catalyst particles, the Carberry and Wheeler–Weisz criteria have been adopted (14, 15). The Carberry number, Ca, and the Wheeler–Weisz group $\eta\varphi^2$ have been calculated by the expressions

$$\mathrm{Ca} = \frac{V_{\mathrm{obs}}}{k_{\mathrm{ls}}(6 \cdot W/d_p \cdot \rho_p)C}$$

$$\eta\varphi^2 = \frac{d_p^2}{4D_{\mathrm{eff}}} \cdot \frac{1}{V_p} \cdot V_{\mathrm{obs}} \cdot \frac{1}{C},$$

where

V_{obs}	observed rate (mol s^{-1})
k_{ls}	calculated mass transfer coefficient (m s^{-1})
W	catalyst weight (g)
d_{p}	mean particle diameter (m)
ρ_p	catalyst apparent density (g cm^{-3})
C	solubility in water of H_2, C_6H_6 C_6H_{10} (mol cm^{-3})
D_{eff}	calculated diffusion coefficient (m^2 s^{-1})
V_{p}	catalyst volume $(cm)^3$.

k_{ls} and D_{eff} were calculated according to Refs. (13) and (16), respectively. Values of k_{ls} of 4.44×10^4 m s^{-1}, 1.65×10^{-4} m s^{-1} and 1.54×10^{-4} m s^{-1} were used for H_2, C_6H_6, and C_6H_{10}, respectively. Values of D_{eff} of 6.83×10^{-9} m^2 s^{-1}, 2.17×10^{-9} m^2 s^{-1}, and 2.09×10^{-9} m^2 s^{-1} were used for H_2, C_6H_6, and C_6H_{10}, respectively.

TABLE 2

Carberry Values (Ca), Wheeler Weisz Group ($\eta\varphi^2$), Selectivity to Cyclohexene, and Rate of Disappearance of Benzene Calculated on Catalyst A (0.1 wt% Ru): $T_r = 333$ K, $P_{H_2} =$ 3 MPa, $W = 0.1047$ g

Conv. (%)	$SelC_6H_{10}$ (%)	$v_{obse}C_6H_6$ (mol/s) (10^7)	$Ca_{C_6H_6}$ (10^3)	$Ca_{C_6H_{10}}$ (10^3)	Ca_{H_2} (10^3)	$\eta\varphi^2{}_{C_6H_6}$ (10^2)	$\eta\varphi^2{}_{C_6H_{10}}$ (10^2)	$\eta\varphi^2{}_{H_2}$ (10^2)
6.97	17.36	1.85	1.83	4.52	2.00	1.55	3.99	1.50
11.07	15.89	1.84	1.82	4.11	2.00	1.54	3.49	1.50
15.62	14.21	1.85	1.83	3.70	2.00	1.55	3.26	1.50
22.29	11.30	1.85	1.83	2.94	2.00	1.55	2.59	1.50
27.56	10.84	1.85	1.83	2.82	2.08	1.55	2.49	1.56
39.95	8.76	1.84	1.82	2.27	2.12	1.54	1.93	1.59
60.42	3.87	1.84	1.82	1.00	2.16	1.54	0.85	1.62
78.75	2.43	1.85	1.83	0.63	2.12	1.55	0.55	1.59

The values of V_{obs} ($V_{obs} = dn/dt$) used to calculate the Carberry and Wheeler–Weisz group for C_6H_6, C_6H_{10}, and H_2 are, respectively, the observed rate of disappearance of C_6H_6, the observed rate of formation of C_6H_{10}, and the observed rate of consumption of H_2. A value of Ca smaller than 0.05 indicates that diffusion retardation by external mass transport may be neglected (13), whereas a value of $\eta\varphi^2$ smaller than 0.1 means that pore diffusion limitation is negligible (13).

Tables 2– 4 report the Carberry and Wheeler–Weisz values for C_6H_6, C_6H_{10}, and H_2, calculated on the catalysts A, B, and D. As shown in Table 2, which reports the results obtained on the catalyst with the lowest ruthenium loading (catalyst A), the Carberry numbers are far less than 0.05 for all substrates in all ranges of conversions. Also the values of the Wheeler–Weisz group are less than 0.1 at all reaction times. This indicates that the reaction is always under kinetic control.

Table 3 reports the Ca numbers calculated when the reaction is carried out on catalyst B. The Ca numbers found for C_6H_6 and H_2 are very near the limiting value of 0.05. The Ca values for C_6H_{10} are higher and in the range 0.1–0.2. Also, the $\eta\varphi^2$ values are higher than 0.1. These results indicate that on catalyst B the reaction is carried out mainly under cyclohexene liquid–solid diffusion constraints and pore diffusion limitations.

Table 4 reports the Ca numbers calculated on catalyst D. In this case the Ca numbers for all substrates are higher than 0.05, showing that there is a strong resistance of the liquid–solid diffusion for all substrates. The $\eta\varphi^2$ values calculated for all substrates are higher than 0.1 and indicates that also in this case the reaction is influenced by pore diffusion limitations.

It is noteworthy that in our case the rate of disappearance of benzene is practically constant in almost all ranges of conversions investigated. This is in agreement with the fact that due to its low solubility the concentration of benzene in the water phase is constant regardless of the conversion. The decline of the rate of reaction with time observed by Struijk *et al.* (3) could be instead related to a poisoning of the catalyst by iron salts originating from the stainless steel reactor walls.

Figures 2A and 2B show the yields and the selectivities to cyclohexene measured on catalysts A, B, and D as a function of benzene conversion.

At low conversion (<20%) selectivity to cyclohexene is similar on all three catalysts investigated regardless of diffusion constraints. Differences are instead observed at higher

TABLE 3

Carberry Values (Ca), Wheeler Weisz Group ($\eta\varphi^2$), Selectivity to Cyclohexene, and Rate of Disappearance of Benzene Calculated on Catalyst B (0.5 wt% Ru): $T_r = 333$ K, $P_{H_2} = 3$ MPa, $W =$ 0.309 g

Conv. (%)	$Sel_{C_6H_{10}}$ (%)	$v_{obe}C_6H_6$ (mol/s) (10^6)	$Ca_{C_6H_6}$	$Ca_{C_6H_{10}}$	Ca_{H_2}	$\eta\varphi^2{}_{C_6H_6}$	$\eta\varphi^2{}_{C_6H_{10}}$	$\eta\varphi^2{}_{H_2}$
7.40	16.75	8.08	0.08	0.19	0.08	1.39	3.47	1.37
13.77	15.68	8.08	0.08	0.18	0.08	1.39	3.25	1.38
17.19	14.77	8.07	0.08	0.17	0.08	1.39	3.05	1.35
21.46	11.88	8.03	0.08	0.14	0.08	1.38	2.44	1.36
42.14	10.51	7.92	0.08	0.12	0.09	1.36	2.13	1.39
53.91	8.92	7.99	0.08	0.10	0.08	1.37	1.83	1.38
62.39	8.49	7.92	0.08	0.09	0.08	1.36	1.72	1.38

TABLE 4

Carberry Values (Ca), Wheeler Weisz Group ($\eta\varphi^2$), Selectivity to Cyclohexene, and Rate of Disappearance of Benzene Calculated on Catalyst D (2 wt% Ru): $T_r = 333$ K, $P_{H2} = 3$ MPa, $W = 0.2007$ g

Conv. (%)	$Sel_{C_6H_{10}}$ (%)	$v_{obs}C_6H_6$ (mol/s) (10^5)	$Ca_{C_6H_6}$	$Ca_{C_6H_{10}}$	Ca_{H_2}	$\eta\varphi^2{}_{C_6H_6}$	$\eta\varphi^2{}_{C_6H_{10}}$	$\eta\varphi^2{}_{H_2}$
1.78	15.48	1.39	0.22	0.48	0.29	7.93	18.27	3.69
16.42	12.99	1.38	0.21	0.40	0.29	8.20	15.84	3.65
36.85	10.85	1.38	0.21	0.33	0.30	8.20	13.23	3.72
47.48	9.41	1.38	0.21	0.29	0.29	8.23	11.52	3.71
53.41	8.95	1.38	0.21	0.27	0.30	7.93	10.56	3.73
61.48	8.07	1.38	0.21	0.25	0.30	8.20	9.84	3.76
62.24	7.29	1.38	0.21	0.22	0.30	8.09	8.78	3.74

degrees of conversion. On catalyst A, on which the reaction is carried out under kinetic regime, cyclohexene yields reach a maximum at a conversion of about 40% and then decreases following the known behavior of a consecutive reaction. On catalyst B, where the reaction is carried out under cyclohexene liquid–solid diffusion constraints and pore diffusion limitation for all substrates (Table 3), the decrease of selectivity to the cycloolefin with conversion is slower and the yield increases in all ranges of conversion investigated. On catalyst D, where the reaction is carried out under mass transfer limitations for all substrates and under strongly pore diffusion limitation, selectivity to cyclohexene follows the same trend already observed on catalyst B. Moreover it has been observed that on all samples the selectivity to cyclohexene remains constant regardless of the H_2 pressure (0.1–4 MPa). The possibility that the observed differences are related to the different metal particle sizes present on the investigated catalysts is quite unlikely. As will be discussed later, at conversion <20%, where the influence of cyclohexene mass transfer diffusion is lower, the cyclohexene selectivity was found almost constant in all ranges of metal particle size investigated.

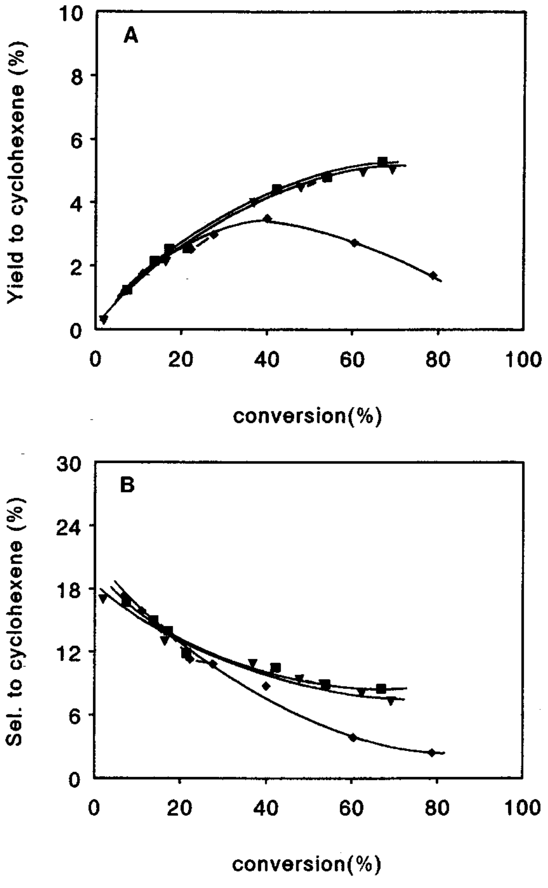

FIG. 2. (A) Yield to cyclohexene as a function of benzene conversion measured on catalysts A(◆), B(▼) D(■). Reaction conditions: $T_r = 333$ K, $P_{H2} = 3$ MPa. (B) Selectivity to cyclohexene as a function of benzene conversion measured on catalysts A(◆), B(▼), D(■). Reaction conditions: $T_r = 333$ K, $P_{H2} = 3$ MPa.

From the reported results some interesting considerations can be made. Selectivity to cyclohexene seems to be scarcely dependent on the liquid–solid diffusion limitations of H_2. In all ranges of conversion investigated, selectivity to cyclohexene is the same on catalyst B, where liquid–solid diffusion resistance for H_2 is almost negligible ($Ca_{H2} = 0.08$), and on catalyst D, where it cannot be neglected ($Ca_{H2} = 0.30$). This can be explained if we consider that the availability of hydrogen on the catalyst surface can affect the reaction selectivity if the hydrogen concentration in the rate expressions for competing reaction appears to a nonequal power (17). Hydrogenation of C_6H_6 and C_6H_{10} have been reported to show the same order of reaction with respect to H_2 (18, 19), therefore hydrogen-rich or hydrogen-poor conditions should influence in same way the hydrogenation of the two substrates causing no variations in the selectivity to the intermediate cyclohexene. This is also in agreement with the results of the runs carried out at different H_2 pressure, which showed no variations in the reaction selectivity.

The liquid–solid diffusion resistance of cyclohexene seems instead to influence greatly the cyclohexene yields, especially at higher conversions (Fig. 2A). It can be suggested that under a kinetic regime (Fig. 2A and 2B, catalyst A), cyclohexene can easily escape from the catalytic surface to the organic phase where it is more soluble. Increasing the amount of cyclohexene, it can be easily readsorbed and hydrogenated to cyclohexane. In fact at higher conversion the selectivity decreases rapidly (Fig. 2B).

When, instead, the liquid–solid diffusion resistance of C_6H_{10} cannot be neglected (catalyst B) it is observed that whereas the initial selectivity to cyclohexene (up to 20% of conversion) is similar to that observed on catalyst A, at higher conversions a higher selectivity is found on catalyst B (Fig. 2B). It can be suggested that at low conversion the rate of hydrogenation of cyclohexene is low due to its low concentration and the diffusion phenomena do not influence the cycloolefin selectivity. At higher conversions, instead, the resistance of cyclohexene to migration towards the catalytic surface decreases its rate of hydrogenation to cyclohexane.

Accordingly with Struijk *et al.* (3) our results confirm that in order to obtain a higher cyclohexene yield, it is important to operate under mass transfer limitations which slow down the rate of cyclohexene readsorption. However, to reach high cycloolefin yields it is also necessary to have a high initial value of selectivity, which is obtained with addition of water.

The question which remains open is: what is the role of water on cyclohexene formation?

Niwa *et al.* (7) have suggested that on a hydrophylic catalytic surface, water is adsorbed more strongly than benzene and cyclohexene. Therefore water expels easily the formed cycloolefin from the catalytic surface through a competitive adsorption. Struijk *et al.* (20) have instead reported that water can bind the intermediate cyclohexene through hydrogen bonding, thus decreasing the adsorption strength of the cycloolefin. A preferential adsorption of water molecules on strongly bonding ruthenium sites on which cyclohexane is preferentially formed has been also proposed (20).

It is interesting to note that the selectivity to cyclohexene ($S = 14\%$) measured on catalyst D at a conversion of about 50% ($T_r = 423$ K), even though it is too low for an industrial exploitation of our system, is about two times higher than that reported (in the absence of additives) by Struijk *et al.* (3) on similar Ru/Al_2O_3 catalyst at the same conversion value.

Catalyst Pretreatment

The influence of different catalyst pretreatments on the selectivity to cyclohexene has also been investigated. An influence of catalyst pretreatment inside the reaction vessel has been previously reported on unsupported Ru catalysts and attributed to the effect of metal cations originating from corrosion of the stainless steel wall of the reactor which are adsorbed on the catalyst surface (1, 4, 9). For this systematic study, catalyst D and reaction conditions of $T_r = 333$ K and $P_{H2} = 3$ MPa were used. Pretreatments of the catalyst sample were carried out within the reaction vessel in the presence of liquid water under H_2 or N_2. The effect of catalyst pretreatment was evaluated comparing the selectivity to cyclohexene calculated at 10% of benzene conversion, where the diffusional limitations have been found to scarcely influence the cyclohexene formation. Selectivity to cyclohexene doesn't change when pretreatment is carried out at different temperature (300–423 K), pretreatment time (1–6 h), or gas pressure (0.1–3 Mpa) under N_2 atmosphere. After a treatment under H_2 we have found, instead, that selectivity to cyclohexene increases from 9 to 16%, raising the pretreatment temperature from 300 to 423 K and the H_2 pressure from 0.1 MPa up to 3 MPa.

To verify the positive effect of an hydrogen pretreatment on the selectivity to cyclohexene, we have reduced the catalyst at 423 K under H_2 pressure (in the absence of liquids). Then avoiding any contact of the catalyst with air, we added water and the catalyst was treated under N_2 pressure (3 MPa) for 1 h at 423 K. The selectivity to cyclohexene measured under these conditions (14%) is similar to that obtained after pretreatment in H_2 in the presence of water. This result suggests that the higher selectivity to cyclohexene is related to a more reduced catalyst.

Metal Particle Size and Ruthenium Precursor

The influence of ruthenium particle size on the selectivity to cyclohexene is reported in Table 5. The selectivity has been measured at 10% conversion, where it was found to be scarcely influenced by the diffusional limitations.

From the results reported in Table 5, it can be noted that within each series of catalysts prepared from the same pre-

TABLE 5

Selectivity to Cyclohexene Measured on Catalysts Prepared by Different Precursors (Reaction Conditions: $T_r = 333$ K, $P_{H2} = 3$ MPa)

Catalyst	Precursor	d (nm)	Selectivity[a] C_6C_{10}	N (mol g Ru_s^{-1} s^{-1}) (10^2)
B	$RuCl_3$	7.1	16	2.76
C	$RuCl_3$	4.8	15	2.46
D	$RuCl_3$	7.4	16	1.92
E	$RuCl_3$	8.4	17	2.74
F	$RuCl_3$	13.2	18	2.77
G	$Ru(acac)_3$	1.6	10	0.48
H	$Ru(acac)_3$	3.0	8	1.03
I	$Ru(acac)_3$	5.4	11	2.33
L	$Ru(NO)(NO_3)_3$	5.8	6	0.92
M	$Ru(NO)(NO_3)_3$	5.8	6	1.39
N	$Ru(NO)(NO_3)_3$	5.2	7	1.48
O	$Ru(NO)(NO_3)_3$	7.0	8	0.43

[a] Measured at 10% conversion.

cursor, a variation of the Ru particle size in the range 2–13 nm does not change the selectivity to cyclohexene. Even though the range of particle size investigated is relatively narrow, it is in this region that the largest variations would be expected (21). The insensitivity of the selectivity to cyclohexene to variations of the ruthenium particles size suggests that hydrogenation of benzene and cyclohexene occur on the same sites or at least on sites of similar coordination number. Table 5 also reports the overall turnover rate N (per gram of Ru on the surface) for all catalysts investigated. No attempt has been made to correlate the metal particle size with the turnover rate due to the fact that on most of the samples the reaction is carried out under mass transfer limitations.

From Table 5 it can be also noted that the selectivity to cyclohexene depends on the precursor used for the preparation of the samples. Catalysts obtained from $RuCl_3$ are more selective than the catalysts prepared by using $Ru(acac)_3$ or $Ru(NO)(NO_3)_3$. A higher selectivity to cyclohexene on catalysts prepared from $RuCl_3$ has been previously reported for unsupported samples (1).

After having ruled out the influence of the metal particle size on the selectivity (Table 5), the better performance of the samples ex-$RuCl_3$ is likely to be related to residual chlorine present on the catalyst surface. It has been reported that on Ru/Al_2O_3 prepared from $RuCl_3$, chlorine is not completely eliminated even after treatment in H_2 at 800°C (22). Several hypothesis can be advanced about the positive effect of chlorine. The presence of residual chlorine could modify the electronic state of the ruthenium sites favoring the formation of $Ru^{(\delta+)}$ species. This hypothesis, however, cannot explain the higher selectivity on the chlorine-containing samples. In fact, it has to be recalled that from our investigation on the effect of the catalyst pretreatment it has been concluded that the selectivity is higher on a more reduced Ru sample. It is possible that due to the presence of chlorine the strongest bonding sites are preferentially occupied by Cl, leaving the weakly bonding sites for the adsorption of cyclohexene. This indeed would enhance the selectivity to cyclohexene. Another possible explanation could be related to a higher hydrophilicity of the surface caused by adsorbed chlorine. The chloride ions anchored on the catalyst surface can bond water molecules through hydrogen bonding. This increases the strength of the water–surface bond, thus improving cyclohexene production.

CONCLUSIONS

The results reported in this paper have shown that in the hydrogenation of benzene carried out in the presence of water the formation of cyclohexene cannot be simply ascribed to physical effects. The presence of cyclohexene mass transfer limitations are, however, important to obtaining high yields by slowing down cyclohexene readsorption.

Catalysts pretreated under more severe reduction conditions show a higher selectivity to cyclohexene. A significant effect of the precursor used has also been observed. Samples containing residual chlorine are more selective towards cyclohexene formation.

ACKNOWLEDGMENTS

This work has been carried out with the financial support of C.N.R. and M.U.R.S.T. The authors thank Professor S. Galvagno for helpful discussions.

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