SUPPORTED HETEROPOLYACIDS AS HETEROGENEOUS CATALYSTS FOR PROPENE METATHESIS*

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Catalysts containing tungsten or molybdenum in the form of Keggin type heteropolyacids, like $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$, supported on silica gel were prepared. The acid and surface properties of heteropolyacids and their supported forms are discussed. Keggin type heteropolyacids supported on silica gel have been found active for propene metathesis, the activity was compared with those of the classical catalyst WO_3/SiO_2 . The highest activity and selectivity for studied reaction showed catalyst prepared on the base of $H_3PW_{12}O_{40}$.

In the last several years there has been an increasing interest in the catalytic properties of heteropolyacids (HPA's) and their salts¹. This fact partly arises from the structural and chemical properties as well as from their combined acid and redox nature². HPA's are complexes with high molecular weight anions having from 2 to 18 hexavalent molybdenum or tungsten, or pentavalent vanadium or niob atoms around one or more central atoms³. The central atoms are commonly P, Ni, As, Te and Mn, although approximately 36 different elements have been used for building of the HPA structure. For example, in $[PW_{12}O_{40}]^{3-}$ anions each tungsten atom is at the center of an octahedron and each oxygen atom is situated at each vertex. The phosphorus atom is located in the center of a PO₄ tetrahedron surrounded by WO₆ octahedra which share corners and edges to produce primary Keggin structure. The Keggin structure can form a relatively stable secondary structure with water molecules filling the interconnected space between the Keggin units.

HPA's have been studied for use as the homogeneous catalysts in oxidation⁴ and hydration of alkenes⁵, polymerization of benzyl alcohol⁶ and alcoholysis of epoxide⁷.

The specific properties of HPA's give an opportunity to use them as heterogeneous catalysts when loaded on a suitable support. A number of reaction in vapor phase have

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been reported: methanol conversion^{8,9}, conversion of dimethyl ether into hydrocarbons¹⁰, alcohol dehydration¹¹, decomposition of carboxylic acids¹², methanol addition to isobutene¹³. A brief review on HPA as catalyst for heterogeneous as well as homogeneous reactions has been published¹.

One of possible reactions, utilizing the acid properties of supported HPA heterogeneous catalysts, is alkene metathesis. This reaction opens new synthesis routes to typical petrochemicals (ethylene, propene, butenes), special alkenes (neohexene, higher molecular linear alkenes, α , ω -dienes) and unsaturated polymers (polynorbornene, cyclooctene, dicyclopentadiene) on an industrial scale.

Generally, the process is going on in the presence of heterogeneous, homogeneous or combined type of catalyst. To the heterogeneous catalysts which are most frequently studied, belong mainly transition metal oxides, carbonyls or sulfides of Mo, W and Re deposited on high surface area supports (γ -Al₂O₃, SiO₂).

Homogeneous catalysts are composed of a transition metal coordination compound (typical ones are compounds of W, Mo and Re) in combination with a cocatalyst – an organometallic compound^{14–16}. The activity of a given catalytic system is determined by both the nature and concentration of the active species. There is an evidence that the active species are metal carbenes formed from the transition metal compounds¹⁷, and in the case of catalyst of type W/SiO₂ mainly Lewis acid centers play role¹⁸.

In the present work, supported heteropolyacids were prepared, characterized and tested for the metathesis of propene into ethylene and 2-butenes in vapor phase and compared with the classical WO_3/SiO_2 metathesis catalyst.

EXPERIMENTAL

Catalyst Preparation

Silica gel (Spolana, 383 m²/g) with a particle size of 0.40 - 0.63 mm was used as a support. The supported HPA's were prepared by the incipient wetting of the silica with aqueous solution of H₃PW₁₂O₄₀. *x* H₂O, H₃PMo₁₂O₄₀. *x* H₂O (both Lachema) and H₄SiW₁₂O₄₀. *x* H₂O (Merck). Impregnation was carried out at an ambient temperature and the samples were dried at 373 K and then calcined at 773 K for 4 h. By this method, samples containing from 1 to 11 wt.% of tungsten or molybdenum were obtained.

For comparison, a classical type of catalyst for propene metathesis was prepared by the impregnation of the same carrier with $(NH_4)_2WO_4$.

The samples are symbolized in the text by wt.% of the metal (W or Mo) followed by W for supported classical oxide catalysts and by P–W, Si–W, or P–Mo for catalysts prepared by impregnation with phosphotungsten acid, silicotungsten acid or phosphomolybdenum acid, respectively.

Characterization of Catalysts

Specific surface area, pore volume and pore size distribution were determined by physical adsorption of nitrogen at 77 K (Sorptomatic 1800, Carlo Erba). The specific surface was calculated by the BET

method, pore volume was evaluated from the adsorption isotherm. Before measuring, all samples were calcined at 770 K for 3 h and evacuated at 570 K and 2 Pa for 5 h.

The acid properties of the catalysts and their supported forms were determined by the indicator method (titration with butylamine in benzene) with the following Hammet indicators and arylmethanols: dimethylaminoazobenzene (pK_a 3.3), tolylazo-*o*-toluidine (pK_a 2.0), dicinnamalacetone (pK_a -3.0), chalcon (pK_a -5.7), anthraquinone (pK_a -8.3), triphenylmethanol (pK_a -6.63), diphenylmethanol (pK_a -13.3), trinitrotriphenylmethanol (pK_a -16.27). Samples were activated before measuring at 773 K.

X-Ray diffraction characteristics and DTA–DTG patterns of prepared catalysts were reported in our previous paper¹⁹.

Metathesis Experiments

Metathesis reaction was carried out in a quartz reactor with a fixed bed of the catalyst. Before contact with propene, catalysts (0.3 - 1.4 g) were activated in a stream of air (60 ml/min) at 823 K for 1.5 h and then treated¹⁹ for 15 min at 823 K with CO (40 ml/min). The catalysts were cooled to the reaction temperature in a stream of inert gas (40 ml/min).

Feed and reaction products were analyzed by GC (Hewlett Packard 5890) with capillary columns PONA and HP1. FID detector was used.

The experiments were carried out at reaction temperatures of 603 - 873 K, pressure 0.1 MPa, and space velocities 5 and 10 mmol/s kg. In all experiments, the products were analyzed after 2 - 4 h of stabilization time. Conversion as well as selectivity (production of primary reaction products of propene metathesis – ethene and 2-butenes) were calculated on the base of total reaction products composition in wt.%.

RESULTS AND DISCUSSION

Supported HPA's, as well as pure carrier (SiO_2) are characterized by specific surface area, pore volume and pore size distribution from nitrogen adsorption.

By the loading with HPA or WO_3 from 0 to 11 wt.% of metal, the surface area and pore volume gradually decreased, e.g. for the P–W/SiO₂ from 383 and 0.58 to 289 m²/g and 0.46 cm³/g, respectively. The specific surface area partially depends also on the nature of the HPA, as can be seen from examples for 5 wt.% of metal containing catalysts in Table I.

Sample	$S_{\rm BET}, m^2/g$	$V_{\rm a},{\rm cm}^3/{ m g}$
SiO ₂	383	0.581
W/SiO ₂	332	0.553
P-W/SiO ₂	326	0.504
Si-W/SiO ₂	347	0.527
P-Mo/SiO ₂	342	0.522

TABLE I

Specific surface area (S_{BET}) and pore volume (V_a) of carrier and supported HPA's (content of active metal 5 wt.% W or Mo)

The typical examples of adsorption isotherms for pure carrier SiO_2 and for all catalysts containing 5 wt.% of metal loading on SiO_2 are shown in Fig. 1. The shapes of isotherms are rather similar, differing mainly in the total volume adsorbed (see Table I). It proves that the impregnation of the carrier with quite great molecules of HPA's in comparison with classical $(NH_4)_2WO_4$ impregnation does not change substantially the structure of the pore size distribution of SiO₂ (main pore volume for pore radius of 2 – 4 nm).

The results of the acid strength determination of free HPA's and their supported counterparts are summarized in Tables II and III.

It is seen from Table II that $H_3PW_{12}O_{40}$ was shown to be strongly acidic, with a maximum pK_a at -16.3. $H_4SiW_{12}O_{40}$ was found less acidic, with a maximum pK_a at -8.3. $H_3PMo_{12}O_{40}$ is decomposed under the condition of thermal pretreatment preceding butylamine titration (it was proved by DTA data¹⁹) and the anion of this acid did not have a Keggin structure. It should be noted that the acidity was determined by both types of indicators – Hammets and arylmethanols. Therefore, it is suggested that free HPA's have acid sites of both Brønsted and Lewis character.



Fig. 1

Nitrogen adsorption (open points) and desorption (full points) isotherms (V_a in cm³/g N₂) at 77 K for: 1 pure SiO₂, 2 W/SiO₂ (5 wt.% W), 3 Si-W/SiO₂ (5 wt.% W), 4 P-Mo/SiO₂ (5 wt.% Mo), 5 P-W/SiO₂ (5 wt.% W)

The acidity of supported HPA's were in different sequence as for free HPA's (Table III). The highest acidity was determined for $H_3PMo_{12}O_{40}$ loaded on SiO₂ (the acidity of pure SiO₂ was negligible – below 0.05 meq H⁺/g). Beside this, in the case of supported HPA's only acidity detected by Hammet's indicators was observed. This fact indicates that the most of the acid sites are preserved as a Lewis centers on the surface of the catalysts. The classical metathesis catalyst, containing 5% of W/SiO₂, showed the smallest acidity among all studied samples.

From these results it can be said that interaction between HPA and the carrier plays an important role. There is probably an interaction between the surface OH groups of silica gel and the H ions of HPA on the surface of catalysts. This interaction is the most probable explanation of the increase of the thermal stability of phosphomolybdenum acid on SiO_2 in comparison with its free state.

	Acid strength, meq H ⁺ /g							
Sample	pK _a (Hammets)				pK_a (arylmethanols)			
	3.3	2.0	-3.0	-5.7	-8.3	-6.6	-13.3	-16.3
$\begin{array}{c} H_{3}PW_{12}O_{40} \\ H_{4}SiW_{12}O_{40} \\ H_{3}PMo_{12}O_{40} \end{array}$	2.63 2.43 0	2.42 2.22 0	2.42 1.98 0	2.18 1.76 0	0.97 0.69 0	2.18 1.94 0	0.79 0 0	0.57 0 0

TABLE II		
Acid sites distribution of free H	IPA's of Keggin type,	measured by titration method

TABLE III

Acid sites distribution of supported HPA's of Keggin type, and classical WO_3/SiO_2 catalyst (5 wt.% W or Mo) measured by titration method

		Acid strength, meq H ⁺ /g							
Sample		p <i>K</i> _a (Hammets)					pK_a (arylmethanols)		
	3.3	2.0	-3.0	-5.7	-8.3	-6.6	-13.3	-16.3	
P-W/SiO ₂	0.54	0.48	0.32	0	0	0	0	0	
Si-W/SiO2	0.74	0.58	0.50	0	0	0	0	0	
P-Mo/SiO ₂	0.85	0.75	0.67	0.47	0.37	0	0	0	
W/SiO ₂	0.48	0.32	0.32	0	0	0	0	0	

The catalytic activity of supported HPA's were tested for propene metathesis. Conversion of propene is expressed as an amount of converted propene and selectivity as the conversion to ethylene and 2-butenes (*trans* and *cis*).

$$\begin{array}{c} CH_3-CH=CH_2 \\ + \\ CH_3-CH=CH_2 \end{array} \xrightarrow{\hspace{1cm}} CH_3-CH \\ \hline CH_3-CH \end{array} \xrightarrow{\hspace{1cm}} CH_3-CH \\ \hline CH_3-CH \\ \hline CH_3-CH \\ \hline CH_2 \\ \hline CH_3-CH \\ \hline CH_2 \\ \hline CH_3 \\ \hline CH_2 \\ \hline CH_3 \\$$

The influence of the content of the active metal loaded on SiO_2 is demonstrated on Fig. 2 for P–W catalyst. This figure shows the production of primary metathesis products over loading of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ heteropolyacid at 773 K and space velocity of 4.98 mmol/s kg. The production of ethylene and 2-butenes increases up to about the 5 wt.% of tungsten sharply, further twofold increase of the tungsten content increased the yield of main product only by 2 wt.%.

From Fig. 3 it can be seen the temperature influence on the production of primary metathesis products at space velocity of 9.96 mmol/s kg for 5 wt.% of metal loaded catalysts. An intense increase of the production of ethylene and 2-butenes starts about the temperature of 753 K and reaches 32% at 833 K for $P-W/SiO_2$ catalyst. In comparison with classical W/SiO_2 catalyst, the P-Mo catalyst has only little higher activity at the temperature up to 800 K, further increase of temperature has no possitive effect on desirable hydrocarbons yield, probably for the reason of greater coking by side poly-

TABLE IV

Products	P-W/SiO2 ^a	Si–W/SiO2 ^a	P-Mo/SiO ₂ ^b	W/SiO ₂ ^a
Ethylene	10.4	5.3	3.2	4.0
1-Butene	5.7	3.6	2.0	2.1
2-trans-Butene	6.7	3.9	2.3	2.8
2-cis-Butene	5.1	2.8	1.7	2.1
Pentenes	2.2	8.4	1.1	1.2
Conversion, wt.%	30.1	24.0	10.3	12.2
Selectivity, wt.%	73.8	50.0	69.9	73.0

Products of propene metathesis (in wt.%) over W or Mo catalysts with 5 wt.% of the metal (T = 773 K, F/W = 9.96 mmol/s kg

^a After 2 h of the activity stabilization. ^b After 4 h of activity stabilization.

merization reaction as a result of great acidity. For Si–W/SiO₂ and P–W/SiO₂ catalysts the desired temperature for the same yield of ethylene and 2-butenes is lower by 20 °C and 40 °C, respectively. At the higher temperature the production of these alkenes decreases because more side reactions occurs.

Beside ethylene and 2-butenes, 1-butene is also formed as a consequence of double bond isomerization. The mutual reaction of these two products gives 2-pentenes, that undergo double bond isomerization and results in the formation of 1-pentenes or 3-pentenes. By the metathesis of 1-pentenes with 2-butenes, 3-hexenes are produced. All these substances can be mutually metathesized and then isomerized. All these products are summarized in Table IV as pentenes. This table illustrate the total composition of propene metathesis products at the 773 K and 9.96 mmol/s kg together with the conversion and selectivity of the reaction.

The selectivity of the process over all the catalyst, except $Si-W/SiO_2$ vary between 70 – 75%. Different behavior of $Si-W/SiO_2$ catalyst (only 50% of selectivity) is probably due to the interaction between Si from carrier and Si from HPA. Consequently, sites more suitable for isomerization and dimerization reactions are formed, because a rather high amount of pentenes and hexenes was obtained.

The advantage of using the catalysts of heteropolyacid basis for propene metathesis in the temperature range 753 - 793 K is in the higher production of the primary metathesis products over HPA-catalysts. From this point of view the highest activity has the P–W/SiO₂ catalyst, Si–W/SiO₂ had lower selectivity to the primary products of propene metathesis, and P–Mo/SiO₂ catalyst with stronger acidity showed high side-reaction activity with coking.



Fig. 2

Influence of the metal content (*W*, wt.%) in $P-W/SiO_2$ catalyst on the yield (*Y*, wt.%) of primary products of propene metathesis (ethylene and 2-butenes) at 773 K and *F*/*W* = 4.98 mmol/s kg





Temperature dependence of the yields (*Y*, wt.%) of primary products of propene metathesis (ethylene and 2-butenes) over: 5 wt.% $P-W/SiO_2$ (1), 5 wt.% Si- W/SiO_2 (2), 5 wt.% W/SiO_2 (3) and 5 wt.% $P-Mo/SiO_2$ (4) catalysts. (*F/W* = 9.96 mmol/s kg)

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