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Silver or Copper Promotion of Catalysts Based on Acidic Cesium Salt of Phosphorus-Tungsten Heteropoly Acid for Dimethyl Ether Carbonylation

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Abstract

A new gas-phase process of halogen-free dimethyl ether (DME) carbonylation to methyl acetate is a promising eco-pure preparation method of methyl acetate due to excluding methyl iodide, replacing methanol for cheaper raw materials that are DME and the removal of the separation stage of the reaction products of the catalyst and methyl iodide. The work presents studying an opportunity of using promoted by silver or copper as catalysts for this reaction. Catalysts with composition of $1 \% \text{ Ag/Cs}_{15}\text{H}_{15}\text{PW}_{12}\text{O}_{40}$, 1 % Cu/ $Cs_{1.5}H_{1.5}PW_{12}O_{40}$ and $Cs_{1.5}H_{1.5}PW_{12}O_{40}$ were studied by BET, X-ray phase analysis (XPA), scanning electron microscopy (SEM) and IR spectroscopy of adsorbed pyridine. It was demonstrated that the specific surface of samples was about $60 \text{ m}^2/\text{g}$, the concentration of strong Brønsted acid sites (BAS) was found at a level of 130 µmol/g, and the phase composition of the promoted samples fully corresponded to the initial $Cs_{1.5}H_{1.5}PW_{12}O_{40}$ sample and represented a mixture of two phases that are heteropolyacids and acidic cesium salt. High concentrations of BAS demonstrate superacid character of the resulting catalysts capable of activating a C-O bond in the DME molecule. Trials of the samples under industrial catalysis conditions (pressure of 10 atm, temperature of 200 °C, the composition of the initial mixture of DME/CO = 1:10) demonstrated that 1 $\%~Ag/Cs_{1.5}H_{1.5}PW_{12}O_{40}\ catalyst exceeded the activity of the initial acid$ $Cs_{1.5}H_{1.5}PW_{12}O_{40}$ catalyst in two times, the selectivity by the target product methyl acetate is 60 %. The use of 1 % $Cu/Cs_{1.5}H_{1.5}PW_{12}O_{40}$ does not lead to a change in the activity of $Cs_{1.5}H_{1.5}PW_{12}O_{40}$, the selectivity reduces to 40 %. The data obtained can serve as a basis for elaboration of a silver-containing highly effective catalyst for eco-pure halogen-free DME carbonylation to methyl acetate.

Kew words: carbonylation, dimethyl ether, methyl acetate, acidic cesium salt, heteropoly acid, copper, silver

INTRODUCTION

Currently, the liquid phase methanol carbonylation process over a homogeneous Rh or Ir catalyst with methyl iodide as a promoter is the major industrial method for the preparation of acetic acid [1]. The methanol carbonylation process has a number of disadvantages: 1) methyl iodide refers to cancerogenic substances causing oncological diseases: 2) carrying out the process in the liquid phase causes difficulties of separating the catalyst from reaction products; 3) the use of halides requires alloys to organize the process, additionally, they are poisons for the majority of catalysts, therefore, careful separation of iodides from the reaction products is required in case of the further use of carbonylation products in organic syntheses.

Using dimethyl ether (DME) instead of methanol as raw materials for carbonylation is economically reasonable, since the process of the direct preparation of DME from synthesis gas is much cheaper than a process for preparation of methanol [2]. New process elaboration of halogen-free DME carbonylation into methyl acetate will allow significantly improving eco- and economic indicators of the carbonylation process due to excluding methyl iodide, the stage of separation of the reaction products from the catalyst and methyl iodide, carrying out the reaction in the gas phase and replacing methanol with DME:

 $\mathrm{CH}_3\mathrm{-O-CH}_3 + \mathrm{CO} \rightarrow \mathrm{CH}_3\mathrm{-CO-O-CH}_3$

To perform this reaction superacid catalysts based on heteropoly compounds (HPC) and zeolites were proposed [3-5]. Detailed research of efficient catalysts for DME free-halogen carbonylation based on HPC demonstrated that two kinds of centers were formed herewith on the catalyst surface: acid sites of various nature (Lewis and Brønsted) and metal centers with various reactivities, which allows controlling the activity and selectivity of catalysts. A distinctive feature of these catalysts is their application in a reductive medium, where substantial transformations of the catalyst surface occur, right up to a change in the phase composition. Bifunctional catalysts with high concentrations of strong Brønsted acid centers (BAC) of $Rh/Cs_{x}H_{3-x}PW_{12}O_{40}$ (1.5 $\leq x \leq 2$) demonstrated the maximum activity and selectivity in the DME carbonylation reaction [6]. It is known that the carbonylation reaction on acid sites proceeds by the Koch mechanism [7]. A metal center, rhodium in this case, that passes into rhodium carbonyl and by operating jointly with BAC by the bifunctional mechanism increases the yield of target methyl acetate in 4-5 times [5, 8].

The purpose of this study was the development of a new metal center on the surface capable of forming carbonyls under reaction conditions and leading to an increase in the activity of $Cs_xH_{3-x}PW_{12}O_{40}$ (1.5 $\leq x \leq 2$) by not decreasing the process selectivity.

TABLE 1

Chemical composition, specific surface and concentration of Brønsted acid sites of acidic cesium salt of phosphorus-tungsten heteropoly acid with $Cs_{1.5}H_{1.5}PW_{12}O_{40}$ composition promoted by silver, copper, and without a promoter

Catalysts	Cs/P*	$S_{\rm sp},~{\rm m^2/g}$	Brønsted acid sites, µmol/g
$1~\%~Ag/Cs_{1.5}H_{1.5}PW_{12}O_{40}$	1.4	57	128
$1 \ \% \ Cu/Cs_{1.5} H_{1.5} PW_{12} O_{40}$	1.5	60	130
$Cs_{1.5}H_{1.5}PW_{12}O_{40}$	1.4	57	130

A search for a metal component of a catalyst for halogen-free carbonylation of alcohols and ethers is a complex task, since the known catalysts based on nickel carbonyl or cobalt carbonyls operate at high CO pressure exceeding by an order of magnitude the pressure of carbonylation processes using rhodium catalysts or iridium catalysts. Carbonyl clusters of many other metals have been synthesized and described in the literature [9, 10], but there are almost no data of their possibility to participate in the carbonylation reaction. Several works by Y. Souma and co-workers present results on the use of homogeneous catalysts based on univalent platinum, copper and silver carbonyls in carbonylation reactions of olefins or alcohols in superacidic liquids [11-13]. Application of univalent silver to the surface of solid superacids, such as Nafion, ZSM-5, SO_4/ZrO_2 followed by the formation of the corresponding carbonyl led to an increase in the activity of catalysts in the carbonylation of alcohols in comparison with the initial solid superacid. The reaction was carried out in an organic solvent [14].

This work presents study results of catalysts representing acidic cesium salt of phosphorustungsten heteropoly acid promoted by copper or silver in a gas phase process for halogenfree DME carbonylation to methyl acetate.

EXPERIMENTAL

The precipitation method was used to prepare 1% Ag/Cs_{1.5}H_{1.5}PW₁₂O₄₀ and 1% Cu/Cs_{1.5}H_{1.5}PW₁₂O₄₀ catalysts, a solution of cesium nitrate (0.1 M) was added dropwise with constant stirring to a mixture of solutions of phosphorus-tungsten heteropoly acid (0.1 M) and silver nitrate or copper nitrate (0.1 M) taken in the re-

* Atomic cesium content to phosphorus in samples.



Fig. 1. Scheme of the formation of primary and secondary particles of catalysts based on $Cs_xH_3 - _xPW_{12}O_{40}$ [15].

quired ratio. The resulting suspension was stirred for 24 h, and then the residue was evaporated and calcined at a temperature of 300 °C for 3 h.

The resulting catalysts were characterized by chemical analysis methods, nitrogen adsorption, X-ray phase analysis, IR spectroscopy of adsorbed pyridine. Research techniques are given in [5, 6].

The catalysts were tested in a flow setup with chromatographic analysis of the products at a temperature of 473 K, pressure of 10 atm, the composition of the initial gas mixture of DME/CO = 1:10. Before the reaction, the catalysts were reduced in a mixture of hydrogen and helium at a temperature of 200 °C for 2 h.

RESULTS AND DISCUSSION

Table 1 gives the results of physicochemical studies of the resulting samples; similar data for the initial sample not containing a metal promoter are presented for comparison. It can be seen that regardless of kinds of promoters, the chemical composition, specific surface and the content of BAC in the samples are almost unchanged. One of the most crucial parameters of acid cesium salts of heteropoly acids with the Keggin structure for the use as heterogeneous catalysts is high specific surface of samples, since the initial acid has a surface not exceeding 5 m²/g, does not show high activity in heterogeneous catalysis.

The specific surface of cesium-containing of phosphotungstic acid substantially increases with the increase of the amount of cesium (Fig. 1). The formation of micro- and mesoporous particles showing high specific surface of acid cesium salts happens in the process of the preparation of catalysts. The authors of work [15] suggested that $PW_{12}O_{40}^{3-}$ anions (with the size of 11 Å) form with Cs⁺ cations (size of 2.86 Å) the primary structure, *i. e.* cesium cations are built in between heteropoly anions, forming closely packed primary particles are agglomerated



Fig. 2. Micrograph of a sample with $Cs_{1.5}H_{1.5}PW_{12}O_{40}$ composition.



Fig. 3. Diffractograms of catalysts: $1 - Cs_{1.5}H_{1.5}PW_{12}O_{40}$; $2 - 1 \% Cu/Cs_{1.5}H_{1.5}PW_{12}O_{40}$; $3 - 1 \% Ag/Cs_{1.5}H_{1.5}PW_{12}O_{40}$.

after drying and form the secondary particles with a size of about 500 Å (see Fig. 1).

In fact, it was demonstrated in a microimage of a sample with $Cs_{1.5}HPW_{12}O_{40}$ (Fig. 2) composition that catalysts had a spongy texture with a particle size of 500–1000 nm.

It is demonstrated by X-ray phase analysis results presented in Fig. 3 that for an acid cesium salt with $Cs_{1.5}HPW_{12}O_{40}$ composition and the same salt promoted by silver or copper, a typical face-centered cubic lattice was observed. Two crystalline phases that are pure acid $H_3PW_{12}O_{40}$ and cesium salt were identified in the samples.

Thus, catalysts with almost identical characteristics were obtained resulting from the synthesis: specific surface, the phase composition, BAC concentration, which will allow comparing their catalytic properties when changing one parameter that is promoter's introduction.

The catalysts were tested under industrial conditions; i. e. conditions typical for the process of preparing acetic acid from methanol over a homogeneous rhodium catalyst were selected: pressure, temperature and the ratio of carbon dioxide to the basic reagent, in our case, to dimethyl ether. Table 2 compares the results obtained over catalysts promoted by copper or silver and of the initial sample. It was demonstrated that $1\ \%\ Ag/Cs_{1.5}H_{1.5}PW_{12}O_{40}$ catalyst exceeded the activity of the initial acid $Cs_{1.5}H_{1.5}PW_{12}O_{40}$ catalyst in two times, selectivity for target methyl acetate is 60 %. The use of $1 \ \% \ Cu/Cs_{1.5}H_{1.5}PW_{12}O_{40}$ under equivalent conditions does not lead to a change in the activity of the initial acid catalyst, selectivity reduces to 40 %. Side products for all the studied systems consisted of two major components: methane and a small amount of ethane (to 10%).

Comparison of the results obtained with the data given in work [14] demonstrated that the

reaction rate in case of 1 % Ag/Cs_{1.5}H_{1.5}PW₁₂O₄₀ catalyst increased by two times (see Table 2) in comparison with that for the initial acid salt, while the introduction of silver into acid catalysts Nafion, ZSM-5, SO₄/ZrO₂ increases the reaction rate by 5–25 % depending on the initial reagent and the composition of the catalyst [14].

An increase in the formation rate of methyl acetate due to the introduction of silver into catalysts apparently occurs due to the interconnection to the classic carbonylation mechanism on acid sites known as the Koch mechanism [7], bifunctional carbonylation mechanism of dimethyl ether over two types of centers: acid, in this case, BAC, and silver carbonyl, as was demonstrated earlier by us for catalysts based on acidic cesium salts of phosphorus-tungsten heteropoly acid promoted by rhodium [8].

Thus, the work demonstrated for the first time that the silver promotion of an acid catalyst led to an increase in the carbonylation rate by 100 %. With a view to control the activity and selectivity of promising silver-containing catalysts in halogen-free dimethyl ether (DME) carbonylation to methyl acetate systematic studies of the formation active catalyst centers under reaction conditions and determining the optimum content of silver carbonyls on the surface are required.

CONCLUSION

The paper studied halogen-free dimethyl ether carbonylation to methyl acetate in a gas phase using 1 % Ag/Cs_{1.5}H_{1.5}PW₁₂O₄₀ and 1 % Cu/Cs_{1.5}H_{1.5}PW₁₂O₄₀ catalysts. It was demonstrated that 1 % Ag/Cs_{1.5}H_{1.5}PW₁₂O₄₀ catalyst exceeded the activity of the initial acid Cs_{1.5}H_{1.5}PW₁₂O₄₀ catalyst in two times, the se-

TABLE 2

Activity and selectivity of bifunctional catalysts in halogen-free dimethyl ether (DME) carbonylation to methyl acetate (temperature of 200 °C, pressure of 10 atm, the composition of the initial mixture of DME/CO = 1:10)

Catalysts	DME conversion	Formation rates of methyl acetate,		Selectivity to
	degree, %	10^{-8} mol/(g · s)	10^{-8} mol/(m ² · s)	methyl acetate, %
$\overline{1 \% \text{ Ag/Cs}_{1.5}\text{H}_{1.5}\text{PW}_{12}\text{O}_{40}}$	21.5	20	0.346	60
$1 \% Cu/Cs_{1.5}H_{1.5}PW_{12}O_{40}$	15.2	10	0.164	40
$Cs_{1.5}H_{1.5}PW_{12}O_{40}$	7.6	10	0.173	92

lectivity towards methyl acetate is 60 %. The use of 1 % Cu/Cs_{1.5}H_{1.5}PW₁₂O₄₀ under equivalent conditions does not lead to a change in the activity of the initial acid catalyst, selectivity reduces to 40 %.

The findings can serve as a basis for the development of silver containing a highly efficient superacidic catalyst for an environmentally friendly gas-phase process of halogen-free DME carbonylation into methyl acetate.

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