

Effect of rhodium precursor and thermal treatment on the hydrogenation of 2-cyclohexenone on Rh/SiO₂ Catalysts

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Abstract

The hydrogenation of 2-cyclohexenone in liquid phase was studied at 298 K on Rh/SiO₂ catalysts. The kinetic parameters found were: zero order for the ketone and first order for the hydrogen. The hydrogenation of the C=C double bond was affected by the carbonyl group, i.e., the C=O function of the unsaturated ketone anchors on the metal surface thus increasing the residence time of the molecule on the substrate. In catalysts prepared either with RhCl₃ · 3H₂O or with Rh-acetylacetonate, the reaction was found to be 'structure-insensitive'. A precursor effect was observed: the chlorinated catalysts showed higher activity than the non chlorinated ones. Notable enhancement of the activity per site was observed when the Rh catalysts were thermally treated under hydrogen + water vapor at high temperature. The enhancement in activity was related to the formation of 'weakly' adsorbed hydrogen on the metal surface. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The selective hydrogenation of carbon-carbon multiple bonds of alkenes, alkynes, aromatics and carbonyl groups are important reactions for the synthesis of various fine chemicals [1]. A large number of papers have been published with the aim of establishing the mechanism of hydrogenation of these reducible func-

tions [2–5]. Particular attention has been given to the hydrogenation kinetics of unsaturated C=C double bonds of alkenes. Studies have been made on metals of group VIII, specially on nickel, platinum, palladium and rhodium [5–8]. The reaction order with respect to the alkene at all hydrogen pressures varies generally between one and zero. It has been shown that an additional reducible function such as a C=C in the case of dienes or a C=O function in cyclohexenone, modifies the reaction order of the mono functional compound. For example, the

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reaction order for hydrogenation of 1,3 butadiene was found to be negative: -0.7 on platinum [9], -2 on copper [10] and -0.5 over ruthenium [11], while the order with respect to hydrogen was found to be constant (around 1.0). In the 2-cyclohexenone hydrogenation, a negative order has been observed, in contrast to the positive order found for the cyclohexene hydrogenation [12]. It seems that the kinetic parameters for hydrogenation of poly-unsaturated compounds are well established [13].

Using various supported metal catalysts cyclohexene hydrogenation in gas phase [6,14,15] or liquid phase [15–17], this reaction has been reported as a structure insensitive. However, the effect of particle size on the activity per site (TOF) during the hydrogenation of a C=C double bond associated to a C=O unsaturation has been barely studied [12].

In the present work, the kinetics, the effect of the precursor, as well as the particle size, and the thermal treatment on hydrogenation of 2-cyclohexenone and cyclohexene using Rh/SiO₂ catalysts are reported.

2. Experimental

2.1. Chemicals

High purity hydrogen (99.99%) was used for all catalytic experiments and adsorption measurements. The support used was SiO₂ from AKZO Chemie, which was calcined in flowing air at 773 K before impregnation. Rh-acetylacetonate (Aldrich, 99.8%) and RhCl₃ · 3H₂O (ICN) were used as metal precursors. Reactants were 2-cyclohexenone (Aldrich, 97%) and cyclohexene (Aldrich, 99%), used without further purification.

2.2. Catalyst preparation

Catalysts were prepared by impregnation of the silica support via a solution containing the

Rh precursor, i.e., Rh-acetylacetonate in benzene [13] or RhCl₃ · 3H₂O in water. Metal solution and support were stirred, then the solvent was evaporated in a vacuum evaporator. Afterwards, the solids were dried in an oven at 383 K for 12 h and then reduced under hydrogen flow for 4 h at different temperatures. The catalysts were labeled as 'An' and 'Cn' (A, catalysts prepared with Rh-acetylacetonate and C, catalysts prepared with Rh-chloride), see Table 1.

Some catalysts were treated under hydrogen flow saturated with water vapor (95 + 5 vol.%) at high temperature (≥ 1073 K), in order to induce the sintering of the metal phase ('An_a', and 'Cn_a' catalysts). This treatment was carried out over the catalysts already reduced at the conditions reported in Table 1. Before each characterization, all catalysts were reactivated under hydrogen flow at 673 K for 1 h. The metal contents of the final catalysts were determined by atomic absorption spectroscopy.

2.3. Characterization

The catalysts were characterized by CO, H₂, and O₂ chemisorption and by transmission electron microscopy (TEM) as an independent technique. The chemisorption of CO and H₂-O₂ titration were carried out on a conventional gravimetric apparatus attaining dynamic vacuum. Samples (300 mg) were reactivated under hydrogen stream for 1 h at 673 K and then outgassed at the same temperature. The CO chemisorption was determined by introducing, in the gravimetric system, CO at 343 K and pressure of 13.2 kPa. The irreversible CO adsorbed was calculated from the values obtained after evacuation of the sample for 1 h at the same temperature. In order to apply the H₂-O₂ titration method, hydrogen was put in contact with the outgassed samples under a pressure of 13.2 kPa at 343 K. Following evacuation of H₂, O₂ is then admitted at a pressure of 13.2 kPa. The amount of O₂ employed to titrate H₂ was then determined after evacuation of the sample.

Table 1
Identification and characterization of Rh/SiO₂ catalysts

Catalyst ^a	Rh (wt.%)	Thermal treatment		Temperature (K)	Dispersion (%D)			
		H ₂ (vol.%)	H ₂ O(vol.%)		CO _{ads}	H ₂ -O ₂	TEM	H ₂ _{Irr}
A1	4.4	100	–	773	21	21	19	–
A2	0.3	100	–	673	76	79	78	–
A3 ⁺	4.4	100	–	773	31	–	–	–
A1 ^a	4.4	95	5	1273	8	8	–	–
A2 ^a	0.3	95	5	1073	66	67	–	–
C8	5.0	100	–	873	26	–	–	27
C6	1.5	100	–	1073	27	–	–	–
C2	1.63	100	–	873	51	–	54	–
C9*	1.5	100	–	1073	63	–	–	–
C5	1.5	100	–	873	68	–	66	–
C9	1.5	100	–	673	78	–	–	–
C4	1.5	100	–	673	95	–	–	–
C6 ^a	1.5	95	5	1073	16	–	–	–
C2 ^a	1.63	95	5	1073	18	–	–	–
C5 ^a	1.5	95	5	1073	20	–	–	–
C8 ^a	5.0	95	5	1073	20	–	–	–
C9 ^a	1.5	95	5	1073	48	–	–	44

^a“A” catalysts set: prepared with Rh-acetylacetonate; “C” catalysts set: prepared with RhCl₃ · 3H₂O. “Ana” and “Cna” catalysts set: treated with H₂ + water vapor at high temperature (> 1073 K). C9* catalysts from re-reduction with hydrogen of C9 catalysts at high temperature (1073 K). A3⁺ catalysts calcined before reduction.

A volumetric method was also used for hydrogen chemisorption measurements over some catalysts: the H₂ irreversible chemisorption was evaluated following the double isotherm technique. To calculate the number of active sites, a stoichiometric ratio CO/Rh, H/Rh and O/Rh equal to one was assumed [18,19]. The results were expressed as percentage of dispersion (% D).

The dispersion and particle size calculated by chemisorption were compared with the particle size calculated by TEM using a JEOL 100CX apparatus. There were counted up to 1000 particles per sample, approximately. The histograms showed a monodistribution of the particle size. The average diameter of particle size, d_s , was determined by the following equation $d_s = \sum n_i d_i^3 / \sum n_i d_i^2$ (where n_i is the number of particles with diameter d_i).

The surface area and pore volume of the silica support and Rh/SiO₂ catalysts before and after thermal treatments were obtained from the nitrogen adsorption isotherm using an ASAP 2000 Micromeritics automatic volumetric apparatus. The BET and the BJH methods were used

to calculate the specific surface area and mean pore size diameter, respectively.

2.4. Catalytic activity

Hydrogenation of reactants was carried out in a stainless steel Parr reactor of 1.0 l of capacity, at 298 K and 689 kPa, using 200 ml of either a 0.013 M solution of 2-cyclohexenone or 0.011 M solution of cyclohexene in isopropanol. The catalysts (50 mg), previously reactivated at 673 K (all catalysts were reactivated at this temperature before reaction), and the solution were placed directly in the reactor and then the system was purged with nitrogen and stirred for 20 min. at 2068 kPa. Subsequently, the nitrogen was evacuated from the reactor and the hydrogen was then introduced at 689 kPa of pressure.

The reaction sequence was followed by analyzing samples at time intervals. The chemical analysis was performed in a gas chromatograph using a packed column of 9.84 ft and 1/8 in. packed with Chromosorb W on 10% of FFAP. The sole product detected under the experimental conditions were cyclohexanone and cyclo-

Table 2
Reversible and irreversible hydrogen chemisorption on Rh/SiO₂ catalysts

Catalyst	$H_{\text{Reversible}}$ (atom/g)	$H_{\text{Irreversible}}$ (atom/g)
C8	2.0×10^{19}	2.5×10^{19}
C9a	6.0×10^{19}	4.0×10^{19}

hexanol for the 2-cyclohexenone and cyclohexane for cyclohexene hydrogenation.

Activities expressed as turnover frequency TOF (number of molecules of reactant transformed per unit time per surface metal atom) were determined from Rh dispersion values and initial activities ($t = 0$) and calculated from the slopes of the straight lines that result from plotting the amount of 2-cyclohexenone or cyclohexene vs. time. The selectivity, defined as the molar ratio of cyclohexanone or cyclohexanol formed to the 2-cyclohexenone reacted, is given in mol% and reported at initial time ($t = 0$). The activity and selectivity values were verified at least by two experiments to assure reproducibility. The temperature dependence was determined in the range of 298–373 K and then the apparent activation energy was calculated. The effects of the amount of catalyst and pressure (689–2068 kPa) on the activity were studied at 298 K.

3. Results

3.1. Characterization of the metallic phase

Dispersion values calculated from CO, H₂–O₂ titration, and H₂ chemisorption were com-

pared with those obtained by TEM and are reported in Table 1. A good agreement between the different techniques can be observed. The relative amounts of irreversible and reversible chemisorbed H₂ [20] are reported in Table 2. Results show that the reversible adsorbed hydrogen is higher in the catalyst which undergoes a thermal treatment under H₂ + H₂O vapor (C9a), than for the catalyst reduced only under hydrogen (C8).

3.2. Determination of the specific surface area

The BET surface areas and pore volumes of the support and Rh/SiO₂ catalysts before and after thermal treatments are reported in Table 3. An hydrothermal sintering of the support is observed. The initial surface area of the silica support diminished from 431 to 391 for catalysts treated with hydrogen and to 374 or 372 m²/g for catalysts treated with H₂ + water vapor, respectively. The diminution of the specific surface area for the Rh/SiO₂ catalysts is around 15%, while the pore size changes from 78 to 105 Å.

3.3. Diffusional limitation study

To verify the absence of external diffusion phenomena, the activities of the catalysts were determined by varying the stirring speed in the reactant system. Above 400 rpm rates were independent of stirring speed. The stirring conditions were kept throughout all the experiments.

Table 3
Surface areas and pore volumes of the SiO₂ support and Rh/SiO₂ catalysts before and after thermal treatment

Sample	Temperature treatment (K)	Surface area (BET) (m ² /g)	Pore diameter (Å)
SiO ₂	673 (air)	431	78
Rh/SiO ₂ ^a	673 (H ₂)	391	103
Rh/SiO ₂ ^a	873 (H ₂ + H ₂ O)	374	105
Rh/SiO ₂ ^b	1073 (H ₂ + H ₂ O)	372	105

^aC9 catalyst.

^bC9a catalyst.

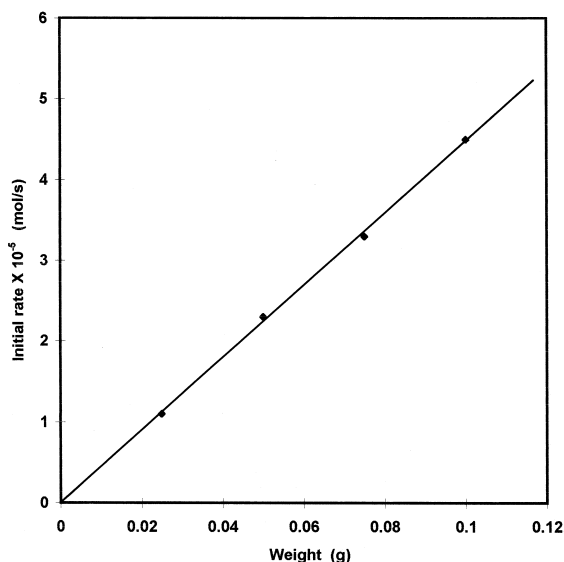


Fig. 1. Initial rate of the 2-cyclohexenone hydrogenation as a function of the weight of catalyst ($C2_a$).

We found a linear dependence by plotting the hydrogenation rate, r , as function of the catalysts weight, w (Fig. 1) [21]. We conclude then that our kinetic values are free of external transport phenomena.

The absence of internal transfer limitations can be demonstrated with the Koros–Nowak criterion [22,23]. For the samples with loadings of 1.5 and of 5.0% of Rh ($C6$ and $C8$ catalysts) and showing very close dispersions (27 and 26%), activity (TOF) values of 2.1×10^4 and $2.0 \times 10^4 \text{ h}^{-1}$ were obtained. A constant value of the turnover frequency is taken as a proof of the absence of internal diffusion limitations [24]. An absence of internal diffusion limitations in the case of catalysts thermally treated under a $\text{H}_2\text{O} + \text{H}_2$ stream was also observed. For example, the activities (TOF) of catalysts $C5a$ and $C8a$, with 1.5 and 5.0 of Rh wt. (20% D) were 6.9×10^4 and $6.7 \times 10^4 \text{ h}^{-1}$, respectively.

3.4. Effect of the amount of substrate

The effect of the substrate concentration on the reaction rate is shown in Fig. 2. It can be seen that rate is not dependent on the concentra-

tion of the 2-cyclohexenone. A zero order with respect to the substrate is then observed.

3.5. Effect of the hydrogen pressure

Rate was determined at various hydrogen pressures. A plot of $\log r$ as a function of $\log p_{\text{H}_2}$ was linear with a slope of about 0.8. The rate is then approximately first order in hydrogen. The hydrogen pressure increases the activity (TOF), while the selectivity towards cyclohexanone is not affected (Table 4). The kinetics of the 2-cyclohexenone can be then expressed by the following expression: $r = -d[A]/dt = kp_{\text{H}_2}$.

3.6. Effect of temperature

An apparent activation energy of 20.9 kJ mol^{-1} for the whole reaction was obtained using 2-propanol as solvent. The apparent activation energy for the two consecutive steps (see Fig. 3) were 20.9 kJ mol^{-1} and 41 kJ mol^{-1} for cyclohexanone and cyclohexanol respectively. The TOF increases with temperature but a non

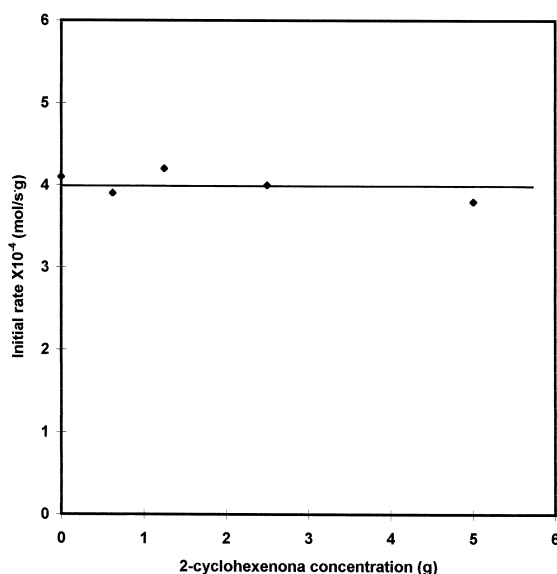


Fig. 2. Initial rate of the 2-cyclohexenone hydrogenation as a function of the 2-cyclohexenone concentration ($C2$).

Table 4

Effect of the hydrogen pressure on the 2-cyclohexenone hydrogenation^a

P_{H_2} (kPa)	Initial rate $\times 10^4$ (mol/s g)	TOF (h^{-1}) $\times 10^{-4}$	Selectivity (%) CyhO ^b
689	4.5	5.7	92
1034	6.2	7.8	90
1379	8.2	10.4	93
1724	8.8	11.2	92
2068	10.9	13.7	90

^aCatalyst C2a, temperature 298 K, solvent 2-propanol.^bCyclohexanone.

important variation of the selectivity pattern was observed at $t = 0$ (Table 5).

3.7. Effect of the metal dispersion on catalytic activity and selectivity

Results of activity and selectivity as function of the dispersion for the 2-cyclohexenone hydrogenation over the Rh/Silica catalysts are reported in Tables 6–8. The TOF, for each set of catalysts (prepared with Rh-chloride, Rh-acetylacetonate precursors and those thermally treated), is constant for the various rhodium dispersions, therefore the hydrogenation of the 2-cyclohexenone over the Rh/Silica is a ‘structure-insensitive’ reaction.

The set of catalysts prepared with the chloride precursor show a higher activity than the

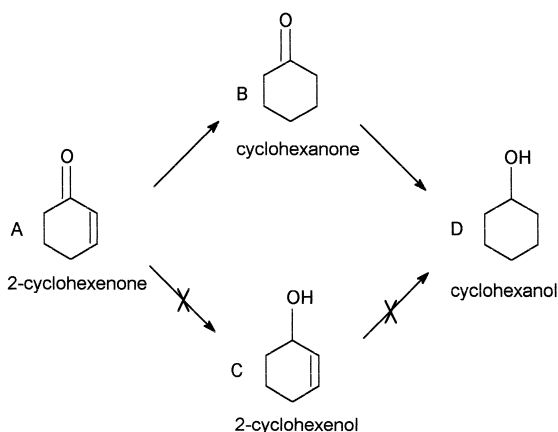


Fig. 3. Reaction mechanism for the 2-cyclohexenone hydrogenation.

Table 5

Effect of the temperature on the 2-cyclohexenone hydrogenation^a

Temperature (K)	Initial rate $\times 10^4$ (mol/s g)	TOF (h^{-1}) $\times 10^{-4}$	Selectivity (%) CyhO ^b
298	4.5	5.7	92
323	9.22	11.6	99
353	14.89	18.8	97
373	20.16	25.4	96

^aCatalyst C2a, temperature 298 K, pressure 689 kPa, solvent 2-propanol.^bCyclohexanone.

set of catalysts prepared with the organic precursor, Tables 6 and 7, respectively. When the catalysts prepared with the organic precursor, were treated with hydrogen saturated with water vapor at high temperature, the activity per site increased 8-fold (Table 8, ‘A’ catalysts). Sintering and a subsequent decrease in the dispersion of Rh particles is observed. However, as we can see, the activity does not change as function of the dispersion; therefore, the structure-insensitiveness of the 2-cyclohexenone hydrogenation is maintained for the thermally treated catalysts. The selectivity pattern at $t = 0$ shows a high formation of cyclohexanone.

The same behavior was observed for the 2-cyclohexenone hydrogenation by the catalysts of Rh/Silica prepared with the chlorine precursor (Table 8, ‘C’ Catalysts). The catalysts treated under hydrogen saturated with water vapor at high temperature (≥ 1073 K) showed higher activities. Thermal treatment provoked the sintering of the metal. Activity and selectivity were not modified with dispersion.

Table 6

Effect of dispersion on activity and selectivity the 2-cyclohexenone hydrogenation over Rh/SiO₂ catalysts prepared with Rh-acetylacetonate^a

Catalyst	% D	TOF (h^{-1}) $\times 10^{-4}$	Selectivity (%) CyhO ^b
A1	21	0.4	94
A3 ⁺	31	0.43	95
A2	76	0.34	98

^aTemperature 298 K, pressure 689 kPa, solvent 2-propanol.^bCyclohexanone.

Table 7

Effect of dispersion activity and selectivity of 2-cyclohexenone hydrogenation over Rh/SiO₂ catalysts prepared with RhCl₃

Catalyst	% D	TOF (h ⁻¹) × 10 ⁻⁴	Selectivity (%) CyhO ^b
C8	26	2.0	91
C6	27	2.1	95
C2	51	1.9	95
C9*	63	1.7	93
C5	68	1.6	93
C9	78	1.5	92
C4	95	1.6	96

^aTemperature 298K, pressure 689 kPa, solvent 2-propanol.^bCyclohexanone.

Hydrogenation of the cyclohexene was carried out with the aim of comparing the hydrogen addition to the C=C bond in this reaction with respect to that of 2-cyclohexenone. The cyclohexene hydrogenation has been largely studied and reported as a structure insensitive reaction [14,15,24–26]. In the present case, the activity for the cyclohexene hydrogenation is also independent of the dispersion of Rh/SiO₂ catalysts as it is shown in Table 9. Hydrogen addition to the carbon-carbon double bond of the cyclohexene shows higher activity for catalysts prepared with the rhodium–chloride precursor than those prepared with rhodium–acetylacetonate. An increase in activity for the rhodium catalysts thermally treated on stream was also observed. Comparing the initial hydrogenation TOF for 2-cyclohexenone and cyclohexene under identical conditions, it is found

Table 8

Activity and selectivity of the 2-cyclohexenone hydrogenation on Rh/Silica catalysts thermally treated^a

Catalyst	% D	TOF (h ⁻¹) × 10 ⁻⁴	Selectivity (%) CyhO ^b
A1a	8	3.3	94
A2a	66	2.8	100
C6a	16	6.1	95
C2a	18	5.8	96
C5a	20	6.9	95
C8a	20	6.7	92
C9a	48	6.2	93

^aTemperature 298 K, pressure 689 kPa, solvent 2-propanol.^bCyclohexanone.

Table 9

Effect of precursor, dispersion and thermal treatment on the activity of the cyclohexene hydrogenation on Rh/SiO₂ catalysts^a

Catalyst	% D	TOF(h ⁻¹) × 10 ⁻⁴
A1	21	1.3
A2	76	1.2
C6	27	3.4
C2	51	2.8
C2a	18	7.4

^aTemperature 298 K, pressure 689 kPa, solvent 2-propanol.

that the activity for the latter is higher, so the presence of a second reducible function such as C=O leads to a lower activity by hydrogen addition to the C=C bond. These results are in agreement with those obtained by Maurel et al. [27,28], where it is shown that hydrogenation of a double bond is very sensitive to the presence of a substituent.

4. Discussion

The zero kinetic order for the hydrogenation of 2-cyclohexenone shows, in terms of Langmuir adsorption, that a strong ketone adsorption covering almost completely the surface of the metal occurs. The order one found for hydrogen implies that it becomes weakly adsorbed on the metal surface. The zero order for the 2-cyclohexenone on Rh/SiO₂ determined here is not observed on Pt/SiO₂ for which the experimental value reported is of -1.4 [12]. Negative orders were also reported for the 1,4 cyclohexanedione and acetophenone [29,30].

The reducible C=O group is considered as an electron donor group with free pairs of electrons that could modify the reactivity of the C=C double bond. Table 9 shows that the activity of one accessible rhodium atom is in all cases higher for the cyclohexene hydrogenation than for the 2-cyclohexenone hydrogenation, Tables 6–8. This could be explained by considering a strong adsorption of the C=O group on the surface of the metal, thus increasing the

residence time of the 2-cyclohexenone. However, concerning the kinetics, the results obtained with 2-cyclohexenone are comparable with those obtained usually for hydrogenation of the mono-olefine: order one for H_2 and zero order with respect to the alkene [31,32].

The hydrogenation of 2-cyclohexenone over Rh/SiO₂ is a consecutive reaction (2-cyclohexenone → cyclohexanone → cyclohexanol), where hydrogenation of the C=O group is made without adsorption–desorption steps [29]. This consecutive mechanism is shown in Fig. 3 [29]. The experimental results show a large conversion to cyclohexanone in almost all determinations and a low conversion to cyclohexanol (Fig. 4).

The C=O functional group is more difficult to reduce than the C=C double bond, the apparent activation energy calculated for the hydrogenation of the C=O group is 41 kJ mol⁻¹, which is close to the 46 kJ mol⁻¹ observed for the partial hydrogenation of 1,4 cyclohexanedione [30]. In Rh/SiO₂ and Ni/SiO₂, Bond reports [6] an apparent activation energy of 35 kJ mol⁻¹ for the hydrogenation of ethylene.

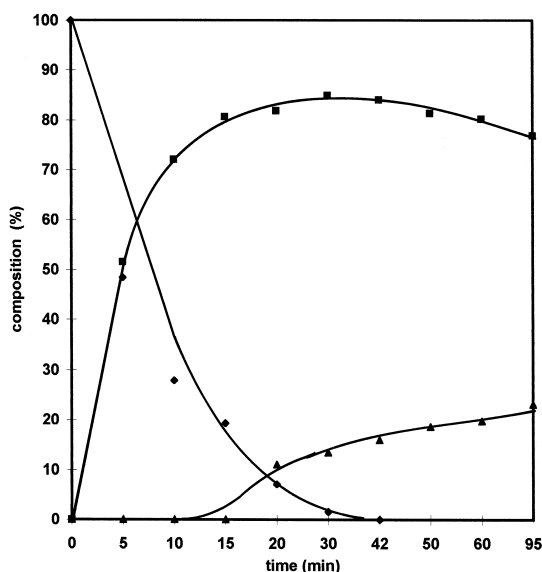


Fig. 4. hydrogenation of 2-cyclohexenone over the C2a Catalyst, (◆) 2-cyclohexenone, (■) cyclohexanone, (▲) cyclohexanol.

The energy of 21 kJ mol⁻¹ obtained for the ethylenic bond in the 2-cyclohexenone is lower and probably due to the effect of carbonyl group electron pairs.

The activity (TOF) for the hydrogenation of 2-cyclohexenone was constant for the three sets of catalysts, showing that this is a structure-insensitive reaction.

As it can be seen catalysts prepared with rhodium-chlorine precursor are more active than those prepared with Rh-acetylacetonate precursor (Tables 6 and 7). The lower activity showed by the catalysts prepared with rhodium acetylacetonate could be due to the presence of carbonaceous deposits on the rhodium metal surface after reduction, then this must be analyzed. Catalyst (A3) that was calcined before reduction, showed a dispersion of 31%, and a TOF of $0.43 \times 10^4 \text{ h}^{-1}$ (Table 6). This TOF value is of the same order of magnitude showed by the catalysts reduced without previous calcination, then the effect of carbonaceous residues is not detected.

During thermal treatment at temperatures higher than 723 K chlorine could have been removed from the surface of the catalyst [33]. Nevertheless chloride plays an important role in the nucleation process, during which the rhodium chloride reduction, rhodium particle shape or metal support interactions are suggested [34]. The higher activity of the chlorinated catalysts is then an effect of the preparation of catalysts using RhCl₃ as metal precursor.

For catalysts treated with hydrogen saturated with water vapor at high temperature a significant increase in activity for the hydrogenation of the 2-cyclohexenone was observed. In this case, the improvement of activity cannot be attributed to the precursor used (chlorinated and non-chlorinated), since the increase in activity is observed for both sets of catalysts.

The specific surface area and the porosity of the catalysts are not substantially modified by thermal treatment (Table 3). Moreover the Koros–Nowak criterion [22] showed that catalysts reduced with pure hydrogen or with hydrogen

on stream are not limited by mass transfer phenomena.

Thermal treatment of the Rh/SiO₂ catalysts leads to the sintering of the rhodium metal particles. The sintering of the metal particles implies a very likely modification of their shape. The crystalline planes exposed are modified and activity modifications can occur in structure-sensitive reactions [35,36]. However, as we showed above the 2-cyclohexenone hydrogenation is a structure-insensitive reaction on Rh/SiO₂, the criterion of shape particle modifications by thermal treatment is ruled out in the present case.

Strong metal support interaction (SMSI) effect has been also observed on supports hardly reducibles like silica [37–42]. Sadi et al. [43] have shown that the silica surrounding the rhodium particles is reduced after a treatment at high temperature in hydrogen (973–1173 K). The silicon thus formed can react with the rhodium to form an intermetallic compound such as Rh₂Si alloy. However, it was observed by XRD, TEM and EDX that H₂O titration destroy the Rh₂Si alloy. High temperature reduction diminishes the hydrogen chemisorption, and it was restored, at least partially, by subsequent hydrogen reduction after titration.

In our case, the catalysts reduced at temperatures between 673 and 1273 K under pure H₂, did not show any suppression of H₂ chemisorption and all techniques employed to measure the metal surface area are in good agreement with the dispersion values. Moreover, formation of the Rh₂Si alloys in our catalysts is not observed, since the hydrogen chemisorption is not suppressed after the thermal H₂ + H₂O water vapor treatments. Therefore, a SMSI effect is not observed in the present catalysts.

In the same way, for Rh/SiO₂ catalysts, Wong and McCabe [44] observed an increase in the particle size but no interactions were observed between the Rh and the support after sequential treatments in O₂ and H₂ at 1095 K. Meanwhile, an effect of the support was observed for the oxidation of Rh/Al₂O₃ at 1095

K, the rhodium diffusion in the Al₂O₃ bulk is proved and a diminution of the activity from five to tenfold for CO oxidation is reported.

Beck et al. [45] studying the effect of high oxidizing temperature on the local structure of rhodium oxide particles in Rh/Al₂O₃ catalysts by XAFS observed that Rh is completely oxidized to Rh₂O₃ after treatment at ≥ 773 K. Baker et al. showed [46] that treatment under an oxidizing environment over pre-reduced Pt/TiO₂ catalysts, initially in SMSI state, with H₂O vapor at 525 K or O₂ at 875 K, causes the three dimensional growth of the Pt particles and partially restores the chemisorption capacity of the metal.

The positive effect of the thermal treatment by a hydrogen + H₂O flow at high temperature (≥ 1073 K), in Rh catalysts is only observed over the catalysts which were previously reduced under H₂ (673–1073 K). Thermal treatment carried out under N₂ + H₂O flow at high temperature, does not have any effect on the improvement of the activity [47].

The kinetics study shows that hydrogenation of 2-cyclohexenone depends on the hydrogen pressure. Concerning the adsorption of hydrogen, two catalysts, the first corresponding to a reduction under pure hydrogen at 873 K (C8) and the second treated under H₂ + H₂O at 1073 K (C9a), were characterized by the isotherms of hydrogen chemisorption (Table 2). The rhodium dispersions calculated from the irreversible adsorbed hydrogen are in good agreement with the accessibility calculated from CO chemisorption; however, the amount of the reversibly adsorbed hydrogen is higher for the catalysts treated under water–hydrogen flow than those catalysts obtained under pure hydrogen flow (Table 2).

An important role of the reversible adsorbed hydrogen in catalytic hydrogenation reactions has been observed by several authors. Van Meerten et al. [20] showed by magnetization measurements that during the hydrogenation of benzene only a small fraction of the nickel surface plays a role in the reaction, and the weakly adsorbed hydrogen was identified as the

active one of the reaction. Richardson and Cale [48] have studied the origin of reversible hydrogen adsorption on dispersed nickel catalysts through analysis in situ magnetization and chemisorption measurements on silica and alumina support catalysts. They found that the ratio of weakly adsorbed hydrogen to the irreversible adsorbed hydrogen increases as the crystallite size increases. In Rh/SiO₂ catalysts, weak adsorbed hydrogen essentially depends on the H₂ + H₂O treatments.

It has also been reported [49] that in the liquid phase catalytic hydrogenation of the C=C double bond of the maleic acid on platinum at different electrochemical potentials, only the weakly bonded hydrogen species are active during the catalytic hydrogenation of the olefinic compound.

In our case, on catalysts pretreated on stream flow the amount of reversible adsorbed hydrogen is larger than that obtained in catalysts non subjected to this pretreatment. This means that the weakly bonded hydrogen is adsorbed in large amount in the thermally treated catalysts. Two hypothesis about the origin of the weakly adsorbed hydrogen can be proposed: (i) its formation is due to a hydrogen spill-over effect, then the hydrogen addition to C=C, which is a structure-insensitive reaction, is promoted by the hydrogen adsorbed on the support; (ii) stream treatment induces a partial oxidation of Rh (at the support-metal interface) increasing the amount of reversible adsorbed hydrogen.

5. Conclusions

The main conclusions of the present work are: (i) in the hydrogenation of the 2-cyclohexenone, the kinetic order for the reactant and for the hydrogen are zero and one, respectively, (ii) hydrogenation of the double bond of the ketone was found to be a structure-insensitive reaction, (iii) an effect of the precursor was observed: catalysts prepared with the chloride compound are more active than those prepared

with the rhodium acetylacetonate, (iv) when the rhodium catalysts were thermally treated in H₂ + H₂O stream, an important increase of the activity was obtained, and (v) it is proposed that weakly bounded hydrogen on Rh/SiO₂ catalysts is responsible for the improvement of the activity in the 2-cyclohexenone and cyclohexene hydrogenation.

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