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OXIDATION OF HYDROGEN BY METAL COMPLEXES OF PLATINUM AND PALLADIUM IMMOBILIZED ON SILICA

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Abstract

The thermal stability of metal complexes immobilized on the surface of silica and its connection with the catalytic activity in the oxidation of hydrogen were investigated. High catalytic activity was exhibited by heterogenized platinum and palladium acetylacetonate near room temperatures in the initial state and by γ-aminopropylsilicas treated with platinum and palladium complexes. The catalytic activity of the metal complexes correlates with their thermal stability and with the ability to undergo oxidation to a metal state with high valence.

Keywords: catalysis, immobilized metal complexes, thermal stability

Introduction

The immobilization of metal complexes on various carriers is one of the methods of obtaining active catalysts for both homogeneous and heterogeneous chemical processes [1–3]. The anchored complexes, which are used in catalysis, have advantages in comparison with homogeneous analogs, such as high catalytic activity, better thermal stability and easy extraction from the reaction environment. The simplicity of regeneration of metal complexes heterogenized on the carrier surface allows the use of these catalysts in a cyclic operational mode of heterogeneous catalysis.

Heterogenized metal complex catalysts have mainly been studied for use in liquid-phase catalytic processes [4]. Little information is available on the application of these catalysts for gas-phase reactions.

Platinum and palladium complexes with γ-aminopropylsilicas (metal contents 0.025 and 0.05 mass%) and the acetylacetonate complexes of these metals with various contents of metal (0.02, 0.06 and 0.6 mass%) immobilized on a SiO_2 surface were investigated as catalysts in the oxidation of H_2.

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Experimental

The quantity of acetylacetone groups in the obtained surface complexes, determined by integral thermal analysis was 0.12 mmol g^{-1} (Q-1500 D, MOM, Hungary; T=25–1000°C, heating rate 10°C min^{-1}, sample mass 0.4 g).

The Pt- and Pd-containing organosilica complexes were obtained [5] by the interaction of modified silicas with different concentrations of H_2PtCl_6 and Pd salt solutions in *i*-propanol and water.

The catalytic oxidation of H_2 with molecular O_2 was investigated under flowing conditions with chromatographic control of the reaction mixture composition. The separation of gases was carried out in a chromatographic column filled with activated carbon (SKT) supported by $NiSO_4$. Catalytic activity was investigated under atmospheric pressure in the temperature range 0–100°C, using various gas mixtures (1.5–38.5% O_2, 1.75–24.5% H_2 and 58.5–93.5% Ar). The gas flow was 0.05–0.1 l min^{-1}.

The catalyst sample had a volume near 1 cm^3 and a mass of about 0.25 g; the catalyst particle size was 0.25–0.5 mm. The reaction was carried out both without and with preliminary temperature treatment. The activities of the catalyst in the various gas mixtures were compared at the temperatures of complete (100%) conversion of H_2 or O_2, which depend on the composition of the reaction mixture.

Results and discussion

The differential thermal analysis of Pt and Pd containing organosilicas was carried out to determine the temperature regime of the catalytic investigations and to establish their stabilities during heating to high temperatures.

The thermal analysis curves for γ-aminopropylsilica containing 0.025% Pd are presented in Fig. 1.

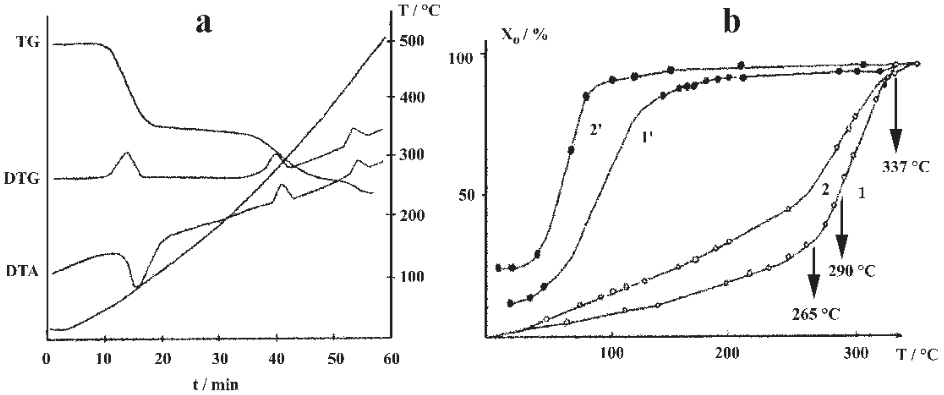

Fig. 1 Investigation of 0.025% Pd – γ-aminopropylsilica: a – thermal analysis; b – catalytic activity; 1 and 1' – reaction gas mixture: 1.5% H_2+38.5% O_2; 2 and 2' – reaction gas mixture 18% H_2+9% O_2

There are exothermic effects at 265 and 462°C in the DTA curve for 0.025% Pd-containing γ-aminopropylsilica. These effects are connected with destruction of the chemically immobilized organic layer: loss of the amino groups of the immobilized γ-aminopropylsilica. Mass losses of 7 and 12% correspond to these effects in the TG curve. Extremes at 290 and 480°C in the DTG curve correspond to these exoeffects.

The thermal analyses of γ-aminopropylsilica with 0.025% Pd allows conclusions about the thermal stability of the Pd complex at temperatures below 265°C. Above this temperature, detachment of the organic layer takes place. Analogous data were obtained during the thermal investigation of the heterogenized Pt complexes.

Thermal analysis of the Pt acetylacetonate (0.024% Pt) catalyst supported on a silica surface reveals the presence of an endoeffect and exoeffect in the DTA curve. These effects are accompanied by losses of 2 and 4% mass in the TG curve. The first corresponds to the removal of physically adsorbed water, and the second to the detachment of grafted acetylacetone fragments. As evidenced by the thermal analysis, this complex is stable up to 200–250°C.

The results of investigation of the catalytic activity of γ-aminopropylsilica with 0.025% Pd are presented in Fig. 1b. The Pd-containing γ-aminopropylsilica catalyst is seen to have insignificant activity in the stoichiometric gas mixture. The conversion degree at 270°C is 30%. On temperature increase, the activity rises sharply and complete conversion of O_2 is observed at 340°C (Fig. 1b). On temperature decrease, the catalytic activity remains high till 140°C and is higher than when the initial temperature increase was carried out. This leads to the appearance of a hysteresis phenomenon (Fig. 1b, curve 1').

The analogous character of the conversion degree *vs.* temperature dependence for 0.025% Pd γ-aminopropylsilica was observed for this catalyst in a gas reaction mixture with a hydrogen excess (Fig. 1b, curves 2 and 2').

Investigation of the catalytic activity for Pt γ-aminopropylsilica with different metal contents showed that catalysts without treatment before the catalytic reaction did not have high activity in any gas mixture. Complete hydrogen conversion on these samples was observed at temperatures higher than 250°C. The hysteresis phenomenon was observed after the decrease of temperature.

The catalytic activity of Pd acetylacetonate (0.024% Pd) was also investigated. The highest activity of this catalyst was observed in a mixture with an oxygen excess.

A sharp increase in the catalytic activity of Pd and Pt γ-aminopropylsilicas was observed in the second cycle of catalysis. The degree of H_2 conversion in a gas mixture with an oxygen excess at room temperature was 65% (Fig. 1b). Analogous investigations in a hydrogen excess showed an increased catalytic activity. However, the activity of this sample in a gas mixture with a hydrogen excess was less than that in the mixture with an oxygen excess. The temperatures of complete hydrogen conversion (x=100%) for Pt and Pd γ-aminopropylsilicas in the second cycle of catalysis are shown in Table 1.

Table 1 Catalytic activity of Pt and Pd γ-aminopropylsilicas in the oxidation of hydrogen in the second catalysis cycle

γ-aminopropylsilica catalyst	T_{100}/°C at different gaseous mixtures		
	Excess of H_2 8.5% H_2+5.1% O_2	Stoichiometric 16% H_2+8% O_2	Excess of O_2 1.5% H_2+38.5% O_2
0.025% Pd	130	160	250
0.05% Pd	80	110	132
0.025% Pt	230	176	70
0.05% Pt	70	80	20

Increase of the metal content in the γ-aminopropylsilica led to higher catalytic activity for both Pd and Pt. This can be explained by increased active site contents on the carrier surface.

Comparison of the catalytic activities of the Pt and Pd-containing γ-aminopropylsilicas with the same quantity of metal (Table 1) shows that in a gas mixture with a H_2 excess the Pd-containing catalyst is the more active. The Pt-containing γ-aminopropylsilica catalyst is the more active in an oxygen excess. This may be connected with the ability of Pt ions to oxidize to the Pt(IV) valence state and to form π-complexes with O_2 molecules. The temperature dependences of the degree of conversion of H_2 (O_2) show that the catalysts can be used in two stationary states (low-active and high-active states) in the same temperature interval in the first and the second cycles of catalysis. Analogous dependences are observed for the immobilized acetylacetonate complexes.

It was earlier observed [5] that the SiO_2 surface with the immobilized 0.024% Pt acetylacetonate has very high catalytic activity in the oxidation of H_2 without preliminary treatment of the catalyst at 60–80°C.

In this work, the influence of the metal content (0.024, 0.064 and 0.64% Pt) of Pt acetylacetonate supported on silica and of Pt-γ-aminopropylsilica (0.025 and 0.05 mass%) on the catalytic activity was examined.

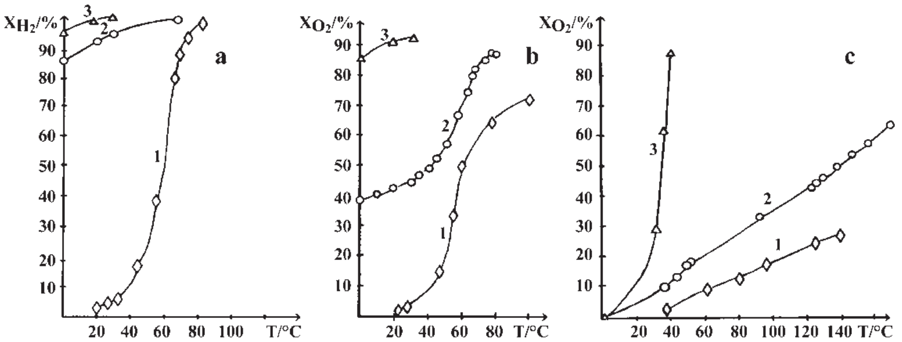

Fig. 2 Catalytic activity of immobilized platinum complexes with various contents of metal (1 – 0.024%Pt; 2 – 0.064%Pt; 3 – 0.64%Pt) in different gaseous mixtures: a – oxygen excess; b – stoichiometric mixture; c – hydrogen excess

The dependence of the hydrogen (or oxygen) conversion degree on the temperature for the acetylacetonate complexes is presented in Fig. 2. According to these data (Fig. 2a), increase of the Pt content in the catalyst leads to a higher catalytic activity. The temperatures of 100% conversion for the complexes containing 0.024, 0.064 and 0.64% Pt are 80, 60 and 20°C, respectively.

Investigation of the catalytic activity of the immobilized complexes showed that the rate of reaction is lower in the stoichiometric gas mixture than in a reaction mixture with an oxygen excess for all catalysts (Fig. 2a and b). The catalytic activity of the complexes in a small (3.3) hydrogen excess (Fig. 2c) is considerably lower for all catalysts in comparison with other mixtures. The complex with 0.64% Pt has the highest catalytic activity for all gas mixtures with various hydrogen and oxygen ratios (Fig. 2).

The Pt- and Pd-containing acetylacetonate catalysts displayed maximum activity in the mixture with an oxygen excess. The catalytic activities of the Pt and Pd acetylacetonates with metal contents of 0.024% (without preliminary treatment in the oxidation of hydrogen) are shown in Table 2.

Table 2 Catalytic activities of Pt and Pd acetylacetonates (0.024% metal) in the oxidation of hydrogen

Acetylacetonate catalyst	Content of gaseous mixture		
	Excess of H_2 8.5% H_2+5.1% O_2 T_{30}/°C	Stoichiometric 16% H_2+8% O_2 T_{50}/°C	Excess of O_2 1.5% H_2+38.5% O_2 T_{100}/°C
0.025% Pd	170	160	100
0.025% Pt	90	70	80

As seen from Table 2, the catalytic activity of Pt acetylacetonate is higher than that of the immobilized Pd compound.

Conclusions

The connection of the thermal stability and the catalytic activity of metal complexes immobilized on SiO_2 in the oxidation of H_2 was investigated. In the case of complexes immobilized on γ-aminopropylsilica, their catalytic activity correlates with their thermal decomposition. Immobilized Pt acetylacetonate has lower thermal stability than those of Pd and Pt γ-aminopropylsilicas, which are very active catalysts both in the initial state and in the oxidized or reduced state.

In contrast, the immobilized γ-aminopropylsilicas of Pt and Pd have relatively high catalytic activity only after preliminary treatment with the gaseous reactant mixture. The investigation of the catalytic activities of the immobilized acetylacetonate catalysts showed that they have higher catalytic activity both without and with preliminary treatment. This may be connected with the lability of these heterogenized compounds and their ability to bind the reagent molecules on the active sites during the catalytic reaction.

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