Activation of *cis*-ReOBr$_3$(PPh$_3$)$_2$ by means of photoimmobilization

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Abstract

The possibility to activate *cis*-ReOBr$_3$(PPh$_3$)$_2$ (inactive under homogeneous catalysis conditions) by photoimmobilization on different supports is demonstrated. The systems obtained are active in the liquid-phase hydrogenation of 1-hexene and *m*-nitrobenzoic acid. We propose various mechanisms for grafting the complex in darkness and under UV irradiation. The samples photoimmobilized on anatase are the most active.

Keywords: Photoimmobilization; Hydrogenation; Rhenium complex; Activation

1. Introduction

Previously it was established [1] that the thiourea complex of rhenium(V) with a composition of [ReOClThio$_4$]Cl$_2$ displays catalytic activity in the hydrogenation of nitrobenzene only after treatment under a hydrogen atmosphere at a pressure of 4.0 MPa and a temperature of 368 K for 3–4 h, while the photoimmobilized complex on various supports does not require preliminary activation and catalyzes the hydrogenation of the nitro group to an amino group with high selectivity at atmospheric pressure [2].

Rhenium complexes with phosphorus-containing ligands are highly active and selective homogeneous catalysts for hydrogenation of the olefin bond, but slowly reduce the nitro group. Thus, the *trans*-isomer of the oxohalide triphenylphosphine complex of rhenium(V) is active in the hydrogenation of olefins at 5.0 MPa

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hydrogen pressure and 338 K temperature in the presence of excess triphenylphosphine (PPh$_3$) in dimethylformamide solutions. The molar productivity is 540 mol/mol Re h, in the hydrogenation of nitrobenzene under the same conditions it is 2.5 mol/mol Re h [3]. The cis-isomer of the rhenium complex is inactive in the given processes. The cis–trans transformation of ReOBr$_3$(PPh$_3$)$_2$ under UV irradiation was not observed.

The goal of this work was to study the possibility of activating the rhenium complex with triphenylphosphine. cis-ReOBr$_3$(PPh$_3$)$_2$ (inactive under homogeneous catalysis conditions) was immobilized on different supports using UV irradiation, and was investigated in the liquid-phase hydrogenation of 1-hexene and m-nitrobenzoic acid (m-NBA).

2. Experimental

The supports were: small pore silica gel [specific surface area (SSA) = 345 m^2/g], aerosil (SSA = 90 m^2/g), differently modified titanium dioxides (anatase and rutile, SSA = 5–10 m^2/g). The photoimmobilized catalysts (P) were synthesized in isopropanol in the presence of benzophenone as in [4]. The reaction of ReOBr$_3$(PPh$_3$)$_2$ photoimmobilization was carried out in a glass reactor under the action of light of wavelength $\lambda > 310$ nm [5,6]. In practice 15–45 mg of complex (about 400 mg for grafting on aerosil) was dissolved in 25 ml of 0.1 M benzophenone solution in isopropanol and then 96 mg of support was added. After filtration and washing with solvent, the precipitate was dried at a pressure of 500–600 Pa and heated on a water bath to remove isopropanol. Similarly, but without irradiation the immobilized samples (I) were prepared on the same supports and were called 'dark' catalysts.

The amount of rhenium grafted on the surface of the support was determined spectrophotometrically (Specord UV-VIS) as the difference between the total amount used for supporting and that remaining in solution after filtration of the catalyst obtained. 0.1–0.5 ml of the rhenium complex solution with an Re concentration of 10 mg/ml, 5 ml of concentrated hydrochloric acid, 5 ml of aqueous 5% thiourea and 1 ml of 20 wt.-% SnCl$_2$ acidic solution were placed into a standard volume vessel (25 ml) and diluted with isopropanol. The color of the Re(IV) complex with thiourea at room temperature completely developed within 1 h. The amount of rhenium was calculated from the intensity of the absorption peak at 392 nm [5]. Isopropanol was proposed as the diluent for the solutions analyzed because it had a better solubility for the organic components (benzophenone, triphenylphosphine) than water, which allows more reproducible data to be obtained. The analysis results are presented in Table 1.

The substrates (1-hexene and m-NBA) were hydrogenated in dimethylformamide at a hydrogen pressure of 2.0 MPa and a temperature of 353 K in a microau-

Table 1

Catalytic activity of immobilized catalysts in the hydrogenation of 1-hexene and m-nitrobenzoic acid[a]

Catalyst	Re content (wt.-%)	1-Hexene (mol hexane/mol Re h)	m-NBA (mol m-ABA/mol Re h)
cis-ReOBr$_2$(PPh$_3$)$_2$ (homogeneous)	19.25	0.0	0.0
P-silica gel	0.30	48.8	48.8
I-silica gel	0.60	0.0	6.3
P-aerosil	3.37	8.6	1.8
I-aerosil	5.00	3.2	0.0
P-rutile	0.51	133.3	43.5
I-rutile	0.70	0.0	4.0
P-anatase	0.78	339.5[b]	73.5
I-anatase	0.83	0.0	4.5

[a] [hexene] = 1.8 10^{-3} mol, [m-NBA] = 4.8 · 10^{-4} mol, P_{H_2} = 2.0 MPa, m(cat) = 0.04 g, reaction time 4 h.
[b] P_{H_2} = 0.5 MPa, m(cat) = 0.0025 g; P = photoimmobilized, I = immobilized catalyst.

toclave made of stainless steel lined with polytetrafluoroethylene. The volume of the reaction solution was 10 ml, the reaction time was 2–4 h.

The mixture of m-NBA and m-aminobenzoic acid (m-ABA) was analyzed spectrophotometrically using a nomogram [7]. The strongest pH-induced changes in the UV absorption spectra were observed for either m-NBA or m-ABA, in particular in an acidic medium. However, at pH > 5.0 for the isomolar series with a concentration of 5 · 10^{-5}–3 · 10^{-4} M there were two clearly marked isosbestic points at $\lambda = 248$ ($E^{248} = 4980$ cm^2/mol) and $\lambda = 310$ nm ($E^{310} = 1830$ cm^2/mol). They are indicative of an equilibrium between the protonized and deprotonized forms within the concentration range mentioned and additivity of UV spectra:

$$A^{268} = E_1^{268}C_1 l + E_2^{268}C_2 l,$$

$$A^{303} = E_1^{303}C_1 l + E_2^{303}C_2 l,$$

where E_1 and E_2 are the molar absorptivity of m-NBA and m-ABA at maximum absorption (268 and 303 nm, respectively), C the molar concentration and $l = 1$ cm. The content of m-NBA and m-ABA in the reaction mixture after hydrogenation was evaluated from the nomogram (see Fig. 1). The data plotted was calculated from the following formulae:

$$C_1 = 1.468 \cdot 10^{-4}A^{268} - 4.038 \cdot 10^{-5}A^{303},$$

$$C_2 = 6.011 \cdot 10^{-4}A^{303} - 1.880 \cdot 10^{-4}A^{268}$$

using the absorbtivity measured for artificial aqueous solutions of pure acids at pH > 5.0.

1-Hexene and hexane containing mixtures were analyzed with a Tsvet-102 gas chromatograph. The stationary phase was 10% polyethylene glycol adipinate on Rysorb BLK, length of the glass column 2.0 m, diameter 3 mm, carrier gas nitrogen, flow rate 40 ml/min, column temperature 313 K, vaporizer temperature 333 K.
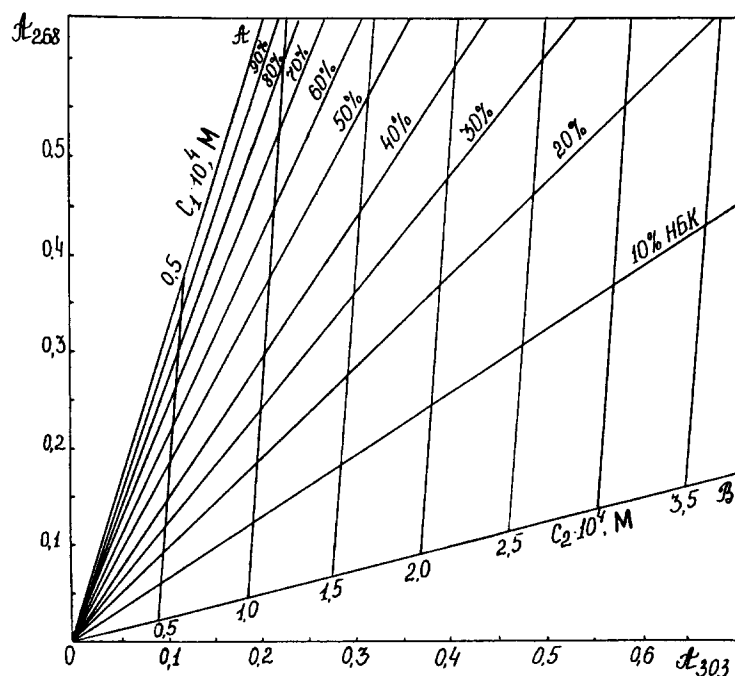
Fig. 1. Nomogram for spectrophotometric analysis of m-NBA and m-ABA mixtures. $C_1 = m$-NBA, $C_2 = m$-ABA.

The UV diffuse reflection spectra of all catalysts obtained were recorded on a Specord M-40 spectrophotometer in the 220–330 nm region.

3. Results and discussion

Table 1 shows comparative data on the molar productivity of the photoimmobilized and 'dark' catalysts in the hydrogenation of 1-hexene and m-NBA. The values were calculated from the results of the analysis of the product composition, rhenium content in the sample and the reaction time (usually 4 h). Both types of samples are more or less active, but the molar productivity of the impregnated samples is significantly less than that of the photoimmobilized samples in spite of the higher concentration of grafted Re. The photoimmobilized catalyst on anatase, as in [2], had the highest activity.

In Fig. 2 the diffuse reflection spectra of the original complex of cis-ReOBr$_3$(PPh$_3$)$_2$ (curve 1), the silica gel support (curve 2), the 'dark' and photoimmobilized catalysts on silica gel (curves 3 and 4, respectively) are presented. Analogous spectra were obtained on aerosil. The modified titanium dioxides have a characteristic absorption spectrum in the region investigated [2] and for this reason it is difficult to obtain informative spectra. Comparison of absorption curves 1 and 2 with 3 and 4 allows us to draw the following conclusion: in the diffuse reflection spectra of the 'dark' and photoimmobilized samples a new broad absorp-
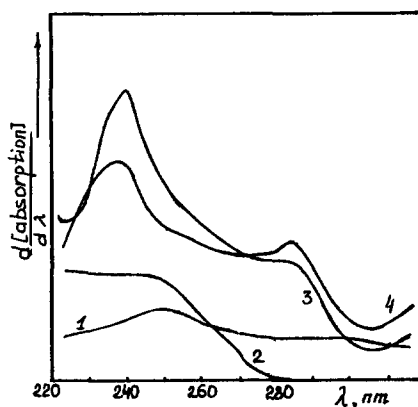
Fig. 2. Differential diffuse reflection spectra of the samples. (1) cis-ReOBr$_3$(PPh$_3$)$_3$, (2) silica gel, (3) I-SiO$_2$, (4) P-SiO$_2$.

tion band appears in the 280–290 nm region, characteristic for tetravalent rhenium ions. According to [8] the absorption band at 281 nm is formed upon photoreduction of rhenium(V) by ethanol in hydrochloric acid and corresponds to the presence of Re(IV) ions. There was no absorption in this region of the oxohalide triphenylphosphine complex of rhenium(V) (curve 1). Upon immobilization of the rhenium(V) compound, partial reduction to Re(IV) occurs under the influence of irradiation and under the action of the reducing mixture isopropanol–benzophenone. However, based on the different catalytic activities, we can suppose that, despite of the greater amount of Re on each support for the immobilized catalysts, the concentration of active centers is significantly lower than that on the photoimmobilized samples. The diffuse reflection spectra of the samples after catalysis showed no remarkable changes.
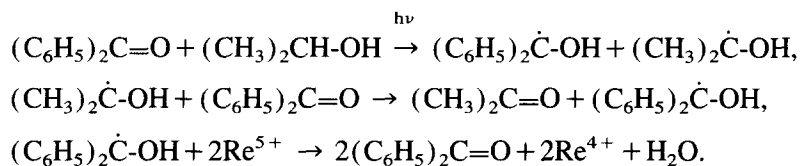
As has been demonstrated, especially in the case of the samples grafted onto the aerosil surface, a substantial increase of the total Re amount up to 0.187 and 0.283 mmol/g for P- and I-catalysts, respectively, did not lead to a corresponding increase in the catalytic activity (see Table 1). This indicates that the nature of the chosen support as a macroligand is very important for formation of the active sites.

On titanium dioxide, having its own photoactivity, the process is facilitated by the fact that upon UV-irradiation dehydroxylation of the surface occurs and additional vacant coordination sites (acceptors) appear. Consequently, catalysts on TiO$_2$ contain more Re in the active form and ensure a higher productivity in the hydrogenation of 1-hexene and m-NBA, which is clear from the data in Table 1.

Certainly, a significant role is also played by the other ligand surrounding Re. Grafting of the complexes under the action of irradiation and under 'dark' conditions occurs by different mechanisms. In the first case, probably under the action of UV light, the rhenyl group is reduced and grafted to the surface as follows lowering the oxidation number of the central ion to +4:
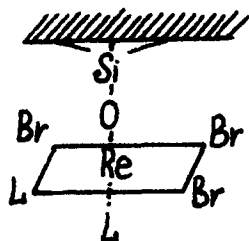
Clearly, the central metal ion reduction under the action of UV-irradiation occurs with participation of the benzophenone ketyl radical as in [4]:

$$(C_6H_5)_2C{=}O + (CH_3)_2CH{-}OH \xrightarrow{h\nu} (C_6H_5)_2\dot{C}{-}OH + (CH_3)_2\dot{C}{-}OH,$$

$$(CH_3)_2\dot{C}{-}OH + (C_6H_5)_2C{=}O \rightarrow (CH_3)_2C{=}O + (C_6H_5)_2\dot{C}{-}OH,$$

$$(C_6H_5)_2\dot{C}{-}OH + 2Re^{5+} \rightarrow 2(C_6H_5)_2C{=}O + 2Re^{4+} + H_2O.$$

Under 'dark' conditions, the rhenium on the surface is fixed preferentially in the pentavalent state through dissociation of the triphenylphosphine ligand and coordination of Re by means of isopropanol bridges (or without them):
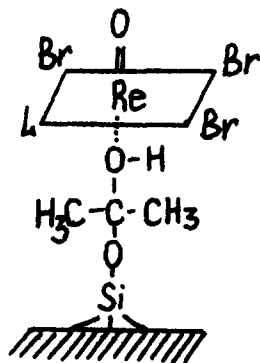
or
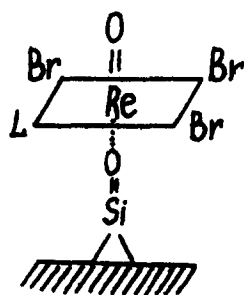
Some amount of isopropanol and traces of it were found in the composition of the I- and P-catalysts, respectively, from the thermography data. Different mechanisms for $ReOBr_3(PPh_3)_2$ immobilization with and without UV-irradiation can be proved indirectly by the following observation: in contrast to the irradiated solutions, the solutions separated after precipitation of the I-catalysts contained more triphenylphosphine than Re remaining in the dissolved state. Despite the larger amount of Re sorbed in this way, the productivity of the catalysts is significantly lower since rhenium is not active with an oxidation state of $+5$ (see Table 1).

As expected, the anatase supported catalysts are significantly more active than samples on rutile because of the smaller photoactivity of the latter due to a more closely packed lattice. The difference between the properties of anatase and rutile in the literature is attributed to different faces emerging on the surface, differing in their degree of hydroxylation. In the case of rutile, the completely hydroxylated face (110) predominates on the surface [9]. While for anatase the data about the predominant face are contradictory [10].

4. Conclusions

The inactive *cis*-isomer of the $ReOBr_3(PPh_3)_2$ complex was prepared in a catalytically active state using immobilization on a support under UV-irradiation. In the hydrogenation of 1-hexene and *m*-NBA, the photoimmobilized catalyst on anatase has the greatest activity, which is connected with the effect of the support itself upon formation of centers for immobilization.

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