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Thermolysis of $Ru(acac)_3$ supported on silica and alumina

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Abstract

Precursors of alumina- and silica-supported ruthenium catalysts were prepared by pore volume impregnation of the dehydrated supports with a benzene solution of $Ru(acac)_3$. The prepared samples were characterized by diffuse reflectance FTIR and TG/DTG–DTA in order to discriminate $Ru(acac)_3$ which interacts with the support surface. Weight loss, experimentally observed upon thermolysis of parent and supported $Ru(acac)_3$, was compared with that calculated using the proposed reaction stoichiometry. Conditions for activating silica- and alumina-supported $Ru(acac)_3$ in an oxidizing atmosphere with complete removal of acetylacetonate ligands from the catalyst precursor are recommended. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Ruthenium (III) acetylacetonate, $Ru(acac)_3$, is considered as a promising precursor for the synthesis of heterogeneous ruthenium catalysts that are active in hydrogenolysis, isomerization and hydrogenation of hydrocarbons [1–4]. The main advantage is the possibility of the complete removal of acetylacetonate ligands under mild conditions which ensures the formation of a pure ruthenium metallic or oxidic phase and prevents its sintering.

The conventional preparation is based on contacting the dehydrated support with a solution of $Ru(acac)_3$ in toluene [1,3–5], trichloroethene [2], benzene [2,3], or tetrahydrofuran [3,4] at room temperature. Afterwards, the solvent is removed by filtration or evaporation followed by oxidative or reductive treatments of the prepared catalyst precursors at elevated temperature. Irrespective of the details of the preparation procedure used, it is generally assumed that upon impregnation the fixation of $Ru(acac)_3$ occurs due to exchange of acetylacetonate ligands with hydroxyl groups of the support [2–4]:

$$x\,[\wr\text{–O–H}]_{\text{surface}} + \text{Ru(acac)}_3 \rightarrow [(\wr\text{–O–})_x\text{Ru(acac)}_{3-x}]_{\text{surface}} + x\,\text{Hacac} \qquad (1)$$

In contrast, according to the observations of van Veen et al. [6–8], $Ru(acac)_3$ dissolved in benzene or toluene does not react at room temperature with γ-Al_2O_3 and TiO_2 and adsorbs only to a minor extent on SiO_2.

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Therefore, it is not clear which conditions are required for $Ru(acac)_3$ to undergo a reaction with the support surface. The question is if this reaction proceeds upon preparation of the supported ruthenium catalysts by impregnation and how the catalyst activation upon thermal treatment occurs.

The present study aims at thermoanalytical characterization of the $Ru(acac)_3$ deposited on the surface of alumina and silica in order to clarify the process of the removal of acetylacetonate ligands and, hence, to optimize the conditions of the catalyst activation.

2. Experimental

The supports, alumina CK-300 ($S_{BET} = 250$ m^2/g, AKZO) and silica Kieselgel 60 ($S_{BET} = 340$ m^2/g, Merck), were initially calcined at 500°C for 2 h in an air flow.

Alumina- and silica-supported $Ru(acac)_3$ samples with Ru loading of 0.2, 1.0 and 5.0 wt.% related to the weight of the dried support (denoted hereafter as $Ru(X)/Al_2O_3$ and $Ru(X)/SiO_2$, where X is the Ru loading) were prepared by pore volume impregnation using $Ru(acac)_3$ (Aldrich) dissolved in dry benzene. They were left for 2 h and then were immidiately dried under vacuum at room temperature for 1 h. All samples were red in color.

Infrared spectra were obtained with a Magna FTIR spectrometer equipped with a reflectance cell. The samples were diluted with KBr (1 : 10), ground and mounted in a microcup. The spectra were normalized against the KBr background and presented in absorbance units.

Thermal studies (TG/DTG–DTA) were carried out with a STA-1500 H thermobalance (PL Thermal Sciences) at a heating rate of 10°C/min in an air flow of ~50 cm^3/min.

3. Results and discussion

Fig. 1 shows the diffuse reflectance FTIR spectra of alumina- and silica-supported $Ru(acac)_3$ as well as of the parent $Ru(acac)_3$ and the initial supports. It is clearly seen that the IR spectra of alumina- and silica-supported $Ru(acac)_3$ have essentially the same bands typical for the parent $Ru(acac)_3$. This means that upon impregnation at room temperature, $Ru(acac)_3$ adsorbs intact on the surface of alumina and silica supports. This result is in complete agreement with the observations of van Veen et al. [6–8]. Moreover, no band at 1295 cm^{-1} is observed in the spectrum of $Ru(1.0)/Al_2O_3$. This band, connected with $Al(acac)_x$ surface species [6,9], should appear due to interaction of Hacac with Al_2O_3 support provided the reaction (1) proceeds.

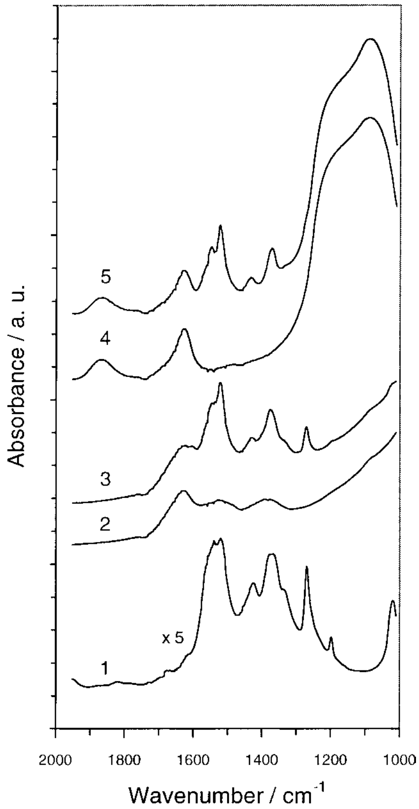


Fig. 1. Diffuse reflectance FTIR spectra of parent $Ru(acac)_3$ (1), initial alumina support (2), $Ru(1.0)/Al_2O_3$ sample (3), initial silica support (4) and $Ru(1.0)/SiO_2$ sample (5).

Parent $Ru(acac)_3$ starts to decompose in air at 200°C and the decomposition is complete at 320°C (Fig. 2). Decomposition proceeds in one step which is clearly seen from both DTG and DTA curves. The exothermic peak on the DTA curve means that the removal of acetylacetonate ligands is accompanied by their oxidative destruction and both processes occur simultaneously. The experimentally observed weight loss was compared with the predicted one which was calculated

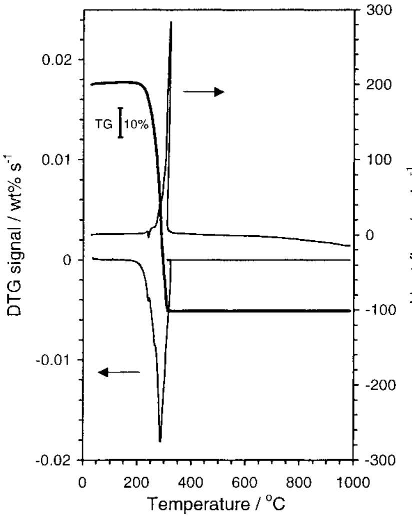


Fig. 2. TG/DTG–DTA curves for parent Ru(acac)$_3$.

assuming the following reaction stoichiometry:

$$\mathrm{Ru(acac)_3} \rightarrow \mathrm{RuO_2} + \text{volatiles} \qquad (2)$$

From Table 1 one can see that the experimental weight loss exceeds the predicted one. Most likely this is connected with sublimation of Ru(acac)$_3$ that occurs in the temperature interval relevant to Ru(acac)$_3$ thermolysis [10].

Thermolysis of the alumina- and silica-supported Ru(acac)$_3$ appeared to be dependent on the Ru loading (Figs. 3 and 4). The first weight loss, observed below 150°C for alumina and below 100°C for silica supported samples, has to be attributed to the removal of the solvent. This conclusion is based on the results of comparison of these thermograms with those of the initial alumina and silica supports soaked with benzene and dried under vacuum. Moreover, the peak on the DTA curve around 450°C, which is present in the supported samples and the initial supports as well, should also be attributed to the removal of a strongly bound solvent.

Table 1
Thermolysis of parent and the supported Ru(acac)$_3$

Sample	Temperature of thermolysis in (°C)		Weight loss in wt. (%)	
	Initial	Final	Calculated	Experimental
Ru(acac)$_3$	200	320	66.6	80.0
Ru(5.0)/Al$_2$O$_3$	200	270	11.0	10.1
Ru(1.0)/ Al$_2$O$_3$	175	350	2.6	3.5
Ru(5.0)/SiO$_2$	150	275	11.0	11.4
Ru(1.0)/SiO$_2$	150	325	2.6	2.6

Thermolysis of the Ru(5.0)/Al$_2$O$_3$ sample (Fig. 3a) occurs similarly to parent Ru(acac)$_3$. A single peak on both DTG and DTA curves is present and centers at 270°C. There is no indication of the influence of the alumina support on Ru(acac)$_3$ thermolysis.

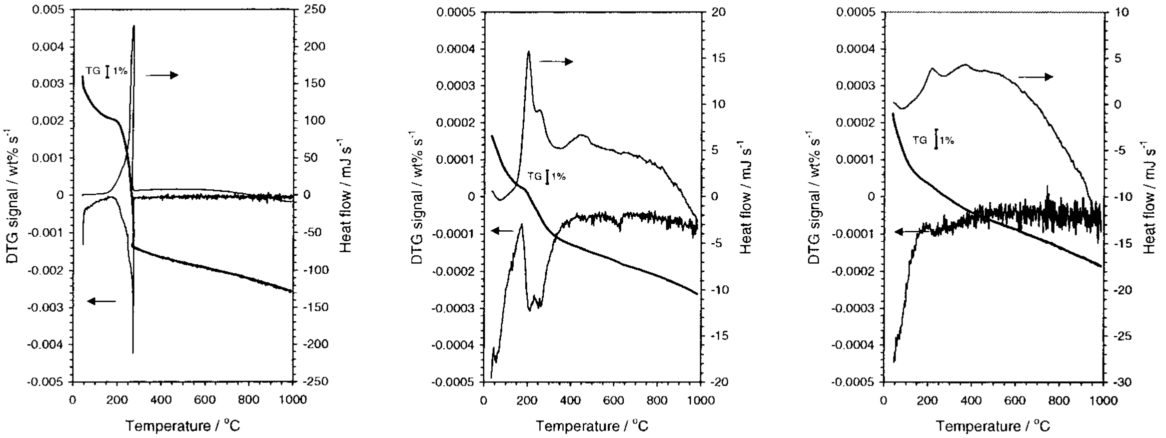
Thermolysis of the Ru(1.0)/Al$_2$O$_3$ sample (Fig. 3b) proceeds via a more complex pathway as compared to that of parent Ru(acac)$_3$ and the Ru(5.0)/Al$_2$O$_3$ sample. It occurs in two steps and, respectively, two peaks on the DTG and DTA curves centered at 200°C and 250°C are observed. So, the influence of the alumina support is clearly seen.

The presence of the low temperature peak can be explained from the viewpoint of the proton-assisted mechanism of thermolysis of the supported acetylacetonates of transition metals [11,12]. The proposed model assumes that the acetylacetonate ligands which are hydrogen-bonded to surface hydroxyls can be eliminated at lower temperature as compared to those which undergo thermal destruction. Since the ruthenium atom in Ru(acac)$_3$ is essentially octahedrally coordinated by six oxygen atoms [13], the acetylacetonate ligands in the supported Ru(acac)$_3$ appeared not to be equivalent with respect to their orientation to the support surface. Two acetylacetonate ligands can be oriented favorably with respect to the support and, hence, are involved in the hydrogen bonding with surface hydroxyls.

Therefore, in the Ru(1.0)/Al$_2$O$_3$ sample the proton-assisted elimination of acetylacetonate ligands at 200°C (see Eq. (1)) can be discriminated from thermal destruction at 250°C of the ligands which do not interact with surface hydroxyls. Consequently, the presence of Ru(acac)$_3$ which interacts with the support surface can be seen in the Ru(1.0)/Al$_2$O$_3$ sample.

For the Ru(0.2)/Al$_2$O$_3$ sample (Fig. 3c), one can assume preferably proton-assisted pathway of Ru(acac)$_3$ thermolysis since only the low temperature peak around 220°C is distinctly seen. This means that Ru(acac)$_3$ which interacts with surface hydroxyls predominate in the Ru(0.2)/Al$_2$O$_3$ sample.

In the Ru(5.0)/SiO$_2$ sample (Fig. 4a) the low temperature peak at 230°C is observed on the DTG and DTA curves along with the high temperature peak at



a b c

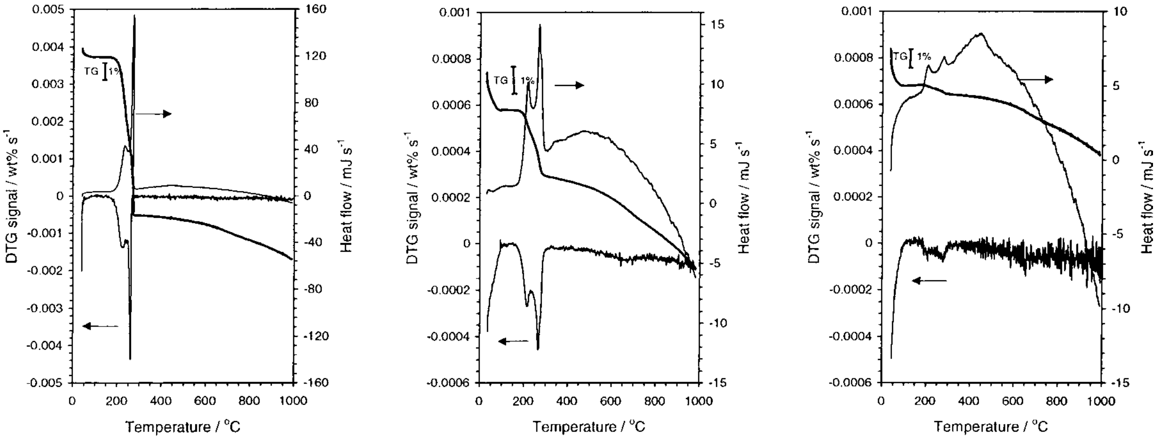
Fig. 3. TG/DTG–DTA curves for Ru(5.0)/Al_2O_3 (a), Ru(1.0)/Al_2O_3 (b) and Ru(0.2)/Al_2O_3 (c) samples.

270°C. Therefore, the presence of $Ru(acac)_3$, which at least partially interacts with hydroxyl groups of silica support upon thermolysis, can be assumed.

Thermolysis of the Ru(1.0)/SiO_2 sample (Fig. 4b) occurs in a somewhat broader temperature interval in comparison with parent $Ru(acac)_3$ and the Ru(5.0)/SiO_2 sample. The peaks at 220°C and 270°C on the DTG and DTA curves are observed. From the ratio of 220°C to 270°C peaks one can conclude about higher proportion of $Ru(acac)_3$, interacting with the support surface, in the Ru(1.0)/SiO_2 sample versus the Ru(5.0)/SiO_2 one.

In the case of the Ru(0.2)/SiO_2 sample, the presence of the peak around 210°C on the DTA curve in Fig. 4c distinctly indicates the proton-assisted pathway of $Ru(acac)_3$ thermolysis.

The results of thermoanalytical characterization of alumina- and silica-supported $Ru(acac)_3$ confirm that on decreasing the Ru loading from 5.0 to 0.2 wt.% the proportion of acetylacetonate ligands which are eliminated upon thermolysis due to surface hydroxyls increases. Correspondingly, the proportion of $Ru(acac)_3$ interacting with the support surface increases in the same order.



a b c

Fig. 4. TG/DTG–DTA curves for Ru(5.0)/SiO_2 (a), Ru(1.0)/SiO_2 (b) and Ru(0.2)/SiO_2 (c) samples.

Separate attention has to be paid to the comparison of the experimental weight loss and the predicted value that was calculated assuming the reaction stoichiometry (see Eq. (2)). Except for the Ru(1.0)/Al_2O_3 sample, a good correspondence of the experimental and calculated weight loss is observed (Table 1). This means that in the as prepared samples, $Ru(acac)_3$ decorates the support surface without elimination of acetylacetonate ligands. A slight difference between calculated and the predicted weight loss is connected most likely with partial sublimation of $Ru(acac)_3$ that occurs under thermolysis. It is self-evident that for the deposited $Ru(acac)_3$ this process has to be less pronounced as compared to that observed for the parent counterpart. In the case of the Ru(1.0)/Al_2O_3 sample, the accuracy of determination of the weight loss, related to $Ru(acac)_3$ thermolysis, is low because of the influence of the support that is clearly seen from the TD curve at the temperatures above 400°C (Fig. 3b).

4. Conclusions

Pore volume impregnation of alumina and silica supports with a benzene solution of ruthenium (III) acetylacetonate followed by solvent removal at room temperature results in decoration on the support surface with $Ru(acac)_3$ without elimination of acetylacetonate ligands. Ligand substitution in the supported $Ru(acac)_3$, assisted by a proton transfer from surface hydroxyl groups, becomes possible at 200–220°C. Thermal destruction of acetylacetonate ligands which do not interact with surface hydroxyls, occurs at higher temperature. As a result, $Ru(acac)_3$ which interacts with the support surface can be distinguished. On decreasing the Ru loading from 5.0 to 0.2 wt.% in the prepared samples the proportion of $Ru(acac)_3$ which can interact with alumina and silica supports increases. Activation of the supported $Ru(acac)_3$ in oxidizing atmosphere requires temperature as high as 350°C in order to ensure a complete removal of acetylacetonate ligands from the catalyst precursor.

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