

Ruthenium surface compounds supported on silica gel

I. Preparation and catalytic properties

Jochem U. Köhler ^{*}, Hans L. Krauss

Laboratorium für Anorganische Chemie, Universität Bayreuth, D-95440 Bayreuth, Germany

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Abstract

In analogy to Phillips catalysts coordinatively unsaturated surface compounds of ruthenium were prepared and their catalytic potential was tested. The impregnated catalysts ($\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ adsorbed on silica gel) were activated either under oxygen (200°C – 600°C) or under vacuum (250°C – 800°C) and reduced with CO (250°C – 350°C). These catalysts show activity with respect to the hydrogenation of olefins (e.g., octenes and cyclooctene) as well as to their isomerization under normal and elevated pressures. The properties of the catalysts depend on the conditions of their preparation. The activity generally increases with increasing activation temperature. The IR spectra of the catalysts activated at temperatures lower than 300°C reveal the presence of carbonyl surface complexes. Their catalytic properties are relatively poor. The catalyst with the best hydrogenation activity was activated at 800°C under vacuum and reduced at 350°C by CO. The IR spectrum shows no CO absorption bands in the carbonyl region after preparation; however, the catalyst reversibly adsorbs carbon monoxide readily at room temperature and two carbonyl bands appear at 2130 and 2070 cm^{-1} . This indicates the presence of unsaturated ruthenium species on this catalyst in oxidation states > 0 . In the absence of hydrogen an isomerization of 1-octene was observed at elevated temperatures (90°C). Reaction mechanisms are proposed for both cases.

Keywords: Ruthenium; Surface compounds; Silica gel; Hydrogenation of olefins; Isomerization of olefins; Phillips catalysts

1. Introduction

The Phillips catalyst (' CrO_3 on silica gel') has been used industrially for the polymerization of ethylene since 1956 [1]. However, a generally accepted mechanism for this reaction has not yet been established. Nevertheless, the first step of the reaction is understood to be a

reduction of Cr(VI) (e.g., by an olefin) to form a coordinatively unsaturated site [2–10]. It has been shown that it is possible to prepare coordinatively unsaturated surface compounds such as Cr(II) as predominant species on the surface of silica gel specifically by reduction with CO [2,3].

Catalytic reactions have been observed not only in the case of Cr(II) but also for unsaturated analogues such as Cr(III) [11–15], V(III) [16–18], Mo(II,IV) [19–21], Fe(II) [22,23], Cu(II) [24] and other transition metal ions [25,26]; the definition of the Phillips system can

^{*} Corresponding author. Present address: Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr, Germany. Tel.: +49-208-3062451; fax: +49-208-3062987; e-mail: jkoehler@dsa.mpi-muelheim.mpg.de.

be extended correspondingly [27]. The ability to polymerize olefins without an additional alkyl source distinguishes it from the Ziegler catalyst system [27]. The goal of this work was to prepare coordinatively unsaturated surface compounds of ruthenium which are analogous to the Phillips system.

Ruthenium compounds are widely used as *homogeneous* catalysts. $\text{RuCl}_2(\text{PPh}_3)_3$ for example, is a useful catalyst for the hydrogenation of carbon–carbon double bonds [28]. Hydrogenation of aldehydes to alcohols is catalyzed by $\text{Ru}(\text{CO})_3(\text{PPh}_3)_2$ [29]. Other reactions of ruthenium complexes include hydroformylation [29], hydrogenation of CO_2 to formic acid in supercritical carbon dioxide [30], hydrogen/deuterium exchange [31], polymerization of ethylene [32], ring opening metathesis polymerization [33], isomerization of 1-pentene [34], and self metathesis of vinyltrimethoxysilane [35]. Ruthenium cluster compounds are used as precursors in the water-gas shift reaction [36].

Ruthenium fixed on supports such as SiO_2 [37–45], Al_2O_3 [46–48], MgO [44,45], TiO_2 , [49], and zeolites [50] have been tested as *heterogeneous* catalysts. A general procedure for the preparation of these catalysts consists in impregnating the oxidic supports with ruthenium salts (for example $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ or $\text{Ru}(\text{NO}_3)_3$) dissolved in water. After drying these catalyst precursors they are usually reduced with hydrogen at temperatures between 300 and 400°C. Under these conditions metallic ruthenium is formed on the surface of the support [48,51,52]. Another approach to anchor metallic ruthenium on oxidic supports is to decompose adsorbed $\text{Ru}_3(\text{CO})_{12}$ at elevated temperatures [38]. Some of these catalysts are of interest due to their ability to hydrogenate CO to methanol and ethanol [46,53–57]. An important application of such Ru/ SiO_2 catalysts is the Fischer–Tropsch reaction where Cu, Ag, and Au may be added as co-catalysts [58]. Heterogeneous ruthenium catalysts may also be used for the hydrogenation of C=C double bonds [59] and the reduction and of benzene to

cyclohexane [60], or even selectively to cyclohexene [61,62].

Altogether, hydrogenation seems to be the dominant catalytic reaction of ruthenium catalysts¹. Most of the work published on ruthenium anchored on oxidic supports starts with a reduction of the catalyst in a hydrogen stream under conditions which lead mainly to the formation of metallic ruthenium. In the present work we specifically tried to prepare coordinatively unsaturated surface compounds of ruthenium (oxidation number > 0), starting with an activation at high temperatures to anchor the ruthenium on the surface of silica gel and proceeding with the reduction under carbon monoxide instead of hydrogen to avoid the formation of metallic ruthenium. It was attempted to exclude the formation of ruthenium carbonyl surface compounds by choosing selective reduction conditions.

2. Experimental

All preparations and reactions were carried out under argon using the Schlenk technique. Argon was dried and purified by passing it through columns of $\text{Mg}(\text{ClO}_4)_2$ and Cr(II) on silica gel [65,66]. All solvents were dried and purged with argon to remove dissolved oxygen. 1-octene, *trans*-2-octene, and cyclooctene were passed through Al_2O_3 , purged with argon, and stored in a Schlenk flask over Mn(II) on silica gel [67]. *cis*-2-octene was passed through Al_2O_3 and distilled in an atmosphere of argon immediately before reaction. All olefins were tested for purity by GC before use. In the case of 1-octene there was approximately 1% *n*-octane present and no isomers were detected.

SiO_2 (Merck 7733) was used as a carrier. After washing with boiling water the silica gel was dried in vacuo at 150°C for 15 h and

¹ For analogous hydrogenation reactions with the chromium (II) Phillips catalyst see [63,64].

calcined in a stream of oxygen while the temperature was slowly increased to 700°C. Afterwards cooling was performed under argon and the silica gel was stored under argon.

Impregnation: 0.9 mmol $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (Aldrich) were dissolved in dry acetone (18 ml, ca. 0.05 mol/l). The brown solution was added to silica gel (20 g for 0.45% Ru and 10 g for 0.9% Ru content in the final catalyst). The mixture was kept for one hour at RT and shaken occasionally. Since a potentiometric titration to determine the amount and the oxidation state of ruthenium on silica gel was not successful (in contrast to the cases of chromium and iron) the solvent was removed completely under vacuum and the content of ruthenium calculated from the amount of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ employed.

The *activation* of the reddish-brown impregnated catalyst was carried out in a quartz tube (assembled vertically in an oven) either in a stream of oxygen or in vacuo.

Activation in oxygen: The temperature was raised from RT to 300°C by 25°C every 20 min and between 300°C and 600°C by 50°C every 20 min. The final temperature was maintained for 45 min. The resulting black product was allowed to cool under argon.

Activation under vacuum: A quartz tube filled with the impregnated catalyst was evacuated for 45 min at RT. The temperature was then increased under vacuum between RT and 200°C in steps of 25°C every 20 min, between 200°C and 300°C in steps of 50°C and between 300°C and 800°C in steps of 100°C every 20 minutes each. A temperature of 800°C was maintained for 1 h and the catalyst (dark brown (0.9% Ru), dark green (0.4%)) was allowed to cool to 600°C under vacuum, and then cooled to RT under a stream of argon.

Reduction of the catalysts: The activated catalysts were heated to 350°C under argon. At this temperature argon was replaced with a CO stream for 15 min, then — reverting to argon — the catalyst was cooled to RT. Reductions under hydrogen were carried out in an analogous way.

‘Blank catalysts’ free of ruthenium were prepared in the same way with the exception that no $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ was added. All catalytic reactions were repeated with these ‘blank catalysts’ to exclude or at least to quantify similar reactions caused by the silica gel itself or by residues of chemicals used for the preparation.

For the *hydrogenation reactions under pressure* a stainless steel laboratory autoclave (Roth, 100 ml, type 10-36.54, maximum pressure: 100 bar (1 bar = 10^5 Pa)) was used. The catalyst (approx. 0.8 g) was placed in a glass tube (with a Schlenk top fitted) together with 40 mmol of 1-octene under argon. This tube was placed in the autoclave which had been set under an atmosphere of argon. After removing the Schlenk top and closing the autoclave, a hydrogen pressure of 20 bar was applied and released three times to minimize the presence of argon. The hydrogen pressure was subsequently increased to 60 bar. The magnetic stirrer was switched on and the pressure was recorded during the reaction. At the end of the reaction (constant pressure) the products were analyzed by GC.

The *hydrogenation reactions under normal pressure* (1 g of the catalyst and 40 ml heptane) was carried out in a flask under argon. The flask could be thermostated to determine the activation energy. However, usually the reactions were performed at room temperature. The suspension was stirred with a magnetic stirrer and hydrogen was bubbled through the liquid by a vertically mounted gas inlet tube. The flow of hydrogen was kept at a constant rate of 7 l/h with a flow meter (Brooks R-2-15-AAA). After 10 min 20 mmol of 1-octene were added. At regular intervals samples were taken from the solution and analyzed by GC.

The *isomerization* reaction was carried out in the same way but without hydrogen in an argon atmosphere and at a temperature of 90°C.

Determination of chloride: Approximately 1 g of the catalyst containing the ruthenium surface compound was titrated with 0.1 N silver nitrate solution in water and under argon to

determine the content of chloride in the catalyst. (Potentiograph Metrohm E 536 connected to a dosimat E 535; silver electrode EA 246 Ag/AgCl/KNO₃ saturated).

Determination of the amount of carbon dioxide which was formed during the reduction of the catalyst was carried out according to the literature [68]. 5 g of catalyst activated at 800°C under vacuum was reduced in a stream of carbon monoxide at 350°C. The effluent stream of gases was passed through a saturated aqueous solution of Ba(OH)₂. The precipitated BaCO₃ was filtered off and dissolved in an excess of 0.1 M HCl. The solution was titrated back with 0.1 M NaOH.

The *determination of the amount of carbon* on the catalyst 800°C vac/350°C CO was carried out according to the literature [68]. 5 g of the catalyst were heated in a stream of oxygen at 600°C. The effluent stream of gases was passed through a catalyst of CuO on quartz wool and then through a saturated solution of Ba(OH)₂. The subsequent procedure is analogous to that described for the determination of carbon dioxide. The amount of carbon on a blank catalyst (free of ruthenium) was also determined as a reference value.

IR spectra were recorded on a FTIR instrument (Bio-Rad Digilab FTS-15/80). For the diffuse reflection spectra the catalysts were placed in a Barnes cell (Spectra Tech, Stamford, CT).

GC: Carlo Erba Instruments HRGC 5300, glass capillary WCOT OV 101.

3. Results

3.1. Preparation of the catalysts, activation under oxygen

After adsorbing RuCl₃ · 3H₂O dissolved in acetone (ca. 0.05 mol/l) on silica gel in an impregnation step, the products were activated by increasing the temperature. It was intended to anchor the ruthenium on the surface and to

reduce the number of neighboring hydroxy groups present on the surface of the gel. During the activation under oxygen an oxidation of the ruthenium (commercial 'RuCl₃ · 3H₂O' actually contains ruthenium in the oxidation states III and IV [69]) to higher oxidation states may occur. The temperature for activation in a stream of oxygen was varied between 200°C (brown product) and 600°C (grey black product). Above 700°C the formation of volatile oxides of ruthenium is reported in the literature [69]. However, in our experiments a sublimation of a black solid from the adsorbate took place already above 600°C. If the temperature was increased further to 800°C, a black mirror separated onto the tube from the oxygen effluent and the silica gel remained finally almost white.

The reduction of the catalysts was carried out in a stream of CO, usually at 350°C. The catalysts were subsequently cooled to room temperature under argon. The colors of the reduced catalysts ($T_{\text{red}} = 250^\circ\text{C}$) depend on the activation temperature: $T_{\text{act}} = 200^\circ\text{C}$: yellow, $T_{\text{act}} = 250^\circ\text{C}$: brown, $T_{\text{act}} = 300^\circ\text{C}$: grey brown, and $T_{\text{act}} = 600^\circ\text{C}$ black grey. Variation of the reduction temperature (250°C, 350°C and 450°C; after constant activation temperature: 600°C) had no effect on the color of the product.

The IR spectra of catalysts activated at relatively low temperatures show absorption bands in the carbonyl region: 200 O₂/250 CO² $\nu(\text{CO}) = 2150, 2143, 2090$ (sh), 2084, 2080 (sh), 2034, 2025 (sh) cm⁻¹ and 250 O₂/250 CO: $\nu(\text{CO}) = 2150$ (sh), 2143, 2079, 2032 cm⁻¹. At activation temperatures above 300°C the absorption bands disappear (Fig. 1a).

3.2. Preparation of the catalysts, activation under vacuum

The impregnation was carried out as described above. The standard concentrations of

² Abbreviation for catalysts: activation temperature in °C, atmosphere / reduction temperature in °C, atmosphere.

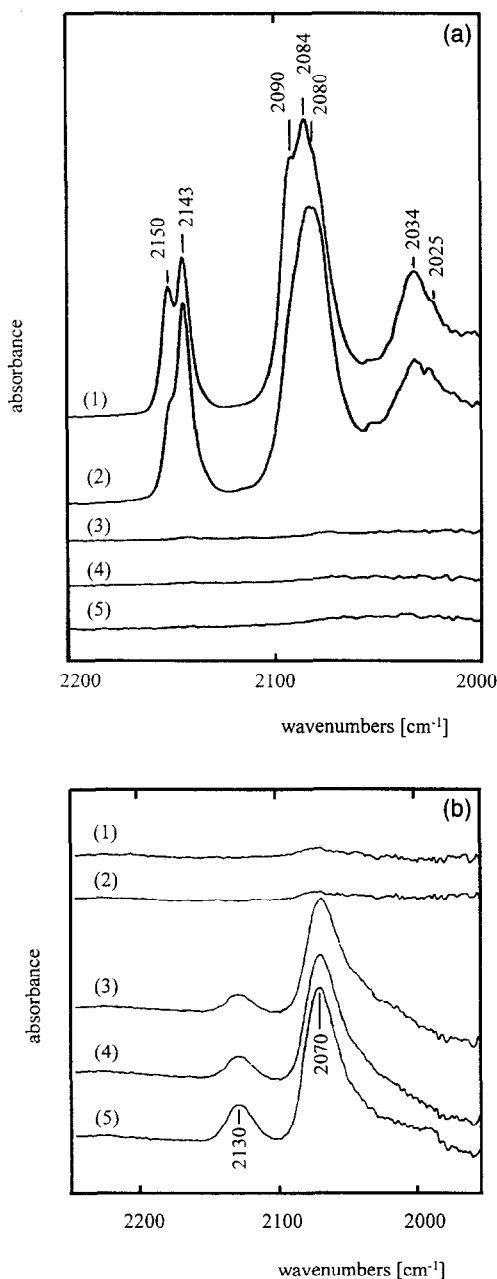


Fig. 1. (a) IR spectra of reduced catalysts (0.3% Ru). Variation of the activation temperature (constant reduction temperature: 250°C). (1) 200°C O₂; (2) 250°C O₂; (3) 300°C O₂; (4) 400°C O₂; (5) 600°C O₂. (b) IR spectrum of the catalyst 800 vac/350 CO (0.9% Ru). Exposure to CO at room temperature and subsequent measurement under argon: (1) catalyst after preparation under argon; (2) exposure to a stream of CO for 5 s; (3) exposure to CO for 10 s; (4) exposure to CO for 20 s; (5) exposure to CO for 5 min.

ruthenium in the catalyst were 0.4 and 0.9%. In contrast to the activation under streaming oxygen the temperature can be increased under vacuum to 800°C without losing ruthenium: Obviously the volatile ruthenium oxides were not formed or immediately decomposed under these conditions. The colors of the activated catalysts depend on the content of ruthenium and were dark green for 0.4 wt% Ru and dark brown for 0.9 wt% Ru (after reaching the temperature 800°C).

The subsequent reduction was carried out at 250°C or 350°C. During this reaction CO₂ was formed in an amount of 70–80 mol% with respect to ruthenium. Again the catalysts were allowed to cool to room temperature under argon. The amount of carbon on the catalyst 800 vac/350 CO was determined as 38 mol% with respect to ruthenium. The colors of the reduced catalysts varied between brown and dark brown. It was not possible to detect any chloride by potentiometric titrations.

The IR spectrum of the catalyst 800 vac/350 CO does not show any CO absorption bands after the preparation. However, if carbon monoxide is pulsed through the IR cell at room temperature two absorption bands appear at $\nu(\text{CO}) = 2130$ and 2070 cm^{-1} . The intensities of these bands increase, however, no shift of the bands is observed (Fig. 1b).

With both activation methods blank catalysts (free of ruthenium) were prepared to exclude misleading artefacts.

3.3. Hydrogenation reactions

Since many ruthenium catalysts are known to be active in hydrogenation reactions, we used the hydrogenation of 1-octene as a test reaction for our catalysts. (All catalysts described show no activity towards polymerization of ethylene or 1-octene neither under pressure nor at 1 bar). The course of the reaction was monitored by GC analysis of the reaction mixture.

At first the hydrogenation of 1-octene was carried out in an autoclave at 60 bar (Usually no

solvent was used. Addition of heptane as a solvent had no influence on the reaction). The reaction did not start immediately. For a certain time which proved to be reproducible the pressure remained unchanged. For this *induction period* an analysis of the reaction mixture showed that neither a hydrogenation nor an isomerization had taken place. During the second part of the reaction the pressure almost suddenly started to decline. The final decrease was approximately 6 bar; the 1-octene was found then to be completely hydrogenated to 99% *n*-octane and 1% 3-methyl-heptane. After approximately 50% conversion, an interruption of the reaction by releasing the pressure and analyzing the reaction mixture revealed the presence of the isomers *cis*-2-octene and *trans*-2-octene. Since hydrogenation is an exothermic reaction a gentle warming of the autoclave was observed.

If 1-octene was added again at the end of the reaction and the autoclave was pressurized again, the reaction passed through a new, identical induction period.

The results of the hydrogenation reactions for

the catalysts prepared under different conditions are compiled in Table 1. Activated catalysts (without the reduction step) work more slowly than catalysts which had been reduced subsequently by CO. The length of both periods of the reaction generally decreased with an increase of the activation temperature for reduced catalysts.

For the catalyst activated at 250°C reduced at 250°C under CO the IR spectra and the catalytic behavior were identical for activation in oxygen and under vacuum (catalysts 3 and 11, Table 1).

For catalysts activated at 600°C under oxygen and reduced under CO at 250, 350, and 450°C (catalysts 8–10, Table 1) the optimum temperature for catalyst activation for the hydrogenation reaction was 350°C. For the series of vacuum activated catalysts a reduction temperature of 350°C also proved to be better than 250°C (catalysts 13 and 14 Table 1).

The influence of a reduction under hydrogen (1 bar) at higher temperatures was also investigated (catalysts 15 and 16, Table 1). These catalysts show significantly longer induction periods compared to the catalyst 800 vac/ 350

Table 1

Influence of activation and reduction temperatures and of the atmospheres for the hydrogenation properties of the Ru/SiO₂ catalysts (0.9% Ru) (reaction conditions: 60 bar hydrogen pressure, 0.8 g catalyst with 0.9% Ru, 40 mmol 1-octene)

No.	Catalysts T_{act} (°C)/ T_{red} (°C)	Induction period (constant pressure) (min)	Period of decreasing pressure (min)
1	200 O ₂ /250 CO	^a	
2	250 O ₂ /—	330	300
3	250 O ₂ /250 CO	120	45
4	300 O ₂ /250 CO	30	18
5	400 O ₂ /250 CO	24	9
6	500 O ₂ /—	^b	
7	500 O ₂ /250 CO	10	5
8	600 O ₂ /250 CO	7	7
9	600 O ₂ /350 CO	3	5
10	600 O ₂ /450 CO	6	9
11	250 vac/250 CO	120	45
12	800 vac/—	^c	
13	800 vac/250 CO	4	11
14	800 vac/350 CO	4	5
15	800 vac/350 CO/350 H ₂	13	4
16	800 vac/350 H ₂	15	5

^a No complete hydrogenation within 48 h.

^b No complete hydrogenation within 15 h.

^c After 4 h still 96% 1-octene.

CO but almost no change in the reaction time after initiation.

A catalyst 800 vac/350 CO was kept under a hydrogen pressure of 60 bar for 15 h at room temperature. It was then tested for the hydrogenation of 1-octene as usual. The induction period significantly increased from 4 min to 55 min compared to an untreated catalyst. The period of decreasing pressure remained almost unchanged at 5 min.

If the initial hydrogen pressure of the test reaction (hydrogenation of 1-octene) was lower than 60 bar, a slower reaction was observed: Both the induction period and the period of decreasing pressure increased with decreasing initial pressure. With the catalyst 600 O₂/350 CO the induction period and the reaction period are lowered from 3/5 min at 60 bar hydrogen pressure to 33/54 min at 10 bar. Similar behavior was observed using the catalyst 800 vac/350 CO (60 bar: 4/5 min; 10 bar: 18/35 min).

To determine the activity of the support itself, a reaction with a blank system (free of ruthenium) 250 O₂/250 CO was carried out in an autoclave at 60 bar hydrogen. After 15 h the system contained 52% 1-octene, 18% octane, 24% *trans*-2-octene and 6% *cis*-2-octene. This result shows that there is some weak activity by the silica gel mostly causing isomerization.

Those catalysts which gave the fastest reactions under pressure with respect to the hydrogenation of 1-octene were tested *under 1 bar hydrogen pressure*. Hydrogen was bubbled through a suspension of 1 g catalyst in 40 ml heptane. After 10 min, 20 mmol of 1-octene were added. (Since the reaction rate depends on the hydrogen flow rate, 7 l/h was chosen as standard. We did not observe any dependence on the agitation speed under these conditions. However, if the stirrer was stopped, the hydrogenation rate dropped dramatically despite the fact that the reaction suspension was vigorously mixed by the hydrogen bubbles). The conversion of 1-octene was monitored by GC.

The decrease of 1-octene follows a rate law of zero order. Surprisingly, no induction period

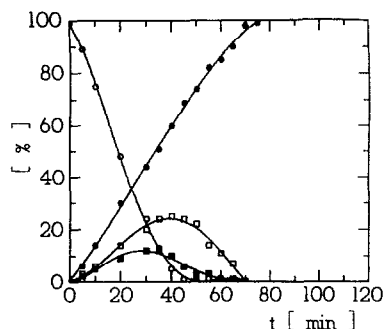


Fig. 2. Hydrogenation of 1-octene (20 mmol) at room temperature at 1 bar hydrogen pressure (7 l/h) in 40 ml heptane (catalyst: 800 vac/350 CO (0.9% Ru) ○ 1-octene, ● octane, □ *trans*-2-octene, ■ *cis*-2-octene).

comparable to that observed in the reactions under elevated pressure appeared and the reaction started immediately. However, at the beginning of the reaction there was a short period of acceleration as shown in Fig. 2. During the reaction, formation of small amounts of *trans*-2-octene and *cis*-2-octene as intermediates were observed. Finally the conversion again yielded *n*-octane with 1% 3-methyl-heptane as side product.

Addition of 1-octene during the hydrogenation did not change the reaction rate. Addition of 1-octene after a completed run caused the appearance of the above mentioned acceleration period.

A small amount of 1-octene was added to a sample of the catalyst in the reflectance cell of the IR-spectrometer. Subsequently hydrogen was passed through the cell and the progress of the reaction was monitored (Fig. 3). The intensity of the absorption band at 3082 cm⁻¹ (C–H stretching frequency at the C=C double bond) decreased and finally disappeared. Correspondingly, the intensity of the band at 3585 cm⁻¹ decreased. This absorption band is probably due to an interaction between an olefinic double bond and a SiOH group [70]. After seven minutes the only absorption bands remaining in the region of the C–H stretching vibrations have to be assigned to octane.

Catalysts employed in the following comparative tests were taken from a single preparation

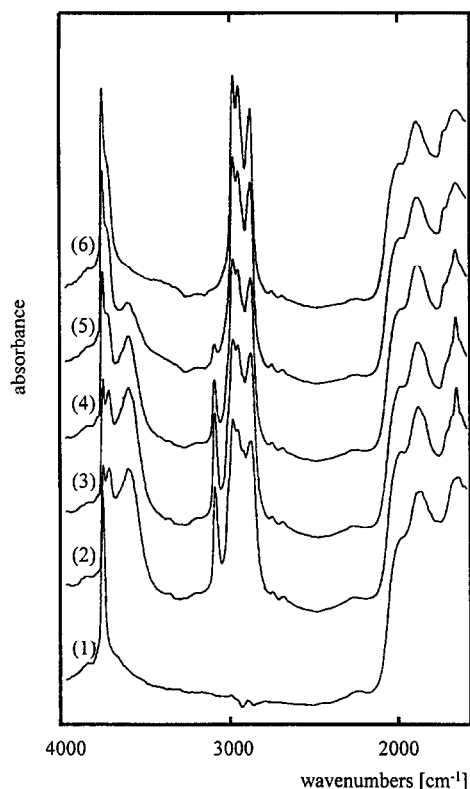


Fig. 3. Hydrogenation of 1-octene monitored by IR spectroscopy (catalyst 800 vac/350 CO (0.4% Ru) at RT: (1) catalyst under argon; (2) catalyst after adding 1-octene under argon; (3) after 1 min H₂ flow; (4) after 3 min H₂ flow, (5) after 5 min H₂ flow, (6) after 7 min H₂ flow.

process each, since the catalytic properties diverged slightly despite apparently identical preparation conditions.

3.4. Treatment of the catalyst 800 vac / 350 CO with O₂ and CO

The catalyst 800 vac/350 CO (0.9% Ru) was treated with O₂ at room temperature and immediately afterwards tested in a hydrogenation reaction. This treatment should reveal the influence of oxygen on the catalyst (oxidation of the ruthenium sites). During the exposure of the catalyst to oxygen, the color changed from brown to black-brown. Compared to an untreated catalyst (as shown in Fig. 2) the reaction rate was slower (duration of the hydrogenation reaction: 105 min) and a smaller amount of

isomers was formed during the reaction (*trans*-2-octene max. 15% at 70 min; *cis*-2-octene max 8% at 60 min).

A similar treatment with CO at room temperature was carried out to study the role of coordination of CO to the unsaturated ruthenium sites and the resulting influence on the catalytic behavior. The color of the catalyst did not change; however, in the carbonyl region of the IR spectrum two absorption bands appeared ($\nu_{\text{CO}} = 2130, 2070 \text{ cm}^{-1}$). The following hydrogenation reaction (duration 180 min) was slower than in the case of an untreated catalyst (as shown in Fig. 2) or even in the case of a catalyst treated with oxygen. The maximum production of isomers was comparable to the results with the untreated catalysts: *trans*-2-octene approx. 30% at 90 min; *cis*-2-octene approx. 12% at 75 min. After finishing the reaction, no CO absorption bands could be detected in the IR spectrum of the catalyst.

3.5. Other catalysts

The catalyst 600 O₂/350 CO which showed the same reaction rate under hydrogen pressure (60 bar) as 800 vac/350 CO (catalysts 9 and 14, Table 1), was also tested under 1 bar hydrogen. The hydrogenation reaction was now significantly slower compared to the catalyst 800 vac/350 CO and was complete after approximately 200 min. Furthermore, only very small amounts of isomers were formed. A blank catalyst (free of ruthenium) showed no catalytic reaction at all after 5 h under 1 bar of hydrogen pressure.

3.6. Variation of the temperature

The influence of the temperature on the reaction rate of the hydrogenation reactions was studied for the catalyst 800 vac/350 CO (0.9% Ru) at different temperatures (10°C, 25°C, 40°C, and 55°C). The increase in temperature caused not only the expected acceleration of the reaction rate but also an increase in the amount of

the isomers formed during the reaction. At 10°C the hydrogenation reaction of 1-octene was complete after approx. 110 min, a period which decreased to approx. 70 min at 55°C. The variation of temperature also affected the amount of isomers formed: The formation of *trans*-2-octene reached its maximum of approx. 20% at 80 min (*cis*-octene 8% at 60 min) at 10°C and approx. 40% after 30 min (*cis*-2-octene 16% after 20 min) at 55°C. The experimental data were used to calculate the rate constants on the basis of the equation of zero order, $[A_0] - [A] = kt$. (55°C: $k = 1.75 \cdot 10^{-2} \text{ mol l}^{-1} \cdot \text{min}^{-1}$; 40°C: $k = 1.25 \cdot 10^{-2} \text{ mol l}^{-1} \cdot \text{min}^{-1}$; 25°C: $k = 9.35 \cdot 10^{-3} \text{ mol l}^{-1} \cdot \text{min}^{-1}$; 10°C: $k = 6.29 \cdot 10^{-3} \text{ mol l}^{-1} \cdot \text{min}^{-1}$). From the values of the rate constants an activation energy of 18 k/mol was determined using the Arrhenius equation. However, it has to be considered that diffusion is the rate limiting step.

3.7. Hydrogenation of isomeric octenes

Since isomeric octenes were formed during the hydrogenation of 1-octene, the hydrogenation of *trans*-2-octene and *cis*-2-octene was also studied using the catalyst 800 vac/350 CO (0.9% Ru). The decrease in *trans*-2-octene was linear up to a conversion of 50%. The reaction rate then became slightly slower in contrast to the behavior observed in the case of 1-octene. The amount of *cis*-2-octene formed during the

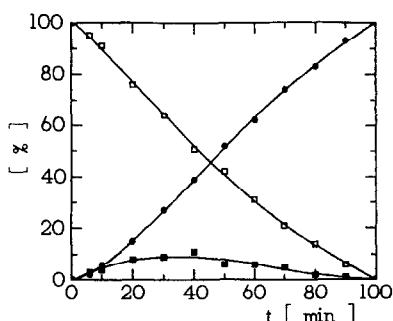


Fig. 4. Hydrogenation of *trans*-2-octene at RT (catalyst: 800 vac/350 CO (0.9% Ru)). □ *trans*-2-octene, ● octane, ■ *cis*-2-octene.

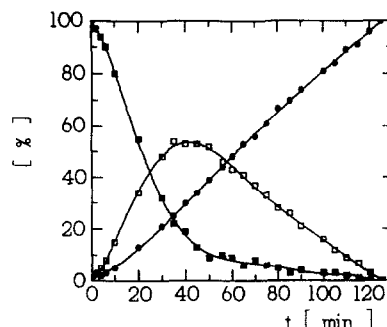


Fig. 5. Hydrogenation of *cis*-2-octene at RT (catalyst: 800 vac/350 CO (0.9% Ru)). ■ *cis*-2-octene, ● octane, □ *trans*-2-octene.

reaction was approximately the same as in the case of 1-octene (Fig. 4).

During the hydrogenation of *cis*-2-octene an isomerization to the thermodynamically more stable *trans*-2-octene (up to 55% conversion) was first favored compared to the hydrogenation (Fig. 5).

A mixture of 1-octene and *trans*-2-octene (1:1) was hydrogenated under the same conditions and with the same catalyst (Fig. 6). The decrease of 1-octene took place in the same way as observed before, with the significant exception that the acceleration period of the reaction rate was clearly longer than usual. Surprisingly, the concentration of *trans*-2-octene increased initially and did not decrease before most of the 1-octene was converted. The amount of *cis*-2-octene formed was within the usual range.

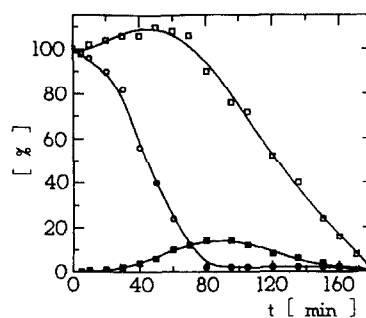


Fig. 6. Decrease of 1-octene and *trans*-2-octene (20 mmol each) at RT in a hydrogenation reaction (catalyst: 800 vac/350 CO (0.9% Ru)). The increase of *trans*-2-octene to more than 100% is caused by its formation from 1-octene by isomerization. ○ 1-octene, □ *trans*-2-octene, ■ *cis*-2-octene.

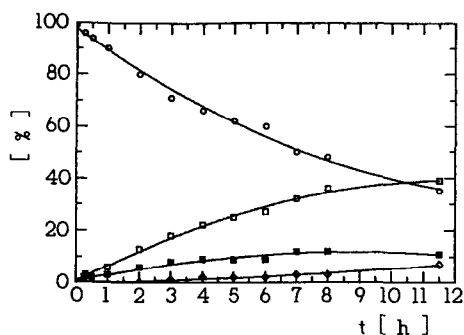


Fig. 7. Isomerization of 1-octene under argon at 90°C (catalyst: 800 vac/350 CO (0.9% Ru)). ○ 1-octene, □ *trans*-2-octene, ■ *cis*-2-octene, ◇ *trans*-3- and *trans*-4-octene.

The hydrogenation of cyclooctene under the same conditions was of zero order as with open chain olefins, but considerably slower (135 min reaction time). No isomers were formed.

3.8. Isomerization

The isomerization activity of the catalyst 800 vac/350 CO (0.9% Ru) with respect to 1-octene was tested at 90°C without hydrogen. The conversion started immediately after the addition of the olefin without any induction period or acceleration; the rate law was observed as first order. Products are given as a function of time in Fig. 7.

4. Discussion

The primary goal of this work was to prepare coordinatively unsaturated surface species of ruthenium on silica gel in analogy to the Phillips system. Therefore, preparation conditions were chosen which proved to be successful for the preparation of coordinatively unsaturated surface species of other transition metals [2]. In those cases an activation was carried out under oxygen followed by a reduction under carbon monoxide. The use of oxygen is limited since volatile ruthenium oxides are formed above 600°C. Therefore the activation preferentially was carried out under vacuum at higher temperatures. Subsequently the activated catalysts were

reduced under CO. Since most of the prepared ruthenium catalysts showed satisfying catalytic activity with respect to the hydrogenation of 1-octene (Table 1), this reaction was chosen as a test reaction to optimize the preparation conditions.

In the case of the hydrogenation reactions of 1-octene under pressure (usually 60 bar) which were carried out as batch reactions in an autoclave, two distinctive sections have been observed. The first comprises an induction period which has been proved to be reproducible; it increases with decreasing pressure. Seemingly, no reaction occurs during this period. During the second section the pressure decreases and the reaction (hydrogenation/isomerization) takes place. The length of this period also depends on the initial pressure and becomes longer at lower initial pressure. In a batch reaction the gas space of the autoclave provides the hydrogen supply. This system is effective if the ratio of the gas space to the volume of the liquid is large and the initial pressure is high [71]. The hydrogen has to diffuse through the liquid phase; that means in this case through the substrate. It can be assumed that the coordinatively unsaturated surface sites are covered by olefin molecules. The hydrogen has to replace an olefin in the neighborhood of another to form the active ruthenium surface species with hydrogen and the olefin in its coordination sphere. This process may account for the induction period beside the diffusion. A lower initial pressure results in a longer induction period as well as in a longer reaction period indicating a slower hydrogen diffusion through the liquid phase. However, catalysts with less good properties show generally longer induction periods as well as longer reaction periods. This indicates that diffusion might not be the only effect responsible for the induction period and the formation of an active species may also be considered.

Catalysts with the best hydrogenation properties under pressure were also tested with 1-octene under 1 bar hydrogen. The induction period was not observed here — in contrast to the

expectation since the induction period was found to increase with decreasing pressure between 60 bar and 10 bar as mentioned above. During reactions at 1 bar the hydrogen was bubbled through the liquid phase consisting of solvent and substrate. By this method a much better gas–liquid mass transfer of hydrogen may be achieved and, more important, a formation of an active ruthenium surface species with hydrogen and the (diluted) olefin in its coordination sphere is more favorable than under the conditions of the autoclave reactions where no solvent is used. The initial period of acceleration may be caused by the formation of the active species. Addition of 1-octene during the hydrogenation reaction does not affect the rate, but if 1-octene is added once again after the complete hydrogenation of the starting material and eventually formed isomers, the acceleration period is observed again³.

A rate dependence on the agitation speed was not observed. However, the mixing of the reaction suspension caused by the hydrogen flow alone was not enough to maintain the hydrogenation rate when the stirrer was switched off. Nevertheless, the reaction may still take place under conditions where the rate of dissolution of the hydrogen determines the rate of hydrogenation even when the reaction mixture is stirred. This means that we observe a reaction of zero order with respect to 1-octene.

In all our experiments an isomerization was observed as a side reaction; however, all these isomers are finally converted to octane. This kind of isomerization under conditions of catalytic hydrogenation has been observed with homogeneous catalysts [74] and in a control experiment with a commercial Pd/C catalyst which we used for a comparison with our catalyst. In the latter case the unusual side product 3-methyl-heptane was observed as well. Overall the reaction on Pd/C proceeded more quickly [75].

Activation and reduction temperatures during the preparation play a crucial role as far as the catalytic properties are concerned. The catalysts ‘activated only’ show less good hydrogenation properties than the reduced ones. Since at higher temperatures oxygen causes a stronger oxidation which finally results in the formation of volatile ruthenium oxides above 600°C, we may assume that the hydrogenation is less favored when the ruthenium is in a higher average oxidation state. Correspondingly, a reduction of the catalysts at elevated temperatures accelerates the hydrogenation in general. It is supposed that coordinatively unsaturated sites of ruthenium are formed during this process — sites which are essential for the coordination of the olefin and hydrogen and therefore for the formation of an active species. The catalyst 200 O₂/250 CO (catalyst 1, Table 1) hardly shows any catalytic behavior. In its IR spectrum we find four absorption bands and three shoulders in the carbonyl region. The catalytically active species might be blocked under these conditions by coordination of CO ligands. Therefore less, or even no, free coordination sites are available for an incorporation into the catalytic circle. The IR spectrum of the catalyst 250 O₂/250 CO (catalyst 3, Table 1) shows fewer and less intensive CO absorption bands — and its catalytic properties are better. The vacuum activated catalyst 250 vac/250 CO (catalyst 11, Table 1) has nearly identical properties as the oxygen activated catalyst and its IR spectrum is the same. Therefore we may assume that the ruthenium species is comparable in both cases.

With an activation temperature above 300°C there is no longer any formation of surface ruthenium carbonyl species during the preparation. Nevertheless, a further increase of the temperature during the activation process improves the catalytic properties. Therefore, the formation of ruthenium carbonyl surface compounds cannot be the only explanation for the slow reaction rate using catalysts activated at relatively low temperatures. Coordinating silanol or siloxane groups in the neighborhood of the

³ A similar behavior is observed in the case of the polymerization of 1-octene with chromium catalysts [72,73].

active center may be responsible for the poor activity as well.

Activations above 600°C were carried out under vacuum instead of oxygen to avoid the formation of volatile oxides of highly oxidized ruthenium. Despite the fact that the oxidizing effect of oxygen was no longer effective we observed a further acceleration of the hydrogenation rate.

The influence of the temperature during the reduction is also important. The results listed in Table 1 reveal that activated catalysts which are reduced subsequently at 350°C show the best properties. Since 'RuCl₃ · 3H₂O' was used as starting material which contains ruthenium mainly in an oxidation state of three (partially four as well) [69], it is assumed that at least a substantial part of the ruthenium anchored on the surface after an *activation under vacuum* remains in the oxidation state three. During a following reduction under an atmosphere of carbon monoxide at 300°C, 70–80 mol% carbon dioxide were formed with respect to the amount of ruthenium on the catalyst (after correction using a blank catalyst).

Therefore, it is likely that most of the ruthenium species are reduced to an oxidation state of two. The IR spectrum of the reduced catalyst shows no absorption bands of CO when the catalyst was cooled under argon to RT. However, this catalyst easily adsorbs CO at room temperature indicating the presence of a coordinatively unsaturated surface species. In the IR spectrum of this catalyst two absorption bands at 2130 and 2070 cm⁻¹ appear. Absorption bands in this range of the spectrum suggest an oxidation state > 0 since CO adsorbed on metallic ruthenium shows absorption bands between 1984–2061 cm⁻¹ depending on the coverage [76]. (For further spectroscopic investigations see [75,77]). Catalysts reduced with hydrogen (catalysts 15 and 16 in Table 1) under conditions where a reduction to metallic ruthenium takes place are less active (*vide infra*).

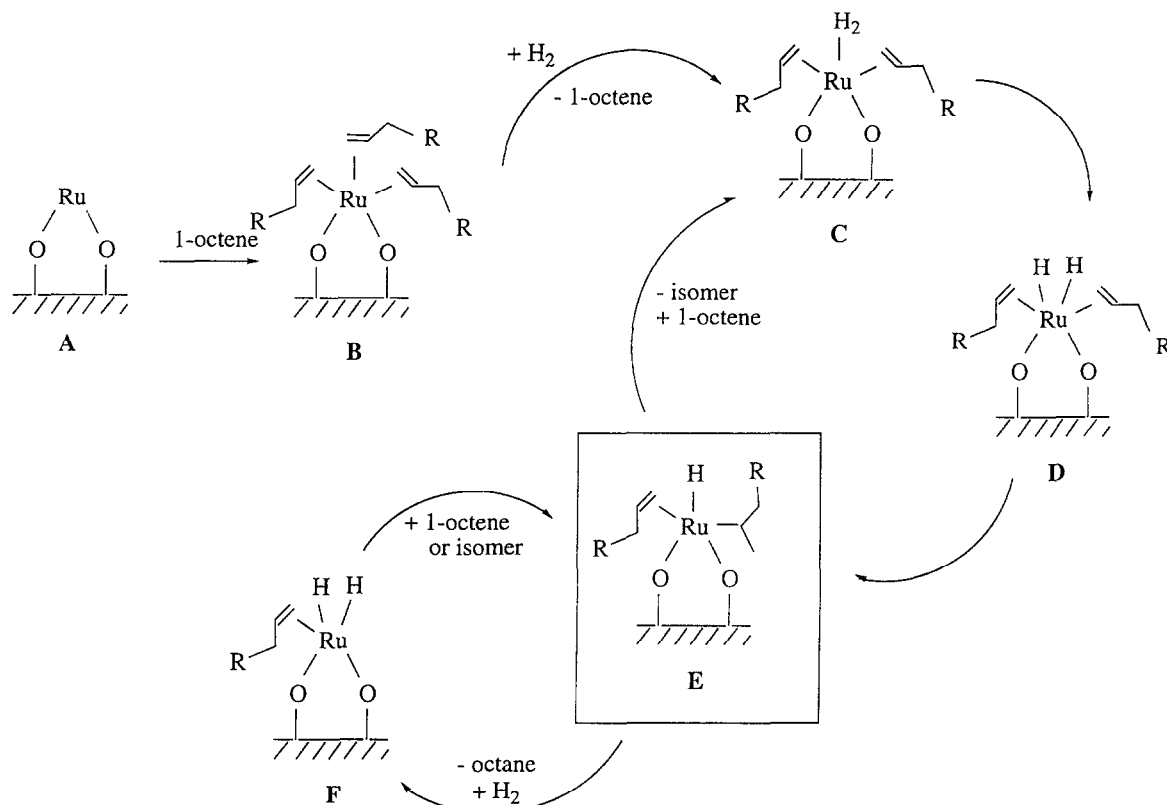
The rate of the hydrogenation (1 bar hydrogen pressure) after CO treatment of this catalyst

is significantly slower since the free coordination sites are now occupied. After completion of the reaction there are no CO absorption bands detected in the IR spectrum anymore. This supports the assumption that CO coordination takes place at the catalytically active sites. However, an acceleration of the reaction rate or a larger induction period at the beginning was not observed. This would indicate that as soon as CO is removed a 'normal' reaction starts. It could be that subsequently only some ruthenium centers may form an active species or the CO causes other changes in the catalyst as well.

By treatment of the catalyst 800 vac/350 CO with O₂ at room temperature the color changes from brown to black-brown. This may be due to an oxidation of coordinatively unsaturated ruthenium sites, since the catalysts activated in O₂ show a similar color. The hydrogenation rate is slower compared to the untreated catalyst under 1 bar hydrogen pressure and less isomers are formed.

To compare the effect of a CO reduction with that of a hydrogen reduction the activated catalyst 800 vac/- was reduced at 350°C in a stream of hydrogen (catalyst 16, Table 1) as well as the CO reduced catalyst 800 vac/350 CO (catalyst 15, Table 1). The hydrogenation properties of these catalysts were tested in a pressure reaction. The obvious difference compared to the CO reduced catalyst 800 vac/350 CO was a much longer induction period with nearly no change in the following reaction period. Remarkably the two catalysts reduced under hydrogen showed almost the same induction period. Diffusion is certainly not the main reason for the induction period in this case: these catalysts seem to need longer to form a catalytically active species. Once this has been formed, they react as observed in the case of the CO reduced catalyst 14. Interestingly the same catalyst 14 stored under a pressure of 60 bar hydrogen at room temperature for 15 h showed an even longer induction period while there was no difference in the hydrogenation period.

In general, catalysts activated at higher tem-



Scheme 1. Proposed mechanism for the hydrogenation of 1-octene, including isomerization in presence of hydrogen.

peratures exhibit the best catalytic properties. However, there are differences with respect to the hydrogen pressure. The catalysts 800 vac/350 CO and 600 O₂/350 CO both catalyze the hydrogenation reaction with the same rate at a pressure of 60 bar (catalysts 9 and 14, Table 1), but under normal pressure the type 800 vac/350 CO is proved to be a superior hydrogenation catalyst. This observation clearly exhibits the limitation of the reaction rate by diffusion in the case of the reaction carried out in the autoclave while under 1 bar atmosphere of hydrogen these catalysts catalyze the reaction with different rates.

In the case of hydrogenation reactions under 1 bar hydrogen pressure the decrease of 1-octene obeys a rate law of zero order in all our experiments independent of the catalyst used. A remarkable result of the hydrogenation experiments at different temperatures is the fact that at

10°C less isomers are formed than at 55°C. Furthermore, the isomerization of 1-octene in the absence of hydrogen (catalyst: 800 vac/350 CO) is favored at a higher temperature (90°C) but proceeds with a slower rate and a different reaction order (first order with regard to 1-octene). This suggests that these reactions proceed via different mechanisms (*vide infra*).

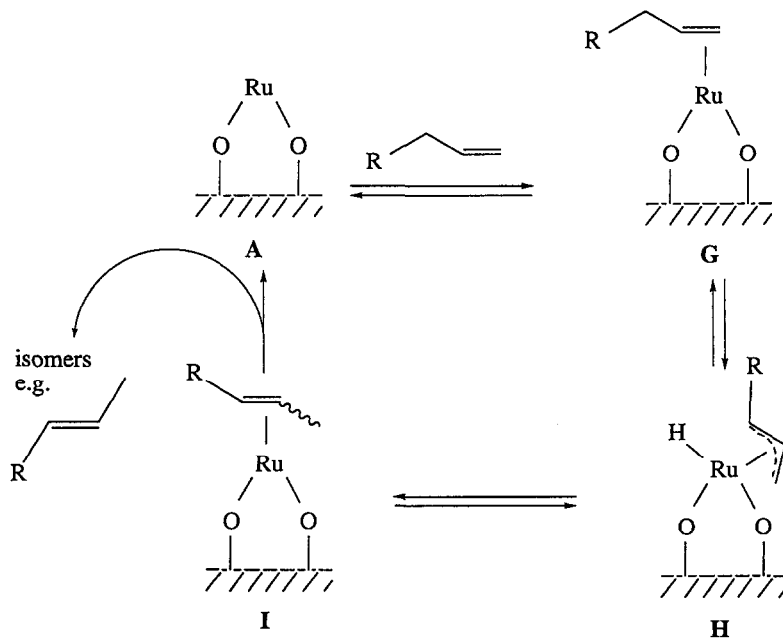
For the hydrogenation rates of isomeric octenes and cyclooctene by the catalyst 800 vac/350 CO the following order (with regard to the decrease of the olefin concentration) was observed⁴: 1-octene > *cis*-2-octene > *trans*-2-octene > cyclooctene.

⁴ For the hydrogenation of 1-butene a different order was reported in the literature: *trans*-2-butene > *cis*-2-butene > 1-butene [59]. However, this reaction was carried out as a gas phase reaction and an isomerization during the induction period was observed.

During the hydrogenation of *cis*-2-octene an initial isomerization to the thermodynamically more stable *trans*-2-octene was observed; obviously the hydrogenation reaction is slower than the isomerization reaction during this period. If a 1:1 mixture of 1-octene and *trans*-2-octene was used for hydrogenation, the 1-octene was hydrogenated first. The *trans*-2-octene even increased to more than the original amount by the concurrent isomerization of 1-octene. The *trans*-2-octene started to react only when most of the 1-octene had been hydrogenated. This shows that the active centers of our catalyst interact most easily with the terminal double bond due to its steric accessibility. The relatively slow hydrogenation of cyclooctene may also be due to steric reasons.

The results of this work allow us to propose a mechanism for the hydrogenation of 1-octene and for the simultaneous formation of isomers (Scheme 1). We assume that the ruthenium surface species (species A) are saturated by coordinated olefin molecules (B) under the conditions of the autoclave reactions. The hydrogen has to diffuse through the liquid phase and it

has to replace one 1-octene molecule to form a hydrido olefin complex (C and D). These steps may account for the long induction period and the fact that no isomers were found during the induction period. In the next step a hydrogen is transferred to one olefinic ligand resulting in a hydrido alkyl complex E which can be considered as the active species. This explains the formation of the isomers by a transfer of a hydrogen from the ligand back to the metal center under formation of a thermodynamically more stable internal double bond as well as the formation of octane when the second hydrogen is transferred from the metal to the ligand. In both cases the hydrocarbon ligand (octane or isomer) leaves the coordination sphere of the ruthenium and species E can start the cycle again via species C under coordination of 1-octene or via species F under coordination of hydrogen and 1-octene or an isomeric octene. In the reaction carried out in a solvent and under 1 bar hydrogen atmosphere a ruthenium hydrido-species can be formed more easily and species C can be formed more rapidly after addition of 1-octene. The period of acceleration may be



Scheme 2. Proposed mechanism for the isomerization of 1-octene in absence of hydrogen.

explained by the formation of species C. A similar mechanism has also been proposed for the homogeneous nickel catalyzed isomerization of olefins [78].

This mechanism does not explain the octene isomerization in the absence of hydrogen. In this case we propose a different mechanism which is shown in Scheme 2. 1-octene is coordinated to the ruthenium surface species G (other coordinated ligands have been omitted for clarity). We assume that a transfer of the hydrogen from the coordinated alkene to the ruthenium results in the formation of the hydrido species H. The hydrogen is transferred back to the allylic ligand and a thermodynamically more stable internal double bond is formed. A similar allylic hydrido nickel complex has been observed in the case of propene coordinated to nickel [79]. In this case the hydrogen which is necessary for the formation of the hydrido ruthenium surface complex originates from the olefin. This is in accordance with the fact that the rate depends on the concentration of 1-octene (first order reaction).

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