

GAS-PHASE HYDROFORMYLATION OF PROPYLENE ON Ru/SiO₂
CATALYSTS

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Ru/SiO₂ catalysts prepared by reduction of supported RuCl₃·xH₂O are active in gas-phase hydroformylation of propylene at low pressure (ca. 0.3 MPa) of H₂ + CO + C₃H₆ mixture and show unexpectedly high selectivity towards unbranched oxo-products. Data concerning the effect of electronic state and dispersity of Ru on their catalytic behavior have been obtained.

Катализаторы Ru/SiO₂, приготовленные восстановлением нанесенного RuCl₃·xH₂O, активны в реакции газофазного гидроформилирования пропилена при низких (~0,3 МПа) давлениях реакционной смеси и проявляют неожиданно высокую селективность в образовании оксо-продуктов линейного строения. Получены данные о влиянии состояния и дисперсности рутения на свойства этих катализаторов.

In practice, olefin hydroformylation is generally carried out under liquid-phase conditions and catalyzed by soluble Co or Rh carbonyls modified by organic ligands [1]. The gas-phase oxo-reaction on supported metal catalysts is less extensively studied. It was previously found that highly dispersed metal catalysts prepared by pyrolysis of Co or Rh carbonyls on various

oxide supports are active in hydroformylation of light olefins even at low partial pressure of CO [2,3]. Under the conditions of Fischer-Tropsch synthesis, the formation of oxo-products is also observed by the addition of olefins to CO + H₂ mixture on supported metal catalysts prepared via high-temperature reduction of supported Ru [4,5], Pd [6,7], Ni [7] or Fe [8] salts, although these systems were not considered earlier convenient catalysts for hydroformylation. In the present work the gas-phase hydroformylation of propylene on Ru/SiO₂ catalysts obtained by reduction of supported Ru chlorocomplexes is studied at low (close to ambient) pressure of reaction gas mixture. Here we also report data concerning the effect of electronic state and dispersity of Ru particles on the properties of these catalysts.

EXPERIMENTAL

Ru/SiO₂ catalysts were prepared by impregnation of silica (S_{BET} = 218 m²/g) with a solution of RuCl₃ · x H₂O (Johnson Matthey Chemicals) in 38% HCl solution (grade "chemical pure") with a subsequent evaporation of the solvent at 300 K. Then the samples were dried under vacuum at 378 K for 2 hours. Further manipulations were performed in a glass apparatus without contact with air. Decomposition of supported Ru compounds was carried out as follows:

A.) The samples were charged into a reactor preheated to the reduction temperature and reduced in flowing H₂ at 423-873 K, atmospheric pressure and space velocity of 2400 h⁻¹ (duration was varied from 15 min to 4 hours);

B.) The samples were heated under vacuum (at residual pressure of 0.01 Torr) or calcined in a flow of O₂ at 723 K for 0.5 h in a preheated reactor with subsequent H₂ reduction at the same temperature for 1 h.

After treatments A and B the catalyst samples were evacuated at the reduction temperature for 0.5 h.

Hydroformylation of propylene was performed in a differential flow reactor at 333 K, total pressure of 0.3 MPa, H₂:CO:

$C_3H_6 = 1:1:1$ and space velocity of $500-1000 \text{ h}^{-1}$ ensuring ca. 5% conversion of reactants. Products were analyzed by an on-line chromatograph. The activity of the catalysts was estimated according to the yield of C_4 aldehydes and alcohols. Prior to any tests, the applied gases (H_2 , CO and propylene) and their mixture were purified in the units containing high-temperature reduced MnO_2 and molecular sieves (5 \AA) to remove trace amounts of O_2 , water and metal carbonyls.

Transmission electron microscopy (TEM) measurements of the samples were taken on a JEM-100CX apparatus. The dimensions of the Ru crystallites were expressed as average diameters, \bar{d} defined as

$$\bar{d} = \frac{\sum_i (n_i d_i)}{\sum_i n_i},$$

where d_i are the diameters of the metal aggregates, as measured by the TEM micrographs. X-ray photoelectron spectroscopic data (XPS) were obtained by a VG ESCALAB spectrometer at 300 K and $P \sim 10^{-7}$ Torr, using the AlK_α radiation. The content of Ru was analyzed spectrophotometrically.

RESULTS AND DISCUSSION

After impregnation of silica with a solution of $RuCl_3 \cdot xH_2O$ in concentrated HCl which is actually the mixture of chlorocomplexes of Ru(III) and Ru(IV) predominantly ($[RuCl_5(H_2O)]^{2-}$ [9], deep-red solid samples are obtained. Upon drying under vacuum at 378 K, they rapidly become darker apparently due to the hydrolysis of supported complexes and formation of the corresponding hydroxides and/or oxides. In the XPS spectra of the Ru/SiO_2 samples before reduction the Ru $3d_{5/2}$ level is observed as a shoulder having a binding energy (E_b) of 281.9 ± 0.1 eV (the intensive C 1s peak overlaps with the Ru 3d peaks). This value differs from those attributed both to the bulk $RuCl_3$ ($E_b = 284.3$ eV) and to Ru in the metallic state ($E_b = 280.6$ eV) [10]. It can be due to partial photoreduction of the supported Ru^{3+} to Ru^{2+} species upon spectra recording. In addition, this spectrum exhibits the Cl 2p peak ($E_b = 199.5$ eV). Treatment of the samples

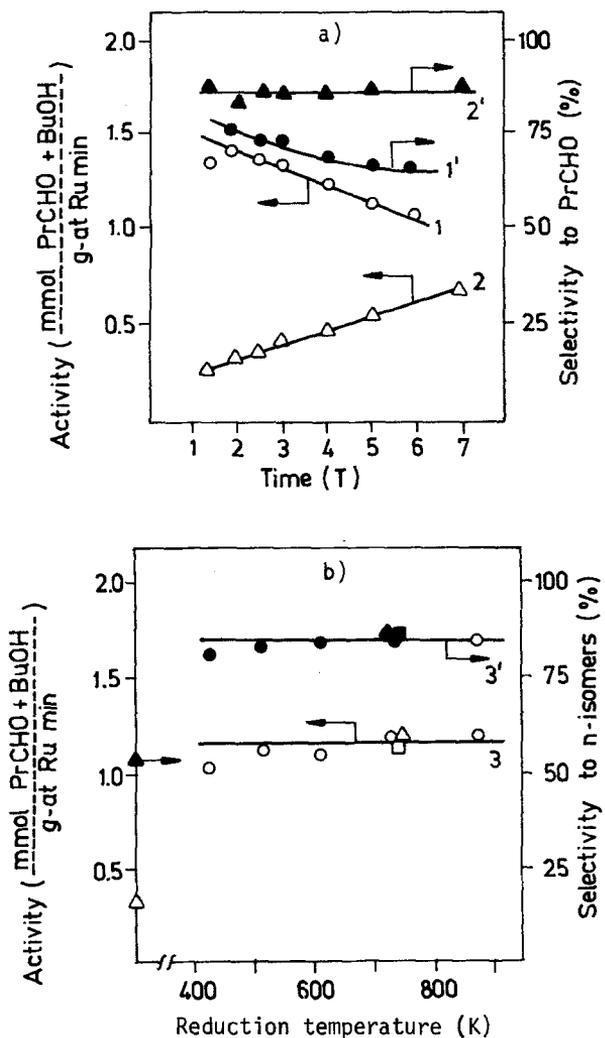


Fig. 1 . Catalytic activity and selectivity in C_3H_6 hydroformylation vs. time (a) and conditions of catalyst preparation (b) (3 h after starting the experiment). Samples: 1,1' - 3% Ru/SiO₂ reduced in flowing H₂ at 723 K; 2,2' - unreduced 3% Ru/SiO₂; 3,3' - 4.6% Ru/SiO₂ reduced in a H₂ flow at various temperatures; duration of the reduction: (◊,◆) - 15 min, (○,●) - 1 h, (□,■) - 4 h, (Δ,▲) - before reduction

Table 1

Properties of 4.6% Ru/SiO₂ catalysts prepared by different methods

Nos	Conditions of the decomposition of supported compound	\bar{d} ^a	Activity ^b	Selectivity n-iso- aldehydes ^c des ^d	
1.	Initial sample	-	0.40	53	86
2.	Reduction in H ₂ flow	31±4 Å (0.30)	1.30 (4.3)	88	71
3.	Pyrolysis in vacuum then H ₂ reduction	50±10 Å (0.19)	0.45 (2.3)	87	68
4.	Calcination in O ₂ flow then H ₂ reduction	80±12 Å (0.11)	0.20 (2.0)	85	77
5.	Sample 2 after 20 h storage in air	32±6 Å (0.29)	1.10 (3.8)	86	80
6.	Sample 2 treated by water	27±4 Å (0.33)	1.20 (3.7)	86	93

^a Average diameter of Ru crystallites ± experimental error (in brackets dispersity values (D) estimated according to [11] are given);

^b Catalyst activities (A) (3 h after starting the catalytic run) are given in mmol (C₃H₇CHO + C₄H₉OH)/mol Ru/min (in parentheses the corresponding turnover frequency (nf = A/D) values are given in min⁻¹ 10³);

^c (n-C₃H₇CHO + n-C₄H₉OH) / (ΣC₃H₇CHO + ΣC₄H₉OH) × 100%;

^d ΣC₃H₇CHO / (ΣC₃H₇CHO + ΣC₄H₉OH) × 100%

in a H_2 flow at 428-873 K for a period as short as 15 min leads to a shift in the Ru $3d_{5/2}$ level towards the E_b values of 280.2-280.6 eV. In this case the Cl 2p peak disappears from the spectra. According to these data, the supported Ru compounds can be rapidly and practically completely reduced under the conditions used.

The results for the hydroformylation of propylene are presented in Table 1 and Fig. 1. The primary products are n- and iso-butyraldehydes. Under the reaction condition, significant fraction of aldehydes is hydrogenated to n- and iso-butyl alcohols. The activity of catalyst 2 reduced immediately after drying is much higher compared to that of the unreduced sample 1 (Table 1). The reduced Ru/SiO₂ catalysts demonstrate an unexpectedly high selectivity to the formation of unbranched oxo-products with the n/iso molar ratio being ca. 6-8. For comparison, when the reaction is carried out under homogeneous liquid-phase conditions in the presence of Ru₃(CO)₁₂ or Ru(CO)₅(PPh₃)₂, the n/iso ratio does not exceed 3 [12]. However, the intensive hydrogenation of propylene to propane accompanies hydroformylation on Ru/SiO₂ catalyst (under the experimental conditions used in this work, the rate of propylene hydrogenation is about 10-15 times higher than the rate of hydroformylation). One can also observe the formation of trace amounts of methane probably due to CO + H₂ reaction.

For catalyst 2 the overall activity gradually decreases in the examined period of the reaction, while the selectivity to alcohols noticeably increases (Fig. 1a, curves 1 and 1') and the n/iso ratio is constant during this period. Since the ruthenium content in the catalyst was found to be unchanged before and after reaction (to within an experimental error of ±5%), this deactivation is apparently due to carbonization and/or poisoning of the metal sites by the reaction products rather than to Ru discharge from the support. In contrast, the activity of catalyst 1 containing Ru in the oxidized state gradually increases during the reaction, probably owing to the reduction of supported complexes during the process (Fig. 1a, curves 2 and 2'). This catalyst is characterized by very low regioselect-

tivity ($n/\text{iso} = 1.0\text{--}1.5$) and comparatively high selectivity to aldehydes.

Unlike metal Co catalysts prepared by pyrolysis of $\text{Co}_2(\text{CO})_8$ [3], the reduced Ru/SiO_2 catalysts can be stored in air or treated by water without loss of their activity (Table 1, catalysts 5 and 6). These treatments lead to a decrease in the share of alcohols. The formation of butyric acids, observed in this case, is likely a result of hydrocarboxylation of propylene by adsorbed water.

An important factor affecting properties of the supported metal catalysts for oxo-reaction is the dispersity of metal particles [3,13]. According to TEM data, catalyst 2 contains supported Ru crystallites with the d value of about 30 \AA , the particle size distribution being sufficiently narrow, i.e. within $20\text{--}25 \text{ \AA}$. Upon variation of the reduction conditions (temperature and duration of reduction, rate of temperature increase), Ru dispersity remains virtually unchanged. Thus, we have not observed any effect of the reduction conditions on the activity and selectivity of Ru/SiO_2 catalysts in propylene hydroformylation (Fig. 1b).

It is known [14,15] that the size of supported Ru crystallites in $\text{Ru}/\gamma\text{-Al}_2\text{O}_3$ catalysts can be changed (enlarged) by pretreatments under thermovacuum or oxidative conditions. It has been suggested that in this case the initially supported Ru hydroxocomplexes are completely converted into oxide particle which can better migrate over the support surface as compared to Ru metal aggregates [16]. In this connection, when preparing Ru/SiO_2 catalysts, some samples after drying and before reduction were treated in vacuum or in flowing O_2 at a high temperature (Table 1, catalysts 3 and 4), XPS data indicate that in these catalysts after reduction ruthenium is also present in the metallic state. According to TEM micrographs, catalysts 3 and 4 contain large metal particles with $\bar{d} = 50\text{--}80 \text{ \AA}$, moreover, some Ru crystallites attain the size of $150\text{--}180 \text{ \AA}$. The activity of catalysts 3 and 4 propylene hydroformylation is 3-7 times lower than that of catalyst 2, while the composition of the reaction products remains the same. One of the reasons of the de-

creased activity of catalyst 2 is apparently the lower dispersity of the supported component.

Turnover frequency of hydroformylation estimated for catalyst 2 is about 2 times higher than that for catalyst 3 and 4. This marked increase can be ascribed to the growth in the fraction of low-coordinated Ru atoms in the surface Ru crystallites taking place when the dimensions of these crystallites decrease. Increasing the concentration of low-coordinated metal atoms has to promote in situ formation of surface Ru carbonyls, which appear to be the active sites in the hydroformylation.

The reasons for high selectivity of dispersed metal catalysts towards unbranched oxo-products, as well as the development of the methods for selective poisoning of olefin hydrogenation sites will be the aim of our further investigations.

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