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**SHORT COMMUNICATIONS**

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UDC 544.478.42

DOI: 10.15372/CSD820180618

## Effect of Rhodium Carbonyls on the Selectivity of Bifunctional Catalysts of Halogen-Free Carbonylation of Dimethyl Ether into Methyl Acetate

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(Received October 09, 2018)

### Abstract

A new gas-phase process of halogen-free carbonylation of dimethyl ether (DME) into methyl acetate is a promising environmental preparation method of methyl acetate. Bifunctional catalysts with a high concentration of strong Bronsted acid sites, *i.e.* rhodium-promoted acid cesium salts of phosphotungstic heteropoly acid with the formula  $\text{Rh}/\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  ( $1.5 \leq x \leq 2$ ), show the highest activity and selectivity in the carbonylation reaction of DME. Their use in a reducing medium, where there are significant transformations of the catalyst surface area until changing the phase composition, is a distinctive feature of these catalysts.

In order to control the activity and selectivity of catalysts in the DME carbonylation reaction, the research on the formation of the active surface of the catalyst was carried out under reaction conditions. The formation of different rhodium carbonyls, such as  $\text{Ph}(\text{CO})_2^+$  and  $\text{Rh}_6(\text{CO})_{16}$ , was detected by FT IR spectroscopy of adsorbed CO on the surface of the *in situ* reduced  $\text{Rh}/\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$  catalyst after filling with CO. The formation of metal particles was identified in case of changing activation conditions. The dependence was found between reduction conditions, the composition of the *in situ* catalyst surface area with selectivity for methyl acetate. The presence of rhodium metal particles causes C–O bond cleavage in the DME molecule and significantly reduces selectivity for methyl acetate, from 95 to 50 %. Catalysts, on the surface of which there are only rhodium carbonyls under reaction conditions upon a complete lack of trace rhodium metal, showed the highest activity and selectivity for methyl acetate. The acquired results may form the basis for developing a highly active and stable catalyst for an environmentally safe process of halogen-free DME carbonylation.

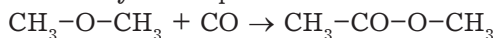
**Key words:** carbonylation, dimethyl ether, acid cesium salt of phosphotungstic heteropoly acid, rhodium carbonyls, *in situ* IR spectroscopy

### INTRODUCTION

The major commercial method of acetic acid production is a liquid-phase process of methanol carbonylation over homogeneous rhodium or iridium catalyst using methyl iodide as a promoter [1]. This process has a number of disadvan-

tages noted earlier [2–4]. A new gas-phase process of halogen-free carbonylation of dimethyl ether (DME) into methyl acetate is a promising environmentally benign preparation method of methyl acetate, owing to elimination of methyl iodide, the replacement of methanol with less expensive raw materials, DME [5], and the removal

of the stage of separating reaction products from the catalyst and promoter:



Heterogeneous catalysts of two types are active in the reaction of halogen-free carbonylation of DME or methanol. The catalytic agents were based on zeolites [6] and heteropolyacids [7]. We have previously demonstrated that Rh-promoted bifunctional catalysts based on phosphorus-tungsten heteropoly acid cesium salts are most efficient among rhodium-containing bifunctional superacid catalysts in series:  $\text{Rh/Cs}_2\text{HPW}_{12}\text{O}_{40} \gg \text{Rh/WO}_x/\text{ZrO}_2 > \text{Rh/SO}_4/\text{ZrO}_2$  [3]. A distinctive feature of these catalysts is their use in a reducing medium, whereat there are substantial transformations of the catalyst surface area, down to changing the phase composition.

In order to control catalytic activity and selectivity in the DME carbonylation reaction, the research on forming catalyst active surface under reaction conditions was carried out. This research lists measurement results for catalytic properties of  $\text{Rh/Cs}_2\text{HPW}_{12}\text{O}_{40}$  upon changed activation conditions. Various states of rhodium on the surface of phosphorus-tungsten heteropoly acid cesium salt were characterised by *in situ* IR spectroscopy of adsorbed CO under reaction conditions.

## EXPERIMENTAL

The deposition method was used to prepare 1 %  $\text{Rh/Cs}_2\text{HPW}_{12}\text{O}_{40}$  catalyst. A solution of cesium nitrate (0.1 M) was added dropwise with constant stirring to a mixture of 0.1 M solutions of phosphorus-tungsten heteropolyacid and rhodium trichloride taken in the required ratio. The resulting suspension was stirred for 24 h followed by precipitate evaporation and calcination at 300 °C for 3 h.

The catalyst was tested in a flow-through setup with the chromatographic analysis of the products at 200 °C, a pressure of 10 atm, and the composition of the initial gas mixture DME/CO = 1 : 10. Prior to the reaction, the catalyst was reduced by two methods: 1) in a mixture of hydro-

gen and helium at 220 °C for 2 h, 2) in high-purity CO at 200 °C for 2 h. The rate of temperature elevation was 2 °C/min in both cases.

In order to determine rhodium carbonyl and metal clusters on the surface of 1 %  $\text{Rh/Cs}_2\text{HPW}_{12}\text{O}_{40}$  catalyst, IR spectroscopy of adsorbed CO was used when *in situ* exploring CO adsorption in a thermostated IR cell [8]. The samples were pressed into tablets ( $c = 30 \text{ mg/cm}^2$ ) containing 50 % of  $\text{BaF}_2$ . Two variants of catalyst reduction were used for *in situ* IR research. They were as follows: 1) with hydrogen, 2) using pure CO. The temperature of sample reduction was 200 °C in both cases, time value of 60 min. The rate of temperature elevation was 2 °C/min. All spectra were recorded in the 400–6000  $\text{cm}^{-1}$  range at 200 °C using a Shimadzu FTIR-8300 spectrometer, a resolution of 4  $\text{cm}^{-1}$ .

## RESULTS AND DISCUSSION

Table 1 lists test results on 1 %  $\text{Rh/Cs}_2\text{HPW}_{12}\text{O}_{40}$  catalyst; they were acquired under various activation conditions. As shown, DME conversion almost does not vary when replacing hydrogen for CO; however, the selectivity for methyl acetate is almost twice reduced, from 95 % to 50 %. In addition to methyl acetate, side products, mainly methane and ethane, are formed (about 10 vol. %). In order to understand the cause for such a dramatic drop in the formation rate of methyl acetate, the research on the catalyst surface area was carried out by *in situ* IR spectroscopy of adsorbed CO. The sample was pre-treated in the thermostated IR cell; catalyst activation conditions were completely repeated in the reactor.

Figure 1 reports IR spectra of CO adsorbed on the surface of 1 %  $\text{Rh/Cs}_2\text{HPW}_{12}\text{O}_{40}$  catalyst reduced with hydrogen at 200 °C for 60 min. After filling with CO (50 torr), absorption bands appear at 2090, 2114, 2127, and 2134  $\text{cm}^{-1}$ . The bands at 2090  $\text{cm}^{-1}$  and 2114  $\text{cm}^{-1}$  correspond to gem-dicarbonyl complexes,  $\text{Rh}(\text{CO})_2^+$  [9].

When the CO pressure is increased till 100 torr, there are the same bands; however, their intensity is increased. When the pressure is 250 torr,

TABLE 1

Activity and selectivity of 1 %  $\text{Rh/Cs}_2\text{HPW}_{12}\text{O}_{40}$  catalyst in the reaction of halogen-free carbonylation of DME into methyl acetate depending on activation conditions. A reaction temperature of 200 °C, pressure of 10 atm, composition of the initial mixture, DME/CO = 1 : 10

Activation conditions	DME conversion, %	Methyl acetate formation rate		Selectivity, %
		$10^{-8} \text{ mol}/(\text{g} \cdot \text{s})$	$10^{-8} \text{ mol}/(\text{g} \cdot \text{s})$	
2 % of $\text{H}_2$ in helium	31.2	43.0	0.42	95
High-purity CO	32.0	22.6	0.22	50

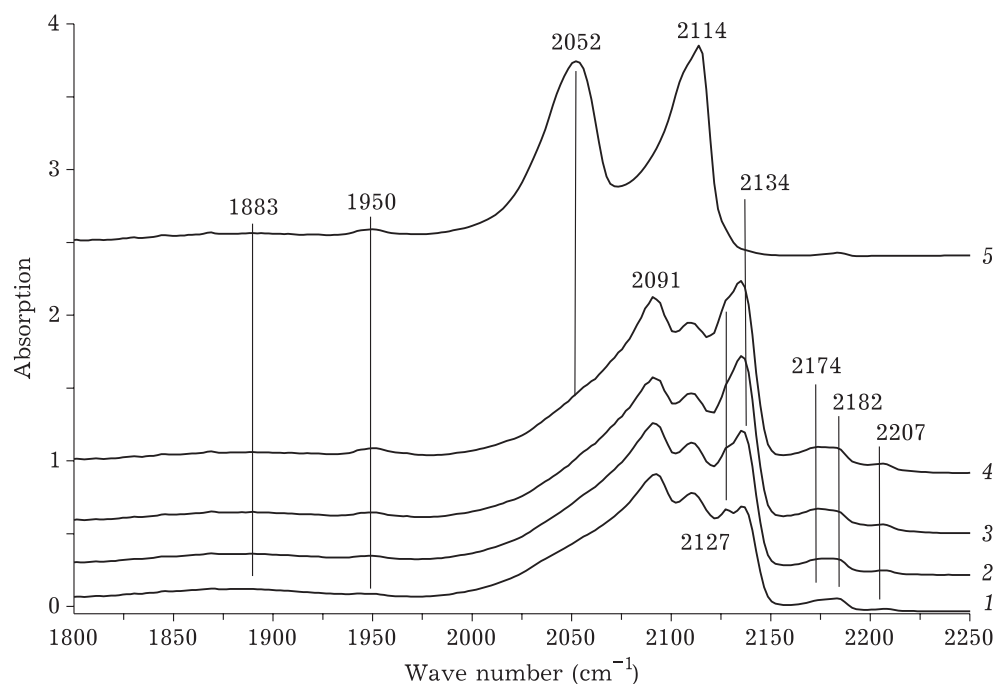


Fig. 1. IR spectra of CO adsorbed over 1 % Rh/Cs<sub>2</sub>HPW<sub>12</sub>O<sub>40</sub> catalyst reduced in a hydrogen atmosphere at 200 °C within 60 min. Amounts of CO fed, torr: 50 (1), 100 (2), 250 (3), and 250 (4) after 60 min and CO desorption (5).

there is a further increase in the intensity of all bands together with the transformation of dicarbonyls to Ph<sub>6</sub>(CO)<sub>16</sub>. There are absorption bands at 2090, 2114, and 2134 cm<sup>-1</sup> for these species [10]. The band at 2052 cm<sup>-1</sup> appears and that at 2114 cm<sup>-1</sup> is significantly increased after CO desorption. The band at 2114 cm<sup>-1</sup> corresponds to

Rh<sub>6</sub>(CO)<sub>16</sub>; the band at 2052 cm<sup>-1</sup> may be referred to the Rh<sup>0</sup>-cluster [9, 10]. This data testifies that rhodium carbonyl complexes exist only in the CO atmosphere. When CO is removed, carbonyls are decomposed and rhodium metal particles are present. Moreover, bands typical for rhodium metal clusters are completely missing at the surface of

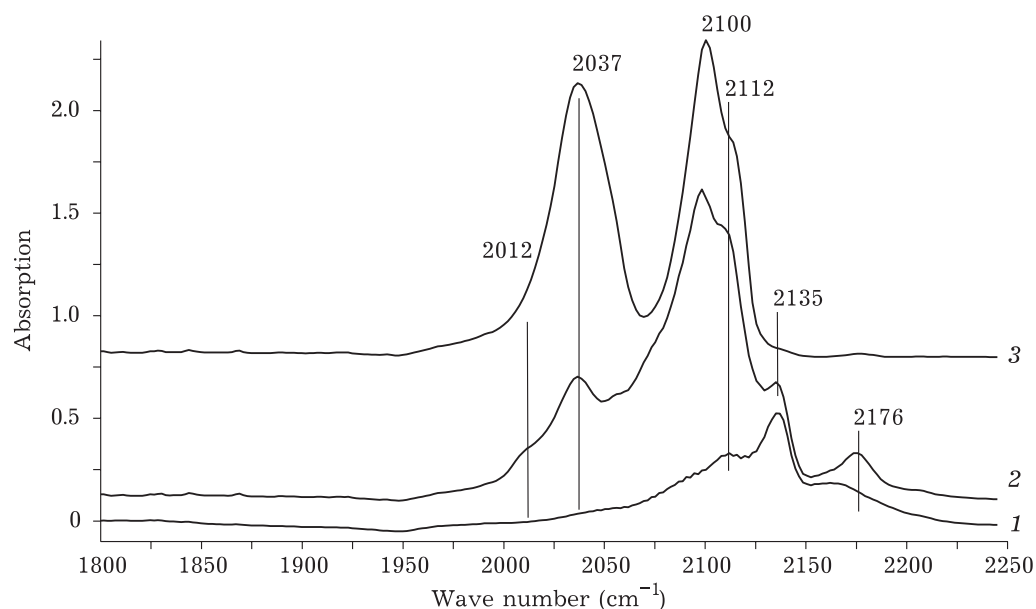


Fig. 2. IR spectra of CO adsorbed over 1 % Rh/Cs<sub>2</sub>HPW<sub>12</sub>O<sub>40</sub> catalyst: 1 – vacuumed at 200 °C within 60 min, 2 – after reduction in CO at 250 torr and 200 °C within 60 min, 3 – after CO desorption.

the sample reduced in, the atmosphere of hydrogen, that of CO (50–250 torr).

Figure 2 represents IR spectra of CO adsorbed on the surface of 1 % Rh/Cs<sub>2</sub>HPW<sub>12</sub>O<sub>40</sub> vacuumed catalyst (curve 1) reduced in CO at 200 °C for 60 min (curve 2) and after CO desorption (curve 3). As demonstrated by the analysis of the IR spectrum of CO (10 torr) adsorbed over the vacuumed sample, there are bands at 2112 and 2135 cm<sup>-1</sup> corresponding to Ph<sub>6</sub>(CO)<sub>16</sub> [10]. Absorption bands appear at 2012, 2037, 2100 cm<sup>-1</sup> after CO adsorption (250 torr). The band at 2100 cm<sup>-1</sup> corresponds to Rh(CO)<sub>2</sub><sup>+</sup>, the band at 2037 cm<sup>-1</sup> refers to the Rh<sup>0</sup>-clusters [10]. The intensity of bands at 2037 and 2100 cm<sup>-1</sup> is increased after CO desorption, in other words, the number of rhodium metal particles is enhanced.

As demonstrated by comparing catalytic test results (see Table 1) and *in situ* IR spectroscopy data, the presence of rhodium metal particles results in a significant decrease of the selectivity for the target product, *i.e.* methyl acetate. Rhodium metal particles cause the breakage of a molecule of DME and side products are formed.

The high activity and selectivity of bifunctional catalysts, on the surface of which rhodium carbonyls are formed under reaction conditions, are ensured due to the involvement of the bifunctional mechanism of carbonylation of dimethyl ether over sites of two types, such as an acid site and rhodium carbonyl, in addition to the classic mechanism of carbonylation over acid sites that is known as the Koch mechanism [11]. We have demonstrated this for catalysts based on Rh-promoted phosphorus-tungsten heteropolyacid acid cesium salts [12].

Thus, the research has shown for the first time the formation of rhodium carbonyls over the surface of heteropoly compounds, phosphorus-tungsten heteropolyacid acid cesium salts in this case. Furthermore, their determining role in the formation of a highly active and selective catalyst for DME carbonylation into methyl acetate has been determined.

## CONCLUSION

Catalytic properties of Rh/Cs<sub>2</sub>HPW<sub>12</sub>O<sub>40</sub> were explored under variation of the activation conditions. It was found by IR spectroscopy of adsorbed CO that various rhodium carbonyls, such as Rh(CO)<sub>2</sub><sup>+</sup> and Rh<sub>6</sub>(CO)<sub>16</sub><sup>+</sup>, were formed on the surface of *in situ* hydrogen-reduced Rh/Cs<sub>2</sub>HPW<sub>12</sub>O<sub>40</sub> catalyst. Rhodium metal particles are formed in case of changing activation conditions. The rela-

tionship was determined between reduction conditions, the composition of the catalyst surface *in situ*, and the selectivity for methyl acetate. The presence of rhodium metal particles causes the CO bond breakage in a molecule of DME and significantly decreases the selectivity for methyl acetate, from 95 to 50 %. Catalysts, on the surface of which there are only rhodium carbonyls under reaction conditions with a complete absence of rhodium metal traces, have demonstrated the highest activity and selectivity for methyl acetate. The findings may form the basis for developing a stable and highly efficient catalyst for an environmentally benign gas phase process of halogen-free carbonylation of dimethyl ether into methyl acetate.

## Acknowledgements

The research was carried out within the state assignment of Federal State Budget Institution of Science, Boreskov Institute of Catalysis (BIC), Siberian Branch, Russian Academy of Sciences (project No 0303-2017-0004). The authors thank A. A. Budneva, an employee of the BIC, Siberian Branch, Russian Academy of Sciences, for her assistance in IR investigations.

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