

Rhodium complexes supported on zinc aluminate spinel as catalysts for hydroformylation and hydrogenation: preparation and activity

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Abstract

The heterogenization of active homogeneous rhodium catalysts on zinc aluminate spinel has been studied. The ZnAl_2O_4 support was prepared by a hydrothermal process and characterized by transmission electron microscope (TEM), RTG, and textural investigations. The rhodium(I) complexes, $\text{Rh}(\text{acac})(\text{CO})_2$, $\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)$, and $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$, supported on the spinel, gave $\text{Rh}(\text{CO})_2^+$, $\text{Rh}(\text{CO})(\text{PPh}_3)^+$, and $\text{Rh}(\text{CO})(\text{PPh}_3)_2^+$ species, respectively, as confirmed by IR spectra. $\text{Rh}(\text{CO})_2^+$ on the spinel with an excess of PPh_3 effectively catalysed the hydroformylation of 1-hexene under 1 MPa of H_2/CO at 356 K. Aldehydes yield of 40–95% were obtained with an *n/iso* ratio of ca. 3. The coordination of 1-hexene to supported $\text{Rh}(\text{CO})_2^+$ species was evidenced by the appearance of a $\nu(\text{CO})$ band at 2053 cm^{-1} . $\text{Rh}(\text{CO})_2^+$ -supported on the spinel catalysed the hydrogenation of nitrobenzene and chloronitrobenzene at 1 MPa of H_2 and 356 K with a TON of 400–500 h^{-1} . © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Zinc aluminate spinel; Hydrothermal process; Supported rhodium complexes; Hydroformylation; Hydrogenation

1. Introduction

Heterogenization of homogeneous catalysts has attracted significant interest in recent years [1]. The main advantage of heterogenization is the easy separation of the catalyst from organic products, which is very important especially when expensive, e.g. chiral, catalysts are applied. The aim of the studies presented in this paper was to prepare and test a new heterogenized rhodium catalyst for hydroformylation and hydrogenation reactions. Zinc aluminate spinel, ZnAl_2O_4 , was selected as the support after preliminary

studies which had shown that typical homogeneous precursors were effectively and stably bound. This contrasted favourably with our previous results on the heterogenization of rhodium complexes on Al_2O_3 , which had shown that only hydroxy-rhodium complexes could be effectively attached to the surface [2].

Recently, there has been a growing interest in ZnAl_2O_4 application for catalysis. The properties of ZnAl_2O_4 , such as high thermal stability, high mechanical resistance, or inertness to water vapour, make it an attractive material both as a catalyst as well as a carrier for active metals to substitute for the more traditional systems. It is active in the dehydrogenation of alkanes [3], shows activity in cyclohexene isomerization [4], and seems to be an attractive catalyst in the synthesis of an important group of compounds, viz

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indenes, from indanones, where a 98% yield of the product has been achieved [5]. It is also a promising support for platinum and copper catalysts [6,7].

2. Results and discussion

2.1. Characterization of zinc aluminate spinel, $ZnAl_2O_4$

The morphology of hydrothermally synthesized zinc aluminate as viewed by transmission electron microscope (TEM) is shown in Fig. 1. It reveals that it is composed of tiny, quasi-spheroidal particles and that most of them are dispersed, maintaining a certain distance from each other. It may also be noted from Fig. 1 that the corresponding selected area diffraction (SAD) pattern confirms the structure of $ZnAl_2O_4$. The as-prepared particles are estimated to be about 3 nm in diameter from TEM measurement, and the particle size is stable up to ~ 673 K on heat treatment. $ZnAl_2O_4$ support calcinated at 873 K consists of spinel particles which enlarged to about 5 nm in diameter. These results were further confirmed by

XRD analysis. The properties of the zinc aluminate support are collected in Table 1.

X-ray diffraction (XRD) analysis can provide more detailed information on the crystalline structure characteristics of hydrothermally prepared zinc aluminate support. Fig. 2 shows the XRD patterns for fresh and heat-treated samples. In the case of an as-prepared sample, the XRD pattern with rather broad diffraction peaks shows a single-phase cubic spinel structure (Fig. 2a), having a lattice constant similar to that of bulk $ZnAl_2O_4$. The average size of the particles determined by XRD was 3.5 nm, which is consistent with the particle size determined by TEM. This means that each particle was composed of a single crystallite. It can be seen from Fig. 2(b) and (c) that after heat treatment at higher temperatures the diffraction peaks became more intense and narrow, indicating that the particles in the samples had grown. However, the nanocrystallinity of the samples was retained, though an increase in the average crystallite size was readily noticeable.

The representative adsorption–desorption isotherms of nitrogen at 77 K and the pore size distribution for the zinc aluminate support (annealed at 873 K) are given

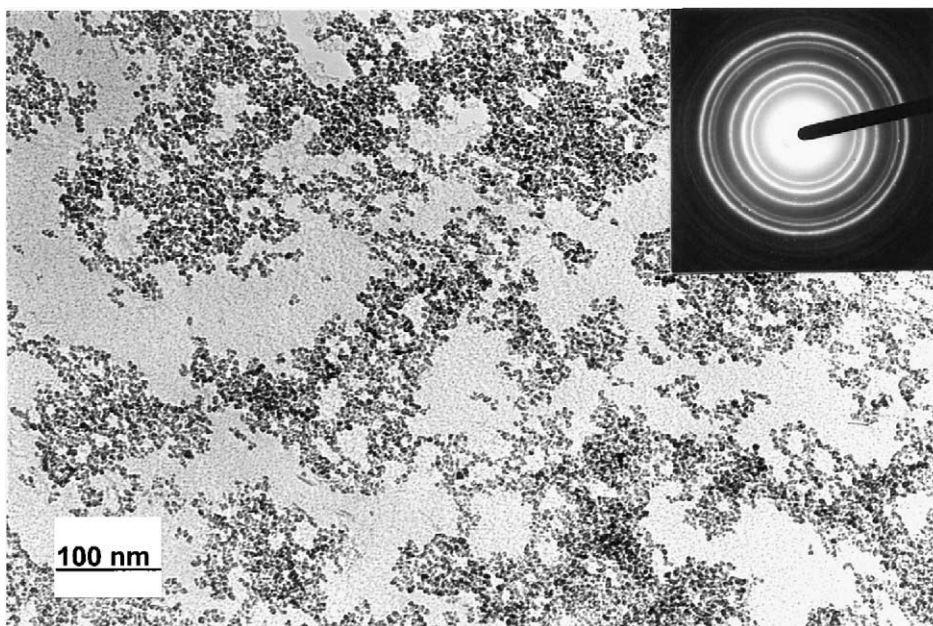


Fig. 1. TEM micrograph of hydrothermally “as-received” zinc aluminate with SAD pattern showing rings that match d-spacings for the spinel structure of $ZnAl_2O_4$.

Table 1
The properties of zinc aluminate support calcined at 873 K

Phase composition	ZnAl ₂ O ₄
Lattice constant of ZnAl ₂ O ₄ (heated at 1423 K), Å	8.0928 (±0.0005)
Average crystallite size, nm	5
Lewis acid sites concentration, μmol Py/g	195
Brønsted acid sites concentration, μmol Py/g	0
Specific surface area (<i>S</i> _{BET}), m ² /g	93
Total pore volume, <i>V</i> _p (at <i>p</i> / <i>p</i> ₀ = 0.95), cm ³ /g	0.14
Mean pore radius, <i>r</i> _p , nm	2.8

in Fig. 3. The obtained isotherms are very similar to those of type IV with a closed and well-defined hysteresis loop described as type H2 in the IUPAC classification, which suggests the presence of mesopores in the material. This type of hysteresis loop is characteristic for solids consisting of particles crossed by nearly cylindrical channels or made up of aggregates or agglomerates of spheroidal particles. Moreover, such hysteresis loops suggest that the pores may have a uniform size and shape. Pore size distribution showed

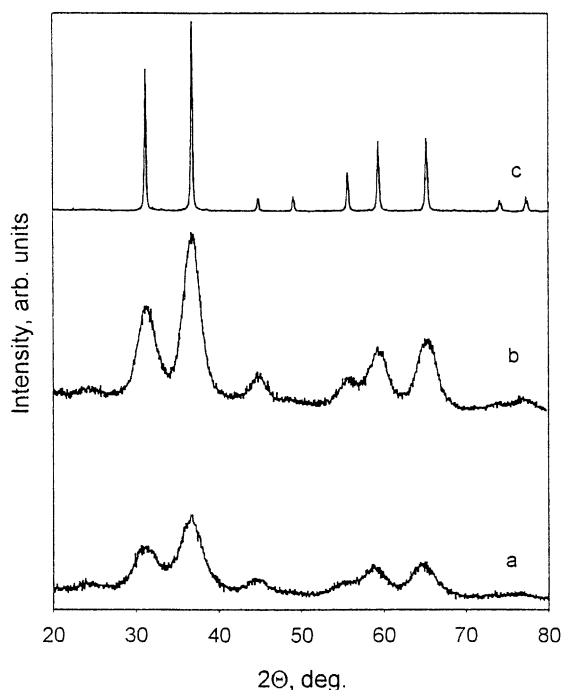


Fig. 2. XRD patterns for the ZnAl₂O₄ support: (a) as-prepared, (b) calcined at 873 K, (c) calcined at 1423 K.

a pore radius *r*_p between 1 and 4 nm, with a maximum centred at about 2.8 nm. Thus, it can be concluded from this narrow size range that hydrothermally obtained ZnAl₂O₄ support is formed from monodisperse particles.

2.2. Characterization of rhodium complexes supported on ZnAl₂O₄

The rhodium complexes, Rh(acac)(CO)₂, Rh(acac)(CO)(PPh₃), and RhCl(CO)(PPh₃)₂ were bound to ZnAl₂O₄ from toluene or benzene solution at room temperature. The heterogenization process was controlled by measurements of absorption decrease in UV–Vis spectra of the solution. The concentration of rhodium left in solution was calculated from the absorption change. When heterogenization was finished, a weighted sample was treated with HCl to extract rhodium from the spinel, and the resulting solution was analysed by the ICP method. The final content of rhodium, an average from both methods, was 0.9–1.1%. This was also the highest content of rhodium on spinel obtained after long-term heterogenization (2 days). The IR spectrum of the Rh(acac)(CO)₂ complex supported on ZnAl₂O₄ showed two ν(CO) bands at 2015 and 2088 cm⁻¹, consistent with the presence of Rh(CO)₂⁺ species [11]. The abbreviation Rh(CO)₂⁺ denotes an Rh(CO)₂⁺ fragment bound to spinel via its O⁻ and O atoms (Scheme 1). A similar structure was proposed by other authors for rhodium species supported on zeolites [8–12]. We proposed that the complexes are bound with the hydroxyl groups of the distorted spinel structure of ZnAl₂O₄ similar to the covalent grafting of these complexes as proposed for γ-Al₂O₃ [13]. During heterogenization, an acetylacetonato ligand is protonated by a proton originating from the spinel and removed from the coordination sphere of rhodium. This conjecture was supported by the detection of Hacac by GC–MS in benzene solution after the heterogenization of Rh(acac)(CO)₂ and Rh(acac)(CO)(PPh₃). The anchoring of the Rh(I) complexes can be interpreted as the location of the rhodium ligands at the other surface of the spinel particles as well as inside mesopores having a diameter of 2.8 nm.

The spectrum containing two ν(CO) bands was, however, obtained only for heterogenized samples

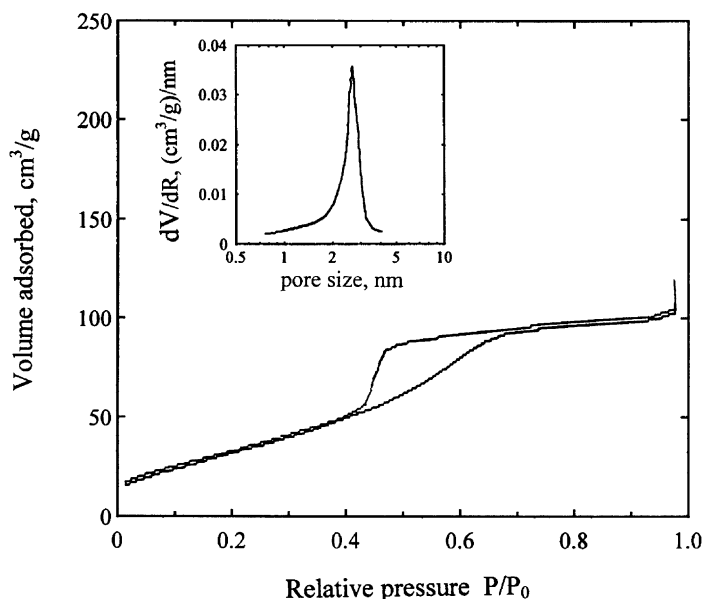


Fig. 3. Adsorption–desorption isotherms of nitrogen at 77 K and pore size distribution for zinc aluminate support.

stored under an N_2 or CO atmosphere. In contrast, a sample of $Rh(CO)_2^+$ on spinel left in an air atmosphere did not exhibit any $\nu(CO)$ bands after ca. 24 h. Exposure of that sample to CO (0.1 MPa) for just 30 min is enough to again observe $\nu(CO)$ bands at 2015 and 2088 cm^{-1} . These results can be explained by the ability of $Rh(CO)_2^+$ on spinel to oxidize CO to CO_2 , which is no longer bound to rhodium. In fact, when the sample of the supported rhodium complex was left in a Schlenk tube filled with a CO/ O_2 mixture at room temperature, an increase in CO_2 concentration was observed already after 3 h. It was calculated that ca. 13 molecules of CO were oxidized to CO_2 on one rhodium atom.

The reaction of $Rh(acac)(CO)(PPh_3)$ with spinel leads to $Rh(CO)(PPh_3)^+$ characterized by $\nu(CO)$ at 1992 cm^{-1} . The same product was also obtained when $Rh(CO)_2^+$ supported on spinel was treated with PPh_3 in toluene solution. Similarly, $RhCl(CO)(PPh_3)_2$ supported on spinel formed $Rh(CO)(PPh_3)_2^+$, characterized by $\nu(CO)$ at 1976 cm^{-1} . In all the three cases, during the formation of a bond between the rhodium complexes and the spinel, we observed a shift of $\nu(CO)$ frequencies to higher values compared to those in the starting complexes (Table 2). This suggests a modifi-

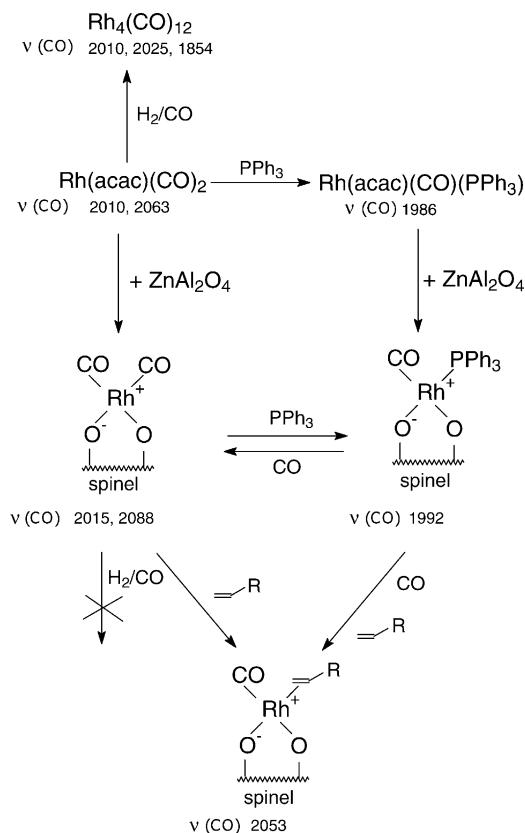
cation of the coordination sphere of rhodium during heterogenization according to Scheme 1.

In a CO atmosphere (0.1 MPa), PPh_3 coordinated in both species ($Rh(CO)(PPh_3)^+$ and $Rh(CO)(PPh_3)_2^+$) was partially substituted by CO, and $Rh(CO)_2^+$ was formed and identified by IR. The reactions were quite fast and already after 15 min of treatment with CO, two $\nu(CO)$ bands appeared at 2015 and 2088 cm^{-1} . It is worth noting that the replacement of PPh_3 by CO was never observed for $Rh(acac)(CO)(PPh_3)$ and $RhCl(CO)(PPh_3)_2$ complexes in solutions. The same

Table 2
IR data (2200–1700 cm^{-1}) of rhodium compounds in KBr

Compound	$\nu(CO)/cm^{-1}$
$Rh(CO)_2^+$ on spinel	2015s, 2088s
$Rh(CO)(PPh_3)^+$ on spinel	1992
$Rh(CO)(PPh_3)_2^+$ on spinel	1976
$Rh(CO)_2^+$ on spinel + 1-hexene	2021w, 2053s, 2089w
$Rh(CO)(PPh_3)^+$ on spinel + CO + 1-hexene ^a	2055
$Rh(acac)(CO)_2$	2010s, 2063s
$Rh(acac)(CO)(PPh_3)$	1986
$RhCl(CO)(PPh_3)_2$	1966

^a 0.1 MPa of CO.



complexes bound to spinel appeared to be more labile under CO.

Rhodium complexes formed stable bonds with ZnAl_2O_4 , preserved also when heated in boiling toluene for 2 h, which was confirmed by UV–Vis analysis of the toluene filtrate after catalyst separation. The analysis showed the absence of rhodium complexes in solution.

2.3. Catalytic activity of $\text{Rh}(\text{CO})_2^+$ supported on ZnAl_2O_4 in the hydroformylation reaction

Before testing the catalytic activity of rhodium-containing catalysts, blank experiments were performed with a pure sample of ZnAl_2O_4 under hydroformylation reaction conditions (1 MPa H_2/CO , 356 K). Tests showed the inactivity of ZnAl_2O_4 in this reaction.

The $\text{Rh}(\text{CO})_2^+$ complex used alone exhibited very limited catalytic activity. Only 2% of 2-hexene was

Table 3

The yields of aldehydes and 2-hexene obtained in hydroformylation of 1-hexene with $\text{Rh}(\text{CO})_2^+$ on spinel^a

Run	[1-Hexene]: [Rh]	Aldehydes (mol%)	<i>n</i> / <i>iso</i>	2-Hexene (mol%)
1	14260	38	2.7	1
2	9420	43	2.8	11
3	8350	69	2.8	6
4	8030	55	2.8	15
5	6510	83	3.0	5
6	5500 ^b	65	3.0	1
7	5360	95	3.1	3
8	4910	95	2.9	2
9	4980 ^c	86	2.8	12
10	4950 ^d	96	3.1	2
11	4800 ^e	–	–	2
12	4260	96	2.9	2
13	4150 ^b	68	2.9	1

^a Reaction conditions: 1 MPa of $\text{CO}/\text{H}_2 = 1$, 356 K, 1.5 ml 1-hexene, 1.5 ml toluene, 3 h, $[\text{PPh}_3]:[\text{Rh}] = 15 \pm 1$.

^b The catalyst was stored before the reaction in toluene solution of PPh_3 at RT for 24 h.

^c $[\text{PPh}_3]:[\text{Rh}] = 8.9$.

^d $[\text{PPh}_3]:[\text{Rh}] = 24.1$.

^e The reaction without PPh_3 added.

found in the reaction products at a [1-hexene]:[Rh] concentration ratio of 4800 (Table 3, run 11).

Much better results were obtained in reactions performed with $\text{Rh}(\text{CO})_2^+$ and free PPh_3 added (Table 3). An excess of ca. 15 mol PPh_3 per mole of supported rhodium was enough to increase the amount of aldehydes to 96% and to achieve an *n*/*iso* ratio of ca. 3. When a lower excess of PPh_3 was used ($[\text{PPh}_3]:[\text{Rh}]$ is 8.9, run 9), chemoselectivity dropped down, and 86% of aldehydes and 12% of 2-hexene were obtained. An increase of the PPh_3 excess to 24 (run 10) led practically to the same results as a 15-fold excess. The dependence of the aldehyde yield on the catalyst concentration ([1-hexene]:[Rh] ratio) is nearly linear (Fig. 4). As the [1-hexene]:[Rh] ratio increased, the reaction slowed down and the yield of aldehydes determined after the same time (3 h) decreased. It is interesting to note that a decrease of the hydroformylation reaction rate was observed when the sample of the supported $\text{Rh}(\text{CO})_2^+$ catalyst was pre-treated with a solution of PPh_3 in benzene or toluene at room temperature for 24 h. It was checked that the above treatment was not sufficient to activate the catalyst and aldehydes were not produced without extra added free PPh_3 .

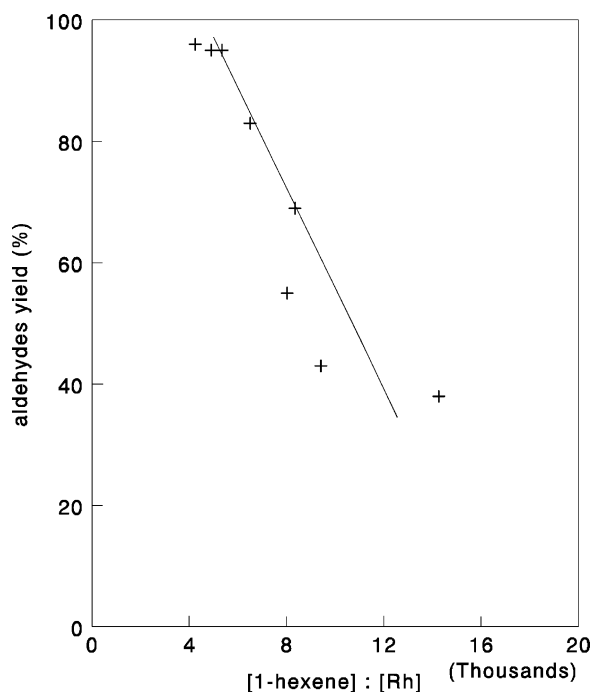


Fig. 4. Dependence of aldehydes yield (%) on [1-hexene]:[Rh] molar ratio.

However, just after the addition of a PPh₃ excess, a 65–68% yield of aldehydes was achieved (run 12).

To exclude the participation of homogeneous (leached) catalysts in the catalytic process, the solution obtained by the filtration of the reaction mixture was introduced to an autoclave together with 1.5 ml of 1-hexene and left under 1 MPa of H₂/CO at 356 K for 3 h. The very small pressure drop (ca. 0.08 MPa) and the lack of aldehydes confirmed the stability of the heterogenized complex.

2.4. Catalytic activity of Rh(CO)₂⁺ supported on ZnAl₂O₄ in the hydrogenation reaction

In some experiments we tested the catalytic activity of Rh(CO)₂⁺ supported on spinel in the hydrogenation of nitrobenzene and chloronitrobenzene. Reactions were performed at 1 MPa of H₂ and 356 K in methanol without free PPh₃ and 50–80% conversion of the substrate was achieved after 1 h. Aniline or chloroaniline was identified as the only product by GC–MS. The TON values calculated were 400–500 h⁻¹.

2.5. Infrared studies of supported rhodium catalysts after treatment with CO/H₂ and 1-hexene

The IR spectra of Rh(CO)₂⁺ and Rh(CO)(PPh₃)⁺ after a hydroformylation reaction performed in the absence of free PPh₃ exhibited three bands in the ν(CO) region, at 2015, 2053, and 2088 cm⁻¹. The absorptions at 2015 and 2088 cm⁻¹ confirmed the presence of unchanged Rh(CO)₂⁺ species. In the case of Rh(CO)(PPh₃)⁺, this result confirmed our observation that CO substitutes PPh₃ in Rh(CO)(PPh₃)⁺.

The most intriguing change in the IR spectrum was appearance of the new ν(CO) band at 2053 cm⁻¹. We suggest that this band originated from a Rh(I) complex bound to the spinel, modified by 1-hexene. This proposition is based on the observation that the appearance of the ν(CO) band at 2053 cm⁻¹ in the spectrum of Rh(CO)₂⁺ on ZnAl₂O₄ is connected with the presence of 1-hexene in the solution used for the heterogenization process (Fig. 5). In all cases where

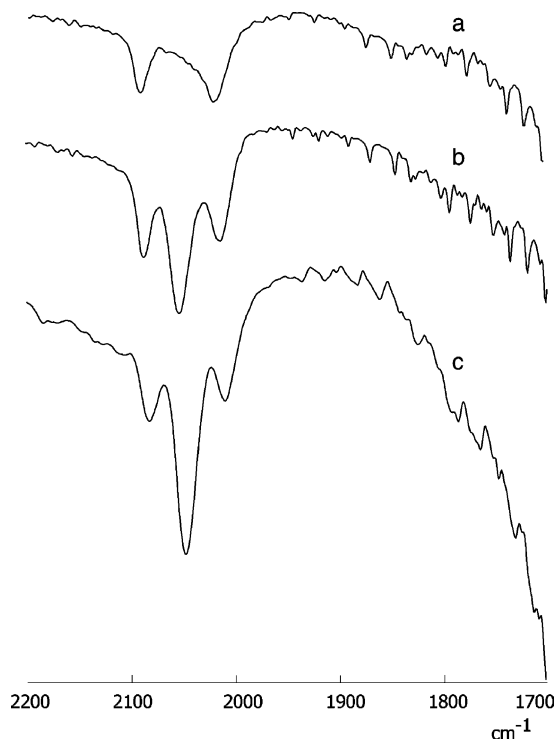


Fig. 5. IR spectra measured in KBr of: (a) Rh(CO)₂⁺ on spinel; (b) Rh(CO)₂⁺ on spinel + 1-hexene + CO (0.1 MPa); (c) Rh(CO)₂⁺ on spinel + 1-heptene + CO (0.1 MPa).

$\text{Rh}(\text{acac})(\text{CO})_2$ was supported from a pure toluene solution, only two $\nu(\text{CO})$ bands were observed in the spectrum of the heterogenized sample (Fig. 5, spectrum a). However, when such a sample was treated with 1-hexene for 3 h and then left under CO (0.1 MPa) for 30 min, an additional band at ca. 2055 cm^{-1} appeared (Fig. 5, spectra b and c). Its intensity increased over time, and after ca. 10 h it became dominating over weak shoulders at 2015 and 2088 cm^{-1} . A spectrum containing three bands was also obtained for samples prepared from $\text{Rh}(\text{acac})(\text{CO})_2$ and spinel in toluene solution containing 1-hexene. Similarly, a new band at 2045 cm^{-1} appeared in the presence of 1-heptene.

The presence of Rh(0) in the analysed samples was also considered. However, different IR spectra have been reported for CO adsorbed on Rh(0) supported on alumina [14] or zeolites [9,15]. A band at 2053 cm^{-1} was observed in the presence of 1-hexene, but when a sample was dried in vacuo it disappeared and only two bands remained at 2015 and 2088 cm^{-1} . In addition, treatment of $\text{Rh}(\text{CO})_2^+$ with H_2/CO (1 MPa) did not cause any changes in the IR spectrum.

It is worth noting that the $\text{Rh}(\text{acac})(\text{CO})_2$ complex in toluene solution is converted by a CO/H_2 mixture to $\text{Rh}_4(\text{CO})_{12}$ and finally to $\text{Rh}_6(\text{CO})_{16}$. In contrast, the heterogenized complex treated with CO/H_2 did not exhibit any bridging $\nu(\text{CO})$ bands (ca. 1800 cm^{-1}) in the IR spectrum, which allows us to rule out the formation of Rh(0) carbonyls.

3. Experimental

3.1. Preparation of the zinc aluminate spinel support

The zinc aluminate support was prepared as follows: appropriate amounts of analytical grade aluminium and zinc nitrates were dissolved in 2.5 l of distilled water at ambient temperature. The pH value of the solution was adjusted to 8.8 by adding the desired amount of aqueous ammonia solution (25 wt.%) with vigorous stirring. After 25 min, the precipitate was filtered off and washed several times with distilled water. Subsequently, 4 l of distilled water was added and the obtained slurry was hydrothermally treated in an autoclave with constant rotation under a pressure of 0.1 MPa for 3 h. After cooling the autoclave in cold

water to room temperature, the obtained product was water-washed and condensed by evaporating at an elevated temperature. The resulting gel was then extruded, air-dried, and calcined at 873 K for 5 h. The material prepared in this way was used as a support for all Rh(I) complexes.

3.2. Support characterization

Methods. Phase composition and mean crystallite size of the support material were determined by the X-ray powder diffraction method. The crystallite size of the spinel phase was calculated from the broadening of the X-ray line (311). The XRD was carried out with a DRON-3 X-ray diffractometer, using Ni-filtered $\text{Cu K}\alpha$ radiation. The unit-cell parameter values were calculated using the least squares fitting program PROSZKI [16]. The particle sizes and the morphology of the support material were estimated from TEM images taken with a TESLA BS-500 TEM using an accelerating voltage of 90 kV. Surface area and porosity were determined using the BET equation and the Dollimore/Heal method, respectively, from nitrogen adsorption data obtained at 77 K by the standard volumetric method using a Sorptomatic 1900 FISONS instrument. Surface acidity, i.e. the concentration of Lewis and Brønsted centres on the surface of the support, was established by means of IR spectroscopy in accordance with a procedure described in the literature [17], using pyridine as the probe molecule. The IR spectra were recorded at room temperature with a Specord M80 spectrometer.

3.3. Synthesis of rhodium complexes

Rhodium complexes have been prepared according to literature: $\text{Rh}(\text{acac})(\text{CO})_2$ [18], $\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)$ [19] and $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ [20].

3.4. Hydroformylation reactions

Hydroformylation reactions have been performed in a steel autoclave with magnetic stirrer at 356 K and 1 MPa $\text{H}_2/\text{CO} = 1$. Reagents, sample of catalyst in small Teflon vessel, 1.5 ml of 1-hexene and 1.5 ml of toluene were introduced to the autoclave in N_2 atmosphere. Autoclave was closed, flushed twice with H_2 (0.5 MPa), filled first with H_2 (0.5 MPa) and with CO

up to 1 MPa. After the reaction (1.5–3 h) the autoclave was cooled down and the liquid sample was analysed by GC–MS.

3.5. Hydrogenation reactions

The procedure was similar to that described for hydroformylation, only instead of H₂/CO 10 atm of H₂ was applied. IR spectra of supported catalysts have been measured on Nicolet Impact 400 FT-IR. UV–Vis spectra have been measured on Diode Array Hewlett-Packard spectrometer. Hydroformylation and hydrogenation reaction products have been analysed on GC–MS Hewlett-Packard instrument: HP 5890 II chromatograph with mass detector HP 5971a.

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