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Cluster - dirived catalysts

# Study of Supported Rhodium Catalysts for Synthesis of Low Alcohols from CO and $H_2$

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Summary

The state of rhodium in the supported catalysts prepared via the adsorption of $Rh_4(CO)_{12}$ on $SiO_2$, $\gamma$-$Al_2O_3$ and $La_2O_3$ was investigated by XPS, EXAFS and IR spectroscopy, TPD and TPR. The existence of "pill-box" shape of rhodium particles on $La_2O_3$ and a decrease of heat of CO desorption in comparison with $Rh/SiO_2$ and $Rh/Al_2O_3$ catalysts were indicative of strong metal support interaction (SMSI) of Rh with $La_2O_3$. The high yield of oxygenated products at CO hydrogenation was characteristic for $Rh/La_2O_3$ catalysts. $^{13}C$-NMR studies suggest that the interaction of CO and $H_2$ over $Rh/La_2O_3$ initially produces species containing $-C\overset{O}{\underset{H}{<}}$ fragments. Formation of $CHO_2^-$ species is also probable. Experimental data are obtained showing that methanol and ethanol formation proceeds through different mechanisms involving different catalytic sites.

At CO hydrogenation by Rh containing catalysts it is possible to obtain either hydrocarbons or oxygenated compounds /1-3/(especially it is necessary to mention the formation of $C_2$ oxygenates /4,5/). The state of Rh in these catalysts is a problem under discussion /2,3,5, 6/. Some important features of the mechanism of CO hydrogenation on Rh catalysts are also not clear. Methanol is suggested to be formed through the hydrogenation of non-dissociatively adsorbed CO. This view is compatible with the results of isotopic mixing technique for $Rh/TiO_2$ /7/. But the type and the location of catalytic sites responsible for the methanol formation however are not known. It was proposed that hydrocarbons and $C_2$-oxygenates are formed via a common $CH_x$ precursor /1,2,6,8/. However, it is not clear if these species are derived from dissociatively adsorbed CO with subsequent hydrogenation of surface carbon or from non-dissociatively adsorbed CO by its direct hydrogenation.

The present paper reports the results of the study of Rh catalysts characterized by different selectivities in CO hydrogenation. This study was performed with an objective to clarify the state of Rh in

these catalysts and the mechanism of alcohols formation.

## Experimental

Rhodium catalysts were prepared via the impregnation of oxide supports preliminary heated at 573-873 K in vacuum with pentane solution of $Rh_4(CO)_{12}$. After evacuation of the solvent supported clusters were decomposed at 423-443 K in vacuum. All the procedures of preparation and treatment of catalysts were carried out without the exposure in air. Some characteristics of the catalysts prepared are given in table 1.

**Table 1**

Properties of rhodium catalysts prepared by supporting $Rh_4(CO)_{12}$. Rhodium content ~1 wt%.

| Support | $T_d$, K[a] | B.E.T. surface area $m^2/g$ | $T_r$ in $H_2$, K | $\frac{H}{Rh}$[b] | $\frac{CO}{Rh}$[b] | $\bar{d}$[c] e.m. nm | $E_b$ and[d] halfwidth of Rh $3d_{5/2}$ line eV |
|---|---|---|---|---|---|---|---|
| $SiO_2$ | 873 | 200 | 673 | 0.7 | 0.6 | 3.7 | 306.8(2.0) |
| $\gamma$-$Al_2O_3$ | 873 | 220 | 673 | 1.6 | 2.1 | $\leq$ 1.0 | 307.7(2.2) |
| $La_2O_3$[e] | 573 | 33 | 473 | 0.6 | 0.9 | - | 307.3(3.5) |
| | | | 673 | 1.15 | 0.4 | - | 307.1(2.9) |
| | | | 873 | 0.6 | 0.2 | - | 307.1(2.2) |
| La-$SiO_2$[f] (10 wt% La) | 773 | 180 | 473 | 1.7 | 1.7 | 2.0[g] | - |
| | | | 673 | 1.9 | 2.0 | 2.0[g] | - |
| | | | 873 | 1.4 | 1.6 | 2.0[g] | - |

a - Temperature of preheating of support; b - measured in Digisorb-2500 at 298 K; c - average diameter of rhodium particles, electron microscopic data; d - XPS data; e - prepared according to ref. 9; f - prepared via impregnation of $SiO_2$ with water solution of $La(OOCCH_3)_3$ and subsequent heating of the support in vacuum at 773 K; g - "pill-box" particles.

XPS studies were carried out using VG-ESCA-3 spectrometer with Al K radiation. The Si 2p (103.7 eV), Al 2p (74.7 eV) and C 1S (284.8 eV) lines were used as internal standards. Electron microscopic

measurements were performed using EMV-100B electron microscope with 0.3 nm resolution. EXAFS K-spectra of rhodium were recorded using synchrotron radiation facilities of the Institute of Nuclear Physics (Novosibirsk). IR spectra of CO adsorbed on catalysts were recorded using Specord 75 IR in a cell providing possibility to treat the wafer of a catalyst without contact with air. TPD of CO and $H_2$ were carried out in a vacuum system ($5\times10^{-6}$ Pa) with a linear heating (5 K/min). The temperature programmed reduction (TPR) of initially oxidized Rh catalysts were studied in the installation by the same technique as described in ref. 10 (7 vol.% $H_2$ in Ar, space velocity 200-400 $min^{-1}$, heating 11 K/min). $^{13}C$-NMR spectra were registered using CXP-300 spectrometer (Brucker) at the constant magnetic field of 7T and frequency of 75.5 mHz. Measurements of activity of CO hydrogenation were carried out at atmospheric pressure in a glass flow differential reactor at 473-573 K and space velocity of the CO and $H_2$ mixture (1:2) of 500-80000 $hr^{-1}$. The products were analyzed chromatographically.

## Results

### Catalytic properties of rhodium catalysts

Table 2 summarizes the properties of rhodium catalysts in CO hydrogenation. The yield of oxygenated compounds (methanol, ethanol and traces of acetaldehyde) significantly depends on the space velocity of CO and $H_2$ mixture (alcohols may be decomposed in the secondary reactions; the rate of methanol formation also decreases with an increase of conversion). So catalytic properties of different samples were compared at the same space velocities. The $Rh/La_2O_3$ and $Rh/La\text{-}SiO_2$ show a higher yield of methanol and ethanol, which accounts for that these catalysts were studied in more detail.

An increase of the temperature of preliminary reduction of $Rh/La_2O_3$ in $H_2$ resulted in an increase of the relative yield of ethanol and a decrease of the yield of methanol (fig. 1). The introduction of $O_2$ in the reaction mixture ($CO:H_2:O_2=1:2:0.002$) resulted in a decrease of the activity of rhodium catalysts.

An addition of $CH_3OH$ in CO and $H_2$ mixture (40% of CO converted) didn't change significantly the yields of oxygenated products in the case of $Rh/La_2O_3$. However, the addition of $CH_3I$ (20-30% of CO converted; the

Table 2

Catalytic properties of supported rhodium catalysts in CO hydrogenation ($CO:H_2$=1:2; 523 K; 10 hours after the beginning of catalytic tests).

| Catalyst | Space velocity $h^{-1}$ | Carbon efficiency [a] | | | | rate of formation $A_i \times 10^5$ | | |
|---|---|---|---|---|---|---|---|---|
| | | hydrocarbons | | $CH_3OH$ | $C_2H_5OH$ | | | |
| | | $C_1$ | $C_2$-$C_5$ | | | $CH_4$ | $CH_3OH$ | $C_2H_5OH$ |
| $Rh/SiO_2$ | 2700 | 43.8 | 56.2 | + | + | 393.0 | + | + |
| $Rh/Al_2O_3$ [b] | 1800 | 42.8 | 57.2 | + | + | 11.0 | + | + |
| $Rh/La_2O_3$ | 3200 | 43.2 | 12.5 | 27.1 | 17.2 | 21.5 | 13.5 (44.5)[c] | 4.3 |
| | 11000 | 29.7 | 7.9 | 36.6 | 25.8 | 25.1 | 31.0 (102.2)[c] | 11.0 |
| $Rh/La-SiO_2$ | 3200 | 71.8 | 10.8 | 8.5 | 8.9 | 83.4 | 9.9 | 5.2 |
| | 16500 | 61.2 | 10.2 | 17.4 | 11.2 | 106.0 | 30.2 | 9.1 |
| $La_2O_3$ | 3600 | - | - | 100 | - | - | -(3.0)[c] | - |

a Carbon efficiency = $(n_i A_i / \Sigma n_i A_i) \times 100$; $n_i$ - number of carbon atoms in product i; $A_i$ = (mol product i x g-at $Rh^{-1}$ x $s^{-1}$) ; b prepared by reduction of $RhCl_3/Al_2O_3$ at 723 K in $H_2$; c rate of methanol formation calculated per 1 $m^2$ of $La_2O_3$ mol $CH_3OH \times (m^2 La_2O_3 \times s)^{-1} \times 10^{11}$.

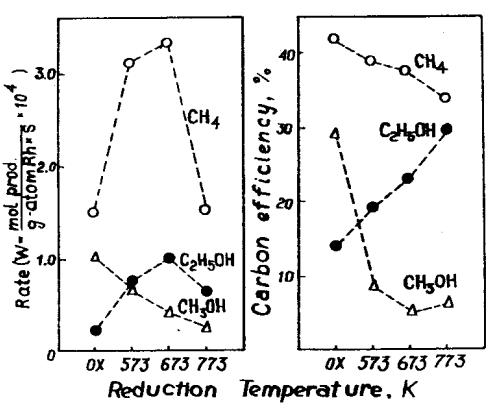


fig. 1

Effect of the temperature of $Rh/La_2O_3$ reduction on the yield of CO and $H_2$ reaction products (523 K, $CO:H_2$=1:2; 3250 $hr^{-1}$). "0x" stands for $Rh_4(CO)_{12}/La_2O_3$ sample oxidized in air at 293 K (reduction in the reaction conditions).

consumption of $CH_3I$ reached 85-98%) led to a drastic decrease of methanol yield, whereas the yield of ethanol somewhat increased (20-25%). When the addition of $CH_3I$ was stopped the yield of ethanol decreased till the value characteristic for $Rh/La_2O_3$ in the absence of $CH_3I$. The rate of methanol formation was still very low.

State of Rh in catalysts

TPR. Hydrogen consumption by oxidized rhodium catalysts was observed at the temperature above 373 K (fig. 2). For $Rh/La_2O_3$ the consumption of $H_2$ (H:Rh=25-30) was much higher than it is necessary for a 3-electron reduction of $Rh^{3+}$. In this case the formation of methane was observed; the amount of $CH_4$ (0.1 mol $CH_4$/g-atom La) was compatible with the amount of hydrogen consumed (0.25 mol $H_2$/g-atom La). $CH_4$ may originate from the hydrogenation of surface carbonate groups of $La_2O_3$ by the hydrogen activated on Rh.

XPS data. The values of binding energies of the Rh $3d_{5/2}$ level are presented in table 1. These values for $Rh/SiO_2$ and $Rh/La_2O_3$ catalysts were close to those typical for metallic rhodium (307.0±1 eV). For $Rh/La_2O_3$ the Rh $3d_{5/2}$ line was however somewhat broader. In the case

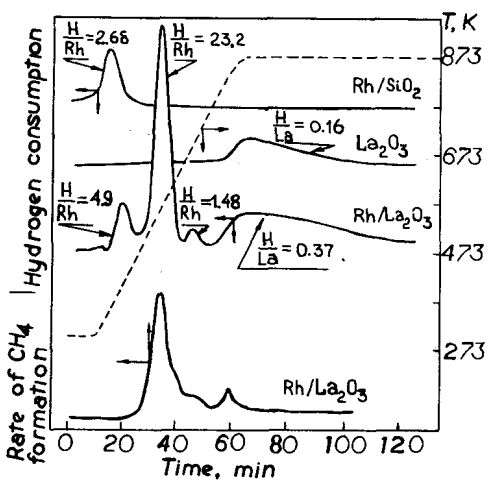


fig. 2

TPR spectra for $Rh/SiO_2$, $La_2O_3$, $Rh/La_2O_3$. $Rh_4(CO)_{12}/SiO_2$ and $Rh_4(CO)_{12}/La_2O_3$ were used for TPR experiments after their oxidation in air.

of $Rh/Al_2O_3$ a significant shift of Rh $3d_{5/2}$ line towards higher bond energies was observed.

Fourier transforms of EXAFS K-spectra of rhodium catalyst with assignment of peaks /11/ are given in fig. 3. For marked peaks the specification of types of atoms and distances was carried out by using the nonlinear least squares fitting method. In the case of $Rh/La_2O_3$ and $Rh/La\text{-}SiO_2$ (reduced at 773 K) the portion of rhodium atoms which have direct contact with oxygen atoms of the support ($r_o - \delta$ =0.18 and 0.2 nm) is greater than for $Rh/SiO_2$ and $Rh/Al_2O_3$. It corresponds to the presence of "pill-box" shape particles of rhodium on the surface of $La_2O_3$ and $La\text{-}SiO_2$. Electron microscopic pictures of $Rh/La\text{-}SiO_2$ show the presence of semitransparent particles less than 2.0 nm /11/.

An increase in the reduction temperature of $Rh/la\text{-}SiO_2$ up to 873 K didn't influence the size of rhodium particles. At the same time in the radial structure function (fig. 3) diminishing of peak of the second coordination shell of rhodium in metal particles ($Rh\text{-}Rh^2$) and shortening of the distance of the first coordination shell of rhodium ($Rh\text{-}Rh^1$) were observed. Such changes in the radial structure function corresponded to the strengthening of the interaction of rhodium with the support. In the case of $Rh/Al_2O_3$ peak (0.16 nm) corresponding to the distance Rh-O in $Rh_2O_3$ was observed.

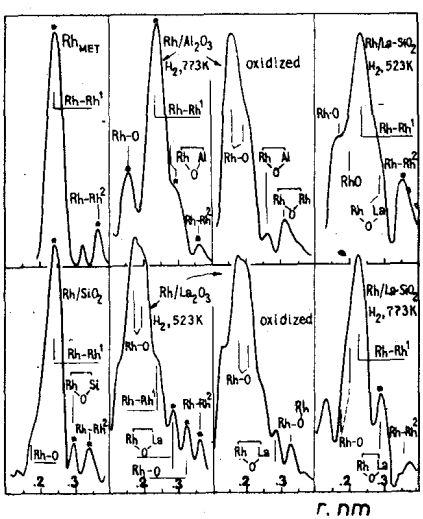


fig. 3

Fourier transforms of EXAFS K-spectra of rhodium catalysts. $Rh/Al_2O_3$(ox) and $Rh/La_2O_3$(ox) were used after the oxidation of $Rh_6(CO)_{16}/Al_2O_3$ and $Rh_4(CO)_{12}/La_2O_3$ respectively in air at 298 K. ($Rh\text{-}Rh^1$ and $Rh\text{-}Rh^2$ stand for the distances in the first and the second coordination shells of metallic rhodium particles). $r = r_o - \delta$ is the distance without taking into account the phase shift ($\delta$); $r_o$ is the true distance.

IR spectra. CO adsorption on $Rh/SiO_2$, $Rh/La_2O_3$ and $Rh/La\text{-}SiO_2$ after their treatment by CO and $H_2$ at 523 K led to the appearance of two types of bands corresponding to linear (I; 2040-2065 $cm^{-1}$) and bridged (II; 1850-1870 $cm^{-1}$) CO groups coordinated on metallic rhodium. In the case of $Rh/Al_2O_3$ twin bands (type III) 2090 and 2015 $cm^{-1}$ along with the bands of CO adsorbed on metallic rhodium were observed. Bands of type III were attributed to symmetric and antisymmetric vibrations of CO groups ($Rh(CO)_2$) coordinated by ions of Rh(I)/12,13/ or atoms of two dimensional particles of metal /6,14/. Treatment of $Rh/SiO_2$, $Rh/La_2O_3$ and $Rh/La\text{-}SiO_2$ at 298-373 K by $O_2$ resulted in the appearance of CO bands of type III. However, in the conditions of CO hydrogenation the bands of type III quickly (1-20 min) disappeared and only bands of type I and II were observed.

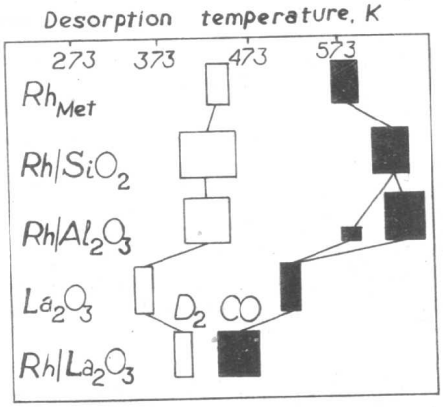


fig. 4

Temperatures of the maximum desorption rate of CO and $D_2$ from rhodium catalysts.

Data on TPD of CO and $D_2$ from Rh catalysts are summarized in fig. 4. We used a low heating rate to provide a uniform heating of catalysts. But because of a possible readsorption of gases it was difficult to calculate the accurate values of desorption heats /15/. However, comparison of relative positions of TPD peaks gives possibility to estimate the difference between values of desorption heats of gases from catalysts. The maximum of desorption rate of CO from $Rh/La_2O_3$ shifted significantly to lower temperatures in comparison with those typical for metallic rhodium, $Rh/SiO_2$ and $Rh/Al_2O_3$. This corresponds to diminishing of the desorption heat of CO by 40-65 kJ/mol /15/.

$^{13}C$ NMR was used for study of surface species formed as a result of CO and $H_2$ interaction on $La_2O_3$, $Rh/La_2O_3$ and $Rh/SiO_2$. $^{13}C$ NMR spectra obtained for $SiO_2$ and $Rh/SiO_2$ were characterized by far lower intensity than those for $La_2O_3$ and $Rh/La_2O_3$. We observed no CO groups chemisorbed on Rh particles due to low concentration of Rh. The spectrum of CO adsorbed on $SiO_2$ exhibits a single line with $\delta$ =184 ppm and