Preparation and properties of ruthenium supported catalysts

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Two types of impregnation solvents were suggested for preparation of the ruthenium supported catalysts. Charcoal, silica, alumina and titania supports were used. Special attention was paid to reduction and activation conditions of nonreduced and passivated forms, respectively. Hydrogenation of 1-heptene, cyclohexene, benzene and acetophenone in the liquid phase were studied using the prepared catalysts.

Keywords: Ruthenium catalysts; supported catalysts; catalyst preparation; benzene hydrogenation; acetophenone hydrogenation; competitive hydrogenation

1. Introduction

Supported ruthenium catalysts have usually been used for hydrogenation of series of organic compounds [1–8], especially for the partial hydrogenation of benzene and toluene to cyclohexene and methylcyclohexene, respectively [9,10]. Application of organic and inorganic reaction modifiers may give rise to increased selectivity of the reaction to cyclo-olefinic intermediates either in gas or in liquid phase [10–17]. According to Struijk et al. [10–12] the addition of various metallic salts to the reaction mixture may result, besides a suppression of the reaction rate, in an increased selectivity to cyclohexene. The salt solution is adsorbed on the catalytic surface, which originally hydrophobic, is rendered hydrophilic [12]. As a result the catalytic particles are surrounded by a stagnant water layer causing a strong diffusional resistance for hydrogen and cyclohexene mass transport to the ruthenium surface which slows down the further hydrogenation of cyclohexene to cyclohexane [10–12]. The action of organic reaction modifiers (aliphatic alcohols, ε-caprolactam, etc.), might be explained in terms of the formation of adsorbate–adsorbate interactions between cyclohexene and the modifier [16–18]

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which are competitively adsorbed on the surface. Owing to that, the overlap of the π-electrons of the double bond of cyclohexene with the ruthenium d-orbitals is diminished. The bonding between the modifier and cyclohexene is weak, which results in desorption of the hydrogen-bonded cyclohexene at a higher rate than of the cyclohexene molecules bonded directly to the ruthenium surface [18].

Dealing with supported metals, one must also be aware of metal particle size effects [19] and metal–support interactions that may change the catalytic behavior of the metal component [20]. The kinetics of hydrogenation reactions has been considered to be structure insensitive, which means, that the rate per unit surface area of the metal seems not to depend on the degree of dispersion of the metal [21].

Recent studies have shown that titania support can have a significant influence on adsorptive properties of a metal component dispersed on its surface [22,23]. This behaviour has been attributed to strong metal–support interactions (SMSI) [24], which include the epitaxial stabilization of preferred crystal faces, transfer of electrons between the metal particles and the support, or a combination of both [25,26].

Reviews of methods which have been used for the catalyst preparation were given elsewhere [27–30]. In the present study we impregnated a support (active C, SiO_2, Al_2O_3, TiO_2) with $RuCl_3$ in excess of an impregnation solvent (water, ethanol) followed by drying and reduction and activation steps. We applied prepared catalysts in hydrogenation of 1-heptene to heptane including a study of isomerization activity of the catalysts in an inert atmosphere, cyclohexene to cyclohexane, benzene to cyclohexene and cyclohexane and acetophenone to 1-cyclohexylethanol assuming alternative reaction pathways.

2. Experimental

2.1. MATERIALS

Except of Ru-1 and Ru-4 (Engelhard) all other catalysts were prepared in the study from active component precursor – ruthenium(III) chloride (Fluka AG) and catalytic supports – charcoal Supersorbon – 1200 m^2/g (Degussa); titanium(IV) oxide – Tiona 472 – 55 m^2/g (SCM-GB); alumina Pural-SB – 150 m^2/g (Condea), silica – 250 m^2/g – prepared from $(C_2H_5O)_4Si$. All substrates used in the study were p.a. and freshly distilled prior to use.

2.2. CATALYST PREPARATION AND KINETIC MEASUREMENT

The catalyst preparation followed the conventional impregnation technique using water and ethanol as impregnation solvents. The reduction conditions are given in table 1. The catalyst was thoroughly activated in the activation furnace prior to use in hydrogen atmosphere at 453 K for 1 h, then covered with a solvent and trans-

Table 1
Conditions of impregnation and reduction of the catalysts

Catalyst code	Solvent	Phase I	Phase II	Phase III
5% Ru/C Ru-1 (Engelhard)		–	–	–
5% Ru/C Ru-2	water	to 393 K 1 h in N_2 at 25 ml/min	to 453 K 1 h in $N_2/H_2 = 1/1$ 40 ml/min	to 593 K 8 h in H_2 30 ml/min
5% Ru/C Ru-3	ethanol	idem	idem	idem
2% Ru/Al_2O_3 Ru-4 (Engelhard)		–	–	–
5% Ru/Al_2O_3 Ru-5	water	to 423 K 1 h in N_2 at 25 ml/min	to 523 K 1 h in $N_2/H_2 = 1/1$ 40 ml/min	at 673 K 6 h in H_2 30 ml/min
5% Ru/Al_2O_3 Ru-6	ethanol	idem	idem	idem
5% Ru/SiO_2 Ru-7	water	to 473 K 1 h in N_2 at 25 ml/min	to 573 K 1 h in $N_2/H_2 = 1/1$ 25 ml/min	at 693 K 9 h in H_2 30 ml/min
5% Ru/SiO_2 Ru-8	ethanol	idem	idem	idem
2.5% Ru/TiO_2 Ru-9	water	to 503 K 1 h in N_2 at 25 ml/min	to 550 K 1 h in $N_2/H_2 = 1/1$ 40 ml/min	at 773 K 5 h in H_2 30 ml/min

ferred to the reactor where it was subjected to the final activation. Typically, it took 10 min with a flow rate of hydrogen of 50 ml/min.

Kinetic measurements were carried out in a semi-batch isothermal stirred reactor connected to gasometric burettes. All experiments were performed at atmospheric pressure and at 303 K. Typically the experiments were carried out in 15 ml of a solvent (isopropanol) with initial volume of a substrate 0.2 ml and the amount of the catalyst varied from 0.1 to 0.5 g. Description of the typical experiment is given elsewhere [30–33]. Mass transfer was not the rate limiting step in the experiments (kinetic regime). Parameters of the power-law kinetic equations (rate constants and reaction orders) were evaluated by means of the Runge–Kutta–Gill method.

2.3. ANALYSIS

The XRD data were obtained using a XRD 3000 P diffractometer (Seifert & Co., Germany) with Bragg-Brentano focusing geometry, Co Kα radiation and graphite monochromator.

The BET surface area was measured on a BET apparatus Pulse Chemisorb 2700 (Micrometrics, USA). The S_{BET} areas were calculated from N_2 adsorption isotherms at 78 K, taking the cross-sectional area of a nitrogen molecule 0.162 nm^2.

SEM micrographs were taken on a Jeol JEM 100 B apparatus (Jeol, Japan). Samples for analysis were fixed on the holder and coated with a thin layer of gold.

The catalyst supports were analyzed on the presence of various ions using atomic adsorption spectroscopy (AAS) Spectr AA 300 (Varian, USA).

Analyses of reaction mixtures were performed on a GC/MC analytical system HP 5970 (Hewlett Packard, USA) with a capillary column (25 m) covered with Carbowax 20M. The temperature varied from 333 to 423 K, the injection split was established at 50 : 1, the pressure of helium was 45 kPa and the injection volume was 0.5 µl.

3. Results and discussion

The selectivity problems usually arising in the performance of ruthenium hydrogenation catalysts (aromatic ring and carbonyl function hydrogenations), might be, to a certain extent, attributed to the effect of various ions adsorbed on the active surface sites. On the basis of the AAS results (table 2) it is seen that the active charcoal support was rich on iron (0.05%), copper (0.02%), zinc (0.06%) and selenium (0.05%) ions. Silica support contained iron (0.07%), nickel (0.01%) and zinc (0.02%) ions and titania–copper (0.02%) ions. Alumina support was relatively very pure (0.003% Fe, 0.001% Cu and Zn), with only insignificant traces of other metals. All these ions, identified in the catalytic supports, may upon drying and reduction steps concentrate themselves on the ruthenium active sites and play an important role as catalyst modifiers. Their possible effect is discussed in the next paragraphs.

3.1. HYDROGENATION OF 1-HEPTENE AND CYCLOHEXENE

No products of 1-heptene isomerization were found in our experiments, including separate study of the isomerization activity of the catalysts in an inert atmosphere. Reaction orders in 1-heptene (m_1) and rate constants (k_1) of 1-heptene hydrogenation ($C_{A_0} = 0.1$ mol ℓ^{-1}) are given in table 3. It is seen, the best activity for this reaction generally was shown by catalysts supported on charcoal and alumina, especially those impregnated in ethanol. On the other hand the activities of silica and also of titania supported catalysts were significantly less. When reduced

Table 2
AAS analysis (%) of catalytic supports used

	Act. charcoal	Alumina	Silica	Titania
K	<0.001	<0.001	<0.001	<0.001
Na	<0.001	<0.001	<0.001	<0.001
Cs	<0.001	<0.001	<0.001	<0.001
Mg	<0.001	<0.001	<0.001	*0.02*
Ba	<0.001	<0.001	<0.001	<0.001
Ti	<0.01	<0.01	<0.01	–
Mn	*0.005*	<0.0005	*0.002*	<0.0001
Fe	*0.054*	*0.003*	*0.069*	*0.005*
Co	<0.0005	<0.0005	<0.0005	<0.0005
Ni	*0.008*	<0.0002	*0.014*	<0.0008
Cu	*0.020*	*0.001*	*0.003*	*0.016*
Zn	*0.065*	*0.001*	*0.023*	*0.005*
Cd	<0.0001	<0.0001	<0.0001	<0.0001
Ga	<0.008	<0.004	<0.004	<0.004
Si	<0.008	<0.008	–	*0.032*
Ge	<0.01	<0.01	<0.01	<0.01
Sn	<0.005	<0.005	<0.005	<0.005
Se	*0.05*	<0.002	<0.002	<0.002

at higher temperatures (above 770 K, table 2), electron-acceptor defect sites are created on titania [23] and the strong suppression in catalytic activity of Ru/TiO_2 after reduction can be, at least partially, explained by a geometric blocking of active sites by TiO_x species formed in the presence of ruthenium [25,34] accompanied by the formation of metal–Ti bonds.

Activities of our catalysts for cyclohexene hydrogenation ($C_{B_0} = 0.13$ mol ℓ^{-1}) were not bad as well with the same increased activity of alcohol impregnated catalysts. The reaction orders in cyclohexene (m_2) varied in the range 0.01 for Ru/silica

Table 3
Data of hydrogenation of 1-heptene and cyclohexene [a]

Catalyst	1-heptene		cyclohexene	
	k_1	m_1	k_2	m_2
Ru-1	12.0	0.53	18.25	0.22
Ru-2	4.0	0.61	8.24	0.10
Ru-3	10.3	0.50	13.24	0.11
Ru-4	4.5	0.19	8.92	0.28
Ru-5	5.3	0.20	10.50	0.10
Ru-6	8.7	0.19	17.78	0.17
Ru-7	1.5	0.53	0.01	0.01
Ru-8	2.0	0.15	4.30	0.07
Ru-9	2.5	0.37	15.50	0.12

[a] $[k_1, k_2] = \mathrm{ml}^m\,\mathrm{mmol}_A^{1-m}/g_{\mathrm{cat}}\,\mathrm{min}$.

(Ru-7) to 0.28 for Ru/alumina (Ru-4), which correlated well with zero order approximation to cyclohexene in consecutive benzene hydrogenation (next section). In hydrogenation of cyclohexene neither benzene nor 1,3- or 1,4-cyclohexadienes were detected in the reaction mixture as described by Ruzicka [35] on palladium catalysts. Comparing reaction orders in 1-heptene and cyclohexene (table 3), it is seen they were generally lower (except of Ru-4) for cyclohexene. This might be caused by better adsorption ability of cyclohexene on the surface of the ruthenium catalysts, which moreover, agrees well with their observed higher activity for cyclohexene hydrogenation. On the other hand, our results were in contradiction with the usual experience in hydrogenation of olefinic compounds over group VIII [36].

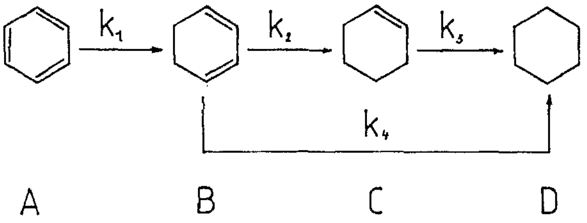
Considering these facts we carried out competitive hydrogenation of the equimolar mixture of 1-heptene (A) and cyclohexene (B) ($n_{A_0} = n_{B_0} = 1.97$ mmol) on Ru-1 catalyst. The results were evaluated in terms of the S_{BA} value, first defined by Rader and Smith [37] in the form $S_{BA} = \log(C_B/C_{B_0})/\log(C_A/C_{A_0})$. The reaction gave us in Rader–Smith's coordinations a linear dependence with $S_{BA} = 1.1$ (although the orders in 1-heptene and in cyclohexene were not the same), which confirmed the higher reactivity of cyclohexene in our experiments.

In a much simpler way, one of the possible explanations of the higher reactivity of cyclohexene in our reactions might also be sought in terms of the fact that ruthenium dissociates the C–H bond. Therefore, 1-heptene is adsorbed on more than one place, which may act as self-poisoning of the surface. On the other hand, cyclohexene π-complexed on the surface, suffers less by this two-point adsorption.

In all experiments no deactivation of the catalysts occurred.

3.2. HYDROGENATION OF BENZENE

The experimental concentration versus time data of benzene hydrogenation and the finding that 1,3-cyclohexadiene and sometimes cyclohexene were formed on the surface of the Ru catalysts led us to the following scheme of the transformation of benzene to cyclohexane over ruthenium supported catalysts:



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At the conditions used in the study, 1,3-cyclohexadiene as one of the possible intermediates was transformed directly to cyclohexane without desorption of cyclohexene to the bulk phase except of the reaction on Ru-1 catalyst ($C_{A_0} = 0.148$ mol ℓ^{-1}, $C_{B_0} = C_{C_0} = C_{D_0} = 0$). Orders of the reaction in benzene (m) and rate constants are given in table 4. Reaction orders (m) in benzene varied in the range of 0.70–0.90. The table does not include orders in 1,3-cyclohexadiene and cyclohexene, since both approached zero. Parameters X_A and S_x have been defined as benzene converted in the reaction until the catalyst had lost its activity and selectivity to individual intermediates or products in the time of their maximum concentration (e.g. $S_B = \%B/[\%B + \%C + \%D]$), respectively. In analogy with the previous experiments similar improved activity of alcohol impregnated catalysts was observed.

The exceptional position of the Ru-1 catalyst in benzene hydrogenation has to be pointed out. Experiments carried out on this well-active catalysts proceeded as consecutive reactions with high selectivities both to 1,3-cyclohexadiene and cyclohexene (table 4). It is a well known fact that the presence of various metal cations on the ruthenium surface may lead to the enhanced selectivity to cyclohexene. According to AAS analysis, the content of 0.1% of Na ions was found in the Ru-1 catalyst. The role of the alkali metal in the promotion of diene and cyclohexene formation is caused by an electron donation from alkali metal to ruthenium [38]. It is reasonable to assume that the intermediate selectivity of the Ru-1 catalyst would be dramatically lowered and the reaction pathway shifted to direct benzene hydrogenation to cyclohexane without the presence of the alkali promoter [39].

Contrary to the Ru-1 catalyst, 1,3-cyclohexadiene was transformed directly to cyclohexane without detection of cyclohexene over the rest of the catalysts. The different reaction pathways might be easily recognized in figs. 1 and 2. Inspecting the AAS results it is seen that no alkali metals were detected in Ru-2 to Ru-9 catalysts. On the other hand considerable traces of Mn, Fe, Ni, Cu, Zn, Se (Ru-2, Ru-3); Mn, Fe, Ni, Cu, Zn (Ru-7, Ru-8); Mg, Fe, Cu, Zn (Ru-9) were found (table 2). As already given above, the alumina support (Ru-5, Ru-6) was relatively very pure with extremely low content of Fe, Cu and Zn ions. When the supports are brought into contact with $RuCl_3$ solution, the HCl released leaches cations out of the support. Upon drying the cations get on the metal precursor surface and after reduction on the metal surface (including Ti and Al ions). Reflecting the fact,

Table 4
Data of hydrogenation of benzene [a]

Catalyst	k_1	k_2	k_3	k_4	m	X_A	S_B	S_C	S_D
Ru-1	3.10	4.60	1.52		0.81	0.99	0.56	0.46	0.18
Ru-2	2.10			6.10	0.77	0.64	0.40		0.49
Ru-3	2.73			7.10	0.73	0.77	0.50		0.71
Ru-4	2.30			8.10	0.87	0.46	0.41		0.46
Ru-5	0.60			1.95	0.78	0.19	0.31		0.24
Ru-6	0.90			2.50	0.70	0.32	0.47		0.53
Ru-7	0.10			0.29	0.75	0.12	0.25		0.10
Ru-8	0.50			1.38	0.79	0.21	0.39		0.34
Ru-9	2.9			9.92	0.90	0.96	0.60		0.82

[a] $[k_1] = \mathrm{ml}^m\,\mathrm{mmol}_A^{1-m}/\mathrm{g_{cat}}\,\mathrm{min}$; $[k_{2-4}] = \mathrm{mmol_A}/\mathrm{g_{cat}}\,\mathrm{min}$.

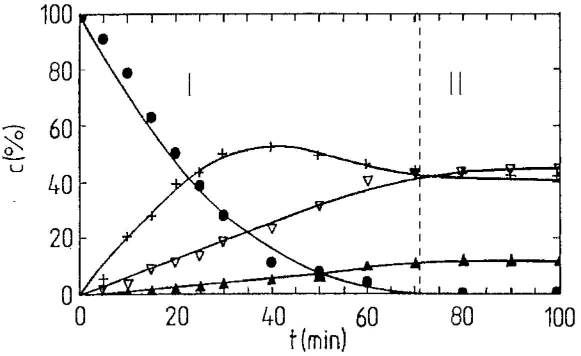


Fig. 1. Hydrogenation of benzene over Ru-1 catalyst. (●) A, benzene; (+) B, 1,3-cyclohexadiene; (∇) C, cyclohexene; (▲) D, cyclohexane.

that the reactions were performed without presence of water, the interpretation of the improved selectivity to dienic intermediate in terms of hydrophilicity (due to promoters) of the metal surface and increased mass transfer resistance cannot be used [10–12]. Since the supported catalysts undoubtedly responded favourably to the presence of small amounts of various metal ions (in view of the improved selectivity to dienic intermediates), the simplest interpretation of their action might be based on the modification of the active sites, promoting the intermediate formation [13]. Generally it also appeared that some of the ions may increase a positive charge on a metal surface and weaken the π-complexing of the –C=C– bonds. The π-complexing is mainly donation to the metal and a positive charge outside the metal makes it less energetically favourable. Less firmly bound intermediates (cyclo-diene) can then appear in the bulk.

Ruthenium supported on titania was very active for partial benzene hydrogenation and produced twice as much 1,3-cyclohexadiene as the Ru-7 catalyst (silica support). The selectivity to dienic intermediate on Ru-9 catalyst attained the maxi-

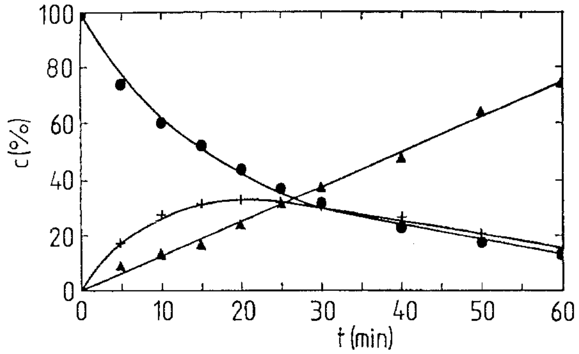


Fig. 2. Hydrogenation of benzene over Ru-9 catalyst. (●) A, benzene; (+) B, 1,3-cyclohexadiene; (▲) D, cyclohexane.

mum level of 60%. It is very well possible that also titanium(IV) oxide on the ruthenium surface has the aforementioned promoting effect on the selectivity of benzene partial hydrogenation. However, since Ti-cation can bind by a π-complex also the dienes and olefins, it has less promoting effect on their selectivities. The promoting effect of TiO_2 might be also ascribed to TiO_x species and the Ti-metal bond formed on the ruthenium surface as it is usual in CO hydrogenation [23] or to special sites created in the interfacial perimeter around the particle [40]. According to this hypothesis, the catalytic activity should increase with the interfacial perimeter, which, in turn, is roughly proportional to the second power of the metal dispersion [40].

Considerable loss of activity of the catalysts was observed in the experiments. It might be assigned either to slow reversible desorption of 1,3-cyclohexadiene and cyclohexene or to formation of strongly physically adsorbed surface species such as 1,4-dicyclohexylcyclohexane. Deactivation of the catalyst might be easily recognized in fig. 1 (areas I and II).

3.3. HYDROGENATION OF ACETOPHENONE

Hydrogenation of acetophenone proceeded via two independent routes to 1-cyclohexylethanol (1-phenylethanol or methylcyclohexylketone as the intermediates). Neither cyclo-olefinic intermediates nor ethylbenzene and ethylcyclohexane were found in the reaction mixtures.

According to our findings (table 5), no competitive hydrogenations of acetophenone to both mentioned intermediates took place ($C_{A_0} = 0.077$ mol ℓ^{-1}, $C_B = C_C = C_D = 0$). Orders of the reaction in acetophenone (m) varied significantly in the range 0.21 for Ru-8 (Ru/silica) to 0.58 for Ru-4 (Ru/alumina). The orders in methylcyclohexylketone and in 1-phenylethanol were assumed to be zero. The X_A and S_x parameters (table 5) have the analogous meaning as those in table 4.

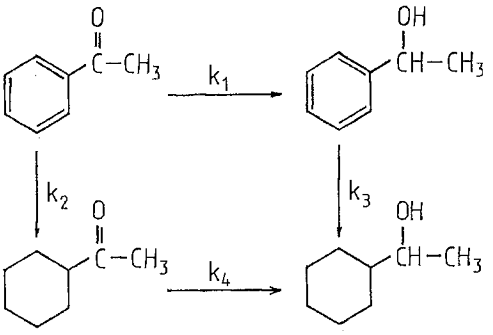
The improved selectivity towards aromatic ring hydrogenation was found only

Table 5
Data of hydrogenation of acetophenone [a]

No.	Catalyst	k_1	k_2	k_3	k_4	m	X_A	S_B	S_C	S_D
1	Ru-1		1.45		0.52	0.37	0.44		0.79	0.18
2	Ru-2	1.30		0.39		0.29	0.41	0.61		0.20
3	Ru-3	1.55		0.35		0.35	0.52	0.78		0.22
4	Ru-4	0.40		0.55		0.58	0.45	0.72		0.26
5	Ru-5	1.12		0.34		0.30	0.23	0.64		0.25
6	Ru-6	1.19		0.37		0.31	0.35	0.71		0.36
7	Ru-7	–		–		–	–	–	–	–
8	Ru-8	0.90		0.21		0.20	0.20	0.69		0.19
9	Ru-9	1.21		0.35		0.23	0.28	0.73		0.28

[a] $[k_{1,2}] = \mathrm{ml}^m\,\mathrm{mmol}_A^{m-1}/g_{\mathrm{cat}}\,\mathrm{min}$; $[k_{3,4}] = \mathrm{mmol_A}/\mathrm{g_{cat}}\,\mathrm{min}$.

for Ru-1 (commercial ruthenium on charcoal). The reactions on this catalyst proceeded exclusively through methylcyclohexylketone intermediate. Reactions performed over the rest of the catalysts followed selectively formation of 1-phenylethanol. The best selectivities to 1-phenylethanol were achieved on Ru-3 (78%) and Ru-9 (73%) catalysts. Furthermore,



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the former showed the highest observed activity and maximum acetophenone conversion attained (52%). Nevertheless, the Ru-9 (titania) and Ru-4 (alumina) catalysts were relatively also very active for carbonyl group hydrogenation, especially bearing in mind the fact that the loads of the metal were only 2.5 and 2%, respectively. The selectivity to 1-phenylethanol was generally better on catalysts prepared in ethanol. As in benzene hydrogenation considerable loss of activity occurred, most likely caused by strong adsorption of intermediates and unspecified surface deposits.

Although the conjugated –C=C– bond is generally less reactive than the isolated one and closer to the reactivity of the –C=O function, the preferential hydrogenation of the –C=O group has to be activated by means of catalytic promoters. The promoters (Sn, Fe, Ge, etc.) are present on the surface as electron-acceptor species and act as adsorption sites coordinating the oxygen atom of the unsaturated aldehyde. It should also be pointed out, that especially on samples having larger ruthenium particles, the steric effects of the aromatic ring facilitate the adsorption of the molecule through the carbonyl function. Considering the above facts, it is seen that the variations in the selectivity to 1-phenylethanol and to methylcyclohexylketone in acetophenone hydrogenation might be attributed to the action of metal ions on the ruthenium surface. Especially iron and zinc (table 2) could be responsible for the reaction pathway observed over the Ru-2 to Ru-9 catalysts. Also the larger ruthenium particle size may play a certain role, especially in Ru-7 and Ru-8 catalysts (next paragraph). Furthermore, an isolated –C=O bond can also be activated by a Ti-cation from the titania support, which may help to explain the high activity and selectivity of the Ru-9 catalyst to 1-phenylethanol, even with the load of the active component as half as of the most active Ru-3 catalyst [26]. On the other hand the exceptional position of the Ru-1 catalyst (analogous to benzene hydrogenation) can be attributed to the presence of alkali metal which increases the relative rate of hydrogenation of the –C=C– bond with respect to the –C=O functional group.

Since the rate constants (tables 3–5) were not evaluated per unit metal surface but per unit weight of the catalyst, it seems reasonable that the difference between the activity of silica and active charcoal, alumina, titania supported catalysts might have been ascribed to a difference in the metal particle size. The XRD analysis of C-supported samples (Ru-1, Ru-2, Ru-3) showed diffused bands corresponding to the support, however, no ruthenium lines were observed (fig. 3). It is evident that ruthenium was either amorphous, or with the particle size in an order of magnitude 0.1–1 nm. Otherwise, in such a weakly absorbing matrix, the crystalline lattice must have been identified. In samples Ru-4, Ru-5, Ru-6 and Ru-9 only γ-alumina and TiO_2 – mainly rutile – were recognized and no ruthenium lines were detected as well (fig. 3). On the other hand the X-ray pattern of both Ru/silica catalysts (Ru-7, Ru-8) showed, except of typical lines of christoballite, evident bands of ruthenium corresponding to the crystallite size in an order of magnitude 10 nm for Ru-8 and <10 nm for Ru-7. This particle size was confirmed by electron microscopy. As an example the SEM micrograph of the Ru-7 catalyst (fig. 4) clearly shows the metal particles in the range of 10–100 nm. The above facts suggest that the tendency – the lower the crystallite size of the metal particles, the higher the hydrogenation activity of the catalyst – correlates well with the observed lower activity of both silica supported catalysts. Also the effect of the impregnation solvent used on

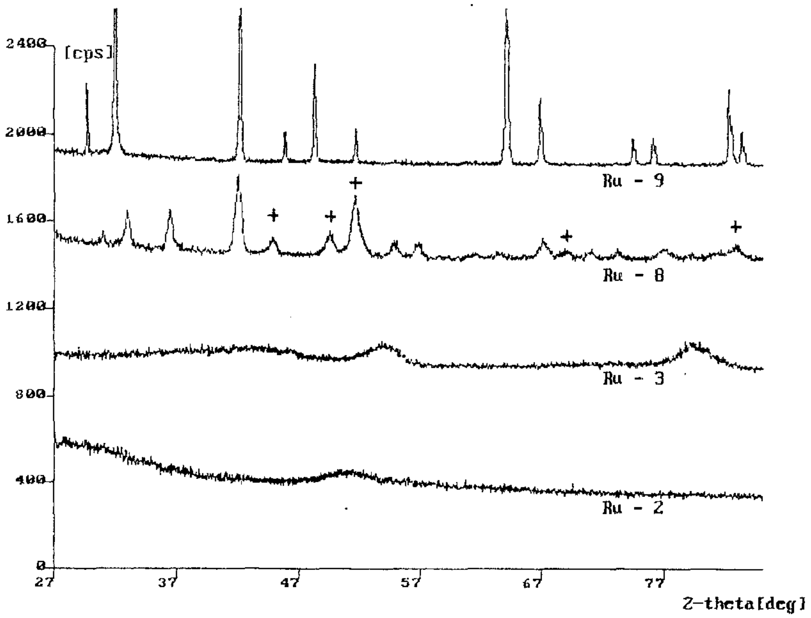

Fig. 3. XRD patterns of Ru-2, Ru-3, Ru-8 and Ru-9 catalysts. (+) Ruthenium lines.

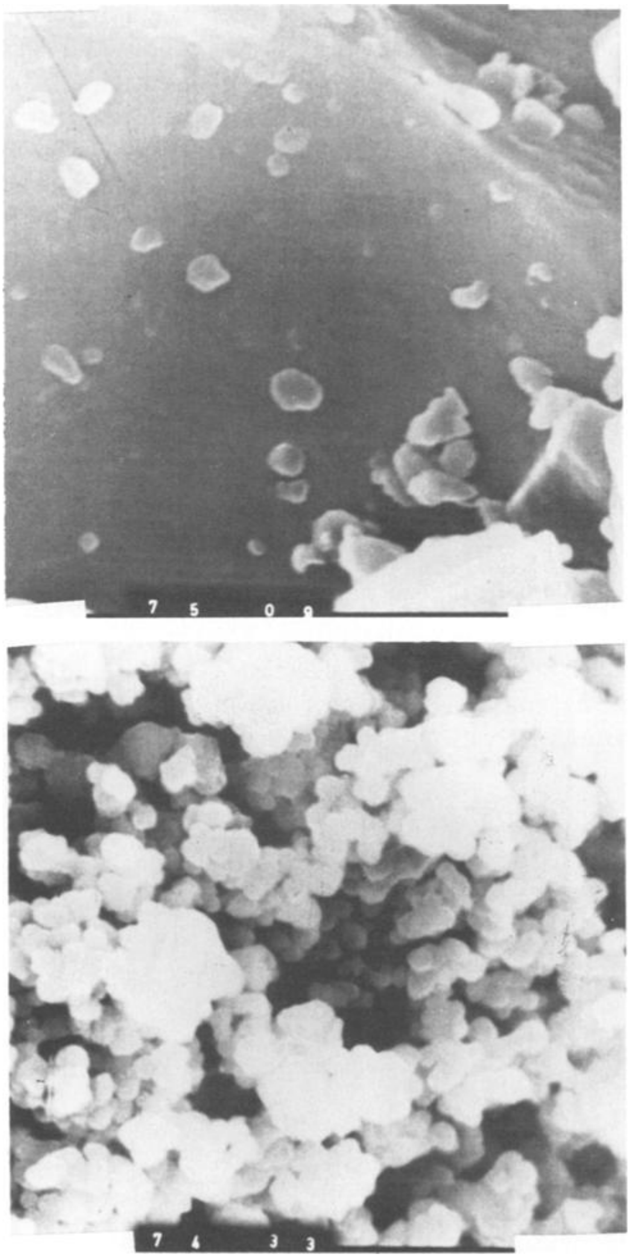

Fig. 4. SEM micrographs of (a) Ru-7 catalyst (0.8 cm = 100 mm), (b) titania support (0.8 cm = 0.3 μm).

the activity of the catalysts should be explained through the metal particle size. Different solubility of $RuCl_3$ in water and ethanol may lead upon drying and reduction to different crystallite size. In spite of that, the difference in metal particle size in alcohol and water prepared catalysts was insignificant (or rather below the detectable level) and the XRD patterns of both water and alcohol impregnated catalysts were almost identical. According to Niwa et al. [4], comparing ethanol and water from the point of view of their coordination ability as the impregnation solvents, the former has weaker complexing ability than the latter. Accordingly, the activity and cyclohexene selectivity of the alcohol prepared ruthenium catalysts were higher due to inclusion of the impregnation solvent in the catalysts after the activation.

It should be emphasized that the presence of metal ions dramatically changes the activity of ruthenium catalysts and selectivity of the hydrogenation reactions. The shift in selectivity can also be attributed to the metal–support interactions as it is usually observed using titania and partly also alumina supports. Lower activity of Ru/silica catalysts in all experiments performed, seemed to be proportional to the larger particle size of these catalysts. The charcoal supported ruthenium was found to be the most versatile catalyst in our experiments.

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