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1. Introduction

Isoprene is among the most important building blocks for the production of a wide variety of synthetic rubbers, elastomers and resins.^{1–4} At the moment, approximately 94% of isoprene latex is produced from the milky sap of rubber trees.^{1–4} However, the quality of this natural latex strongly depends on the growing conditions of rubber trees and could vary within a wide range of parameters such as molecular weight, density, elasticity, *etc.*^{3,4} This peculiarity leads to significant limitations in the utilization of natural isoprene latexes as materials for the critical parts of machines and mechanisms.

Compared to natural latexes, isoprene rubber obtained from an isoprene monomer *via* polymerization over Ziegler– Natta catalysts possesses a well-predicted and narrow distribution of quality-defining parameters. So, technologies which enable isoprene monomer production are highly important in industry.

Isoprene synthesis from formaldehyde and isobutene over Keggin-type heteropolyacids supported on silica†

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Gas phase Prins condensation of isobutene with formaldehyde has been studied over different Keggin-type heteropolyacids supported on amorphous silica. The catalysts were characterized by elemental analysis, X-ray diffraction, low temperature nitrogen adsorption, TPD of ammonia, FTIR of adsorbed pyridine and NMR spectroscopy. The activity of the supported heteropoly compounds was found to increase in the following order: $H_4SiMo_{12}O_{40} < H_3PMo_{12}O_{40} < H_4SiW_{12}O_{40} \approx H_3PW_{12}O_{40}$. The lower activity of the supported molybdenum heteropolyacids was attributed to their low thermal stability and partial decomposition during catalyst activation, which resulted in lower acidity. The variation of HPA content from 5 to 33 wt% was also shown to increase catalyst activity. Based on the relationship between the content of weak Brønsted sites, the amount and type of carbonaceous deposits and the catalytic activity, it was concluded that the generation of "working" active sites over HPA catalysts involves the formation of unsaturated branched surface species over weak Brønsted sites. These active carbonaceous species are responsible for selective isoprene synthesis. The best catalyst performance is observed over the catalyst with 20 wt% of $H_3PW_{12}O_{40}$, which shows an isoprene yield of 48% with a selectivity of 63%.

In the world, a significant amount of isoprene is currently obtained as a by-product of hydrocarbon steam cracking, but due to the extremely low yield its isolation requires a number of expensive extractive distillation steps.⁵ Another on-purpose isoprene synthesis technology consists a two stage reaction of isobutene with formaldehyde in the presence of acid catalysts.^{5,6} The first step involves a liquid-phase Prins reaction of isobutene with formaldehyde catalyzed by aqueous sulfuric acid, and the second the vapor-phase decomposition of 4,4-dimethyldioxane-1,3 (DMD) into isoprene over a solid calcium phosphate catalyst (Scheme 1).

This process has several significant drawbacks: 1) it is a two stage process requiring double the amount of expensive equipment and complicated control systems, 2) the two stages need additional energy consuming separation processes in each step leading to double losses of the main and intermediate products, 3) the selectivity of the overall process towards isoprene is extremely low and does not exceed 50%, and 4) the process uses solutions of sulfuric and phosphoric



Scheme 1 Two-step process for on-purpose isoprene synthesis from isobutene and formaldehyde.



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acids as a catalysts leading to environmental and corrosion problems.⁷ Therefore the development of a one-step selective process for isoprene synthesis based on heterogeneous catalysts is highly desirable. The solid catalysts studied for the formaldehyde and isobutene Prins reaction include zeolites, phosphates, sulfates and oxide catalysts.⁸⁻¹⁵

The best results in terms of both conversion and selectivity have been obtained over sulfate and phosphate solid acid catalysts. Dang *et al.*¹² showed that a formaldehyde conversion of 87% and a selectivity for isoprene of 73% could be achieved over a CuSO₄/SiO₂ catalyst doped with magnesia. Ai¹³ investigated formaldehyde condensation with *tert*-butyl alcohol over vanadium, molybdenum and tungsten phosphates with a yield of isoprene of up to 50%. Although sulfate and phosphate based catalytic systems have shown rather high catalytic activity and selectivity they have demonstrated very short life times and rapid deactivation due to coke formation.^{12,13} In our recent work an isoprene yield of 57% was achieved over a niobium phosphate catalyst which demonstrated stable formaldehyde conversion over 30 hours.¹⁵

However the selectivity of the reaction remains low due to the formation of significant amounts of different by-products. Most important is carbon monoxide, which can be formed by formaldehyde decomposition over Lewis acid sites.^{14,15} Therefore, the application of the catalysts with predominantly Brønsted acid properties such as heteropolyacids may result in a selective catalyst for isoprene synthesis from isobutene and formaldehyde.

Heteropolyacids (HPAs) are a class of solid acids constituting polyoxometalate (POM) units, *i.e.*, metal-oxygen cluster anions, organized in different structures.^{16–20} HPAs exhibiting the Keggin structure are the most stable ones and tungsten and molybdenum based heteropolyacids have found industrial applications as acid and redox catalysts.^{16–18} They are formed of a central tetrahedron (XO₄) surrounded by four octahedral (MO₆) metal units. This anion is stabilized by protons, which are responsible for the high Brønsted acidity of these materials.

In our recent patent we have demonstrated that heteropolyacids supported on silica doped with alumina show high activity and selectivity in the synthesis of isoprene.²¹ The best results were obtained over a 20% $H_3PW_{12}O_{40}$ acid supported on silica. Later, Yu *et al.* confirmed that supported tungsten silicon heteropolyacid is an effective catalyst for isobutene and formaldehyde condensation to isoprene showing a high selectivity of 85 mol%.²² However, the reasons for the high activity and selectivity of HPA catalysts are not yet very clear.

In the present paper we expand the knowledge of the Prins condensation between formaldehyde and isobutene over different types of HPA catalysts, namely $H_4SiMo_{12}O_{40}$, $H_3PMo_{12}O_{40}$, $H_4SiW_{12}O_{40}$ and $H_3PW_{12}O_{40}$ supported on silica, and on the influence of HPA loading. Attention is focused on the elucidation of the relationship between HPA catalyst performance in the Prins condensation, their acidity and the nature of carbonaceous deposits.

2. Experimental

2.1 Catalyst preparation

The catalysts were prepared by incipient wetness impregnation of amorphous silica (CARiACT Q-40c, Fuji Silysia, 355 $m^2 g^{-1}$) with aqueous solutions of the corresponding heteropolyacids (NevaReaktiv). After impregnation the samples were dried overnight at ambient temperature and then at 383 K for 3 h. The samples were then heated in a flow of dry air to 673 K with a temperature ramp of 3 K min⁻¹ and calcined at this temperature for 3 h. Catalysts were denoted as *x*HPA, in which *x* corresponds to the HPA content and "HPA" is represented by two key elements of heteropolyacid structure (*i.e.* PW, SiW, PMo and SiMo).

2.2 Catalyst characterization

The chemical composition of the samples was analyzed using energy dispersive X-ray fluorescence spectroscopy (EDXRF). Prior to analysis the samples were mixed with $B(OH)_3$ and pressed into self-supporting wafers. The wafers were analyzed using a Thermo Scientific ARL Perform'x WDXRF. Sorptiondesorption isotherms of nitrogen were measured at 77 K using an automatic pore analyzer (Micromeritics ASAP 2000). XRD patterns were recorded using a Bruker Phaser D2 diffractometer, applying Cu K_{α} radiation.

TPD experiments were performed on a USGA-101 (UNISIT) in the temperature range from 293 to 1053 K in a flow of dry He (30 ml min⁻¹). The heating rate was 8 K min⁻¹. In a typical experiment, the samples were calcined at 623 K in a flow of dry He, saturated with ammonia at 323 K, and then the physisorbed NH_3 was removed with a flow of He at 373 K. The gas flow composition was monitored using an on-line mass spectrometer (RGA200, Stanford Research Systems).

IR spectra were recorded on a Nicolet Protégé 460 FTIR spectrometer equipped with an MCT detector at 4 cm⁻¹ optical resolution. Prior to the measurements, 20 mg of a catalyst was pressed into a self-supporting disc and activated in the IR cell attached to a vacuum line at 623 K for 3 h. The adsorption of pyridine (Py) was performed at 423 K for 30 min. The excess probe molecules were further evacuated at 373 K for 0.5 h.

TG experiments over the used catalysts were performed on a TA SDT Q600 instrument. Temperature programmed oxidation was carried out in a flow of air (100 ml min⁻¹) in the temperature range of 293–1073 K with the rate of heating of 10 K min⁻¹. ³¹P and ¹³C MAS NMR spectra of fresh catalysts and coked catalysts were recorded using Bruker Avance-400 spectrometer.

2.3 Catalyst evaluation

The condensation of formaldehyde with isobutene was studied in a fixed bed reactor system operated under atmospheric pressure. In a typical experiment, 2 g of catalyst (particle size 0.5-1 mm) was loaded into the reactor. Before the experiment, the catalysts were heated *in situ* in a flow of nitrogen at 623 K. Then, the temperature was decreased to the reaction temperature.

Formalin containing 37 wt% of formaldehyde, 3 wt% of methanol and 60 wt% of water was used as the formaldehyde source without purification. Liquid formalin was fed by a syringe pump, while isobutene was fed by a mass flow controller (Bronkhorst). The isobutene/formaldehyde molar ratio was kept at 7, the reaction temperature was within 540–600 K and the weight hourly space velocity (WHSV) of the feed was 3.0 g g⁻¹ h⁻¹. The products were analyzed by on-line gas chromatography. A Porapak Q column (2 m) was used for the analysis of CO and a capillary column with SE-30 (50 m) was used for analysis of the other products. Methane was used as an internal standard for precise mass carbon balance tests. Formaldehyde concentration was determined by titration with Na₂SO₃. The selectivities towards different products formed from formaldehyde (S_i^F) were calculated as follows:

$$S_j^{\rm F} = \frac{k_j^{\rm F} \frac{m_j}{{\rm Mr}_j} \times 100\%}{n_{\rm reacted, formaldehyde}},$$

where m_j is the weight of product j in the reaction mixture, Mr_j is the molecular weight of product j, and k_j^F is the amount of formaldehyde molecules required for product jformation.

The yield of isoprene was calculated as follows:

$$Y = X_{\rm F} \times S_{\rm isoprene}^{\rm F}$$

where $X_{\rm F}$ is the conversion of formaldehyde.

3. Results and discussion

3.1. Catalysts structure and composition

The main characteristics of the catalysts are presented in Table 1 and Fig. 1. As expected, HPA content on silica measured by elemental analysis was close to calculated values. The specific surface area of the PW samples slightly decreases with an increase of HPA loading. However, even for the catalyst with the highest $H_3PW_{12}O_{40}$ loading the surface area is much higher than that of the bulk HPA (Table 1).

Table 1 Cata	yst characteristics
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The XRD patterns of the supported $H_3PW_{12}O_{40}$ catalysts with different loadings and of bulk HPAs are shown in Fig. 1a. For all the catalysts, the reflections observed can be attributed to the $H_3PW_{12}O_{40}$ · GH_2O^{23-25} phase. Broadening of the XRD reflections in the case of the silica supported catalysts as compared to bulk $H_3PW_{12}O_{40}$ points to the small size of HPA nanocrystals, indicating a high dispersion of heteropolyacid on the surface of silica.²⁶ The same conclusions are valid for the other heteropolyacids (Fig. S1†).

The ³¹P NMR spectra of the catalysts with different H₃PW₁₂O₄₀ loadings reveal the presence of one signal at -15.3 ppm due to the phosphorus atoms in the HPA structure (Fig. 1b).¹⁶⁻²⁰ No signals due to the other phosphorus species are found in the spectra indicating the high stability of H₃PW₁₂O₄₀ during the catalyst preparation procedure. On the contrary, the NMR spectrum of 20PMo catalyst shows the presence of a narrow signal at -3.9 ppm along with a broad signal centered at -13.5 ppm (Fig. S2[†]). The first signal is typical of phosphorus atoms in a H₃PMo₁₂O₄₀ structure, while the appearance of the broad signal can be attributed to HPA decomposition products, which are formed during the calcination of the catalyst. These observations are in line with the previously reported results on the thermal stability of tungsten and molybdenum based heteropolyacids.16-20

To summarize, the deposition of tungsten based heteropolyacids on silica leads to the formation of highly dispersed HPA nanocrystals. In the case of Mo-based catalysts, partial decomposition of HPA is observed due to the lower thermal stability of these acids.

3.2 Acid properties of supported HPAs

The amount and strength of the acid sites of phosphate catalysts were measured using the temperature-programmed desorption of ammonia (Fig. 2 and 3).

The spectrum of bulk $H_3PW_{12}O_{40}$ shows a sharp and intense peak at ~850 K with a small broad peak located at 430 K (Fig. 2) which is assigned to ammonia desorption without decomposition, which is confirmed by mass spectrometry (Fig. S3†). Integration of the high temperature peak gives a value of 990 µmol g⁻¹ which corresponds to the

Sample	HPA content, wt%	Surface area, m ² g ⁻¹	Acidity (TPD NH_3), μ mol g ⁻¹	Acidity (FTIR Py)	Coke	
				BAS, ^{<i>a</i>} µmol g ⁻¹	LAS, ^{<i>a</i>} µmol g ⁻¹	content, wt%
Bulk H ₃ PW ₁₂ O ₄₀	100	10	990	n/a	n/a	n/a
33PW	32.7	330	327	90	23	25.0
20PW	18.8	330	265	15	24	18.6
10PW	9.7	315	161	0	20	14.8
5PW	4.9	300	113	0	19	10.5
20SiW	19.5	315	289	15	26	14.9
20PMo	19.9	325	198	10	41	12.0
20SiMo	19.4	325	144	10	49	4.6

^a BAS - Brønsted acid sites; LAS - Lewis acid sites.



stoichiometric interaction of one molecule of HPA with three molecules of ammonia. Hence, the peak at 430 K could be attributed to weakly bonded ammonia adsorbed on the surface of HPA.

The TPD-NH₃ profiles for supported $H_3PW_{12}O_{40}$ are very different from that of pure HPA and show major desorption peaks in the temperature range of 400–800 K corresponding to weaker acid sites. The shift of ammonia desorption peaks from the high temperature region to low temperature points to the strong interaction between $H_3PW_{12}O_{40}$ and the silica support.^{16–20} By using ³¹P NMR it has been previously shown that the distribution of $H_3PW_{12}O_{40}$ over silica leads to the protonation of surface silanol groups, evidently changing their acid strength in comparison with bulk HPA.²⁷ The Si–OH₂⁺ surface species formed apparently display a lower acidity with respect to the strong Brønsted acid sites of bulk HPA. No peaks in the high temperature region due to the strong acid sites were observed, suggesting uniform HPA distribution on the surface of the silica support.



Fig. 2 TPD-NH₃ profiles for supported $H_3PW_{12}O_{40}$ catalysts in comparison with bulk $H_3PW_{12}O_{40}$. Note the ×0.1 multiplier for bulk HPA.

For the 33PW sample with high HPA loading, a broad shoulder within the temperature range of 600–800 K is observed indicating the presence of acid sites with medium strength. Furthermore, the increase of $H_3PW_{12}O_{40}$ content from 20 to 33 wt% does not lead to an increase in the ammonia desorption peak at 450 K. It can be suggested that at HPA loadings of 20 wt% almost all silanols interact with HPA giving weak acid sites. A further increase in HPA content results in a weaker interaction of the excess HPA with the silica surface, giving acid sites of medium strength.^{16–18}

The total amount of acid sites determined by TPD-NH₃ was found to increase with an increase in $H_3PW_{12}O_{40}$ content in the samples (Table 1). Ammonia can access all Brønsted acid sites in HPA due to its unique "pseudo liquid" state in which protons do not have determined linkages with HPA anions but are dissolved in the bulk HPA structure.^{16–18} Comparison of the experimental values with those calculated from elemental analysis points to slightly higher values measured by TPD-NH₃. These observations could be due to weakly bonded ammonia which desorbs at low temperature as in the case of bulk HPA.



Fig. 3 TPD-NH $_3$ profiles for HPA catalysts with different structure and 20 wt% loading.

Fig. 3 shows the TPD-NH₃ profiles for different HPAs supported on silica. All the samples reveal one desorption peak at *ca.* 450 K pointing to a similar type of interaction with the support for all the catalysts studied. Molybdenum containing HPA shows a lower amount of acid sites in comparison with the tungsten based samples. This observation is due to the partial decomposition of Mo heteropolyacids as confirmed by ³¹P NMR (Fig. S2[†]).

The nature of the acid sites was studied by IR spectroscopy of adsorbed pyridine (Py); the IR spectra for the 33PW sample are shown in Fig. 4. The main bands observed over all the samples are assigned according to the literature data^{28,29} as follows:

- 1600 and 1445 cm⁻¹ – H-bonded pyridine;

- 1638 and 1540 cm^{-1} – pyridine protonated on Brønsted sites;

- 1613 and 1451 cm^{-1} – pyridine adsorbed on Lewis acid sites;

- 1581 and 1438 cm⁻¹ – physically adsorbed pyridine.

Evacuation of the samples at different temperatures leads to gradual vanishing of the IR bands; evacuation at ambient temperature results in desorption of all physically adsorbed Py, whereas heating at 373 K leads to the disappearance of the bands corresponding to H-bonded Py. The bands corresponding to Lewis and Brønsted sites start to decrease only at elevated temperatures (473–573 K), which points to the stronger acidity of the corresponding sites.

Brønsted acidity of the catalysts arises from the protonic sites of heteropolyacids, however H-bonding of Py can also occur through the weak silanols of the support. Pure HPAs do not possess any Lewis acidity³⁰ and the presence of small amounts of Lewis acid sites in the case of supported HPAs can be explained by the partial HPA decomposition during activation at high temperature in the IR cell that leads to the formation of tungsten oxides which can interact with pyridine.

The FTIR spectra of pyridine adsorbed over 20PW, 20SiW, 20PMo and 20SiMo are shown in Fig. 5. The spectra reveal the presence of the similar bands. The only difference is in the frequency of v8a bands; the tungsten based catalysts show a band at 1614 cm⁻¹, whereas the molybdenum containing samples show a band at *ca*. 1610 cm⁻¹. The different positions of this pyridine vibration band point to the different strength of Lewis acid sites observed over the 20PW, 20SiW, 20PMo and 20SiMo samples.

The content of Brønsted and Lewis acid sites measured by the IR spectroscopy of adsorbed Py are summarized in Table 1. For all samples the amount of acid sites determined by IR of Py is significantly lower than those determined by TPD-NH₃ due to lower basicity of Py which can interact only with strong acid sites. These results are in line with the TPD-NH₃ data, confirming the strong interaction of heteropolyacids with silanol groups of the support leading to dramatic decrease of their acidic strength. The higher concentration of Lewis sites observed over Mo-based catalysts with respect to W-based could be associated with the lower stability of molybdenum HPAs and their decomposition during activation at 623 K.¹⁶⁻¹⁸

In summary, the deposition of heteropolyacids on the silica leads to formation of mostly weak Brønsted acid sites due to the strong interaction with the support. The supported catalysts display similar acid site strength as shown by TPD-NH₃. In addition, partial decomposition of HPAs during



Fig. 4 FTIR spectra of pyridine adsorbed over the 33PW catalyst, a) before evacuation and after evacuation at b) 298 K, c) 373 K, d) 473 K and d) 573 K.



Fig. 5 FTIR spectra of pyridine adsorbed over different HPA catalysts with 20 wt% loading after evacuation at 373 K.

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activation at high temperature can lead to the formation of a small amount of Lewis acid sites. The total amount of acid sites determined by TPD-NH₃ is found to increase in the following order for HPA catalysts: $20SiMo < 20PMo < 20PW \approx 20SiW$. The increase of HPA loading leads to a gradual increase in the amount of the acid sites.

3.3 Condensation of formaldehyde with isobutene over HPA catalysts

3.3.1. Reaction network. The reaction network is shown in Fig. 6. The main reaction pathway involves the Prins reaction of formaldehyde with isobutene leading to 3-methylbuten-1-ols, which can be further converted *via* the following routes:^{7,15}

•dehydration of 3-methylbuten-1-ols leading to isoprene which is the main reaction product;

•3-methyl-3-buten-1-ol can react with formaldehyde giving methylcyclopentadiene (MCPD);

•3-methyl-2-buten-1-ol double bond isomerization leading to 3-methyl-1-buten-1-ol which further converts into 3-metylbutanal due to keto–enol tautomerism;

•hydration of 3-methylbuten-1-ols giving 3-methyl-1,3butandiol, of which traces are also observed.

The isoprene formed and its precursors can interact with formaldehyde or isobutene giving secondary by-products. Thus, the addition of formaldehyde to isoprene yields 4-methyldihydropiranes (MDHP). The similar reaction of isoprene with isobutene leads to trimethylcyclohexene formation (Fig. 6). Oligomerization of isoprene gives a complicated mixture of terpenes and terpenols, which are denoted as "other products".

Formaldehyde can also decompose giving hydrogen and carbon monoxide. Dimerization of isobutene over acid sites results in the formation of 2,2,4-trimethylpentenes.

While isoprene is the main reaction product over HPA catalysts, considerable amounts of CO, methylcyclopentadiene (MCPD) and 4-methyl dihydropiranes (MDHP) are also observed. Carbon monoxide formation proceeds via formaldehyde decomposition over Lewis acid sites. Compared with our previous work devoted to isoprene synthesis over phosphate catalysts, the selectivity for CO over the HPA catalysts is significantly lower.¹⁵ This observation can be accounted for by the lower amount of Lewis acid sites found on the HPA catalysts, hence confirming the key role of Lewis sites in the decomposition of formaldehyde. The formation of byproducts with six carbon atoms points to the high activity of formaldehyde in the addition reactions. To avoid a significant impact of the condensation reactions on product distribution and to increase the selectivity for isoprene, a high isobutene to formaldehyde ratio should be applied in the reaction mixture.

3.3.2 Effect of temperature. The effect of temperature on the activity and selectivity of the 20PW catalyst was studied





Fig. 7 Effect of temperature on the a) selectivity for isoprene, b) conversion of formaldehyde, and c) yield of isoprene over the 20PW catalyst.

in the temperature range from 540–600 K. The results are presented in Fig. 7 and Table 2. Conversion of formaldehyde changes from 71 to 85% in the above mentioned temperature range, while the selectivity to isoprene decreases from 63 to 48%. At 560–580 K the reaction is accompanied by the formation of large amounts of MCPD and MDHP. A further increase of the temperature to 600 K leads to a significant decrease in the selectivity for isoprene due to formation of a large amount of terpenes and terpenols. The selectivity towards carbon monoxide changes only slightly. The highest yield of isoprene (48%) was obtained at 563 K; the conversion of formaldehyde was 76% with a selectivity for isoprene of 63%. This temperature was selected for further studies.

3.3.3 Effect of HPA loading. Bulk tungsten phosphoric HPA shows high activity in the reaction of formaldehyde with isobutene (Table 3). It demonstrates the highest conversion of formaldehyde (91%) compared with the supported catalysts. However the selectivity towards isoprene reaches only 24 mol%. This low selectivity is due to the formation of high amounts of MDHP and MCPD and can be attributed to the high strength of acid sites of bulk HPA (Fig. 2). Strong acid sites can provide deep condensation reactions of isoprene precursors with formaldehyde followed by formation of MDHP, MCPD and other heavy products.

The results of the catalytic evaluation of the supported PW catalysts with different HPA loadings are shown in Table 3. The activity of the catalysts increases with an increase in $H_3PW_{12}O_{40}$ content and gives a satisfactory correlation with the amount of acid sites as determined by TPD-NH₃ (Fig. 2). Referring to the results of FTIR spectroscopy of adsorbed pyridine, it can be suggested that formaldehyde condensation with isobutene most probably proceeds over the weak Brønsted acid sites of the heteropolyacids, which is line with the earlier observations.⁸⁻¹⁵

Selectivity towards isoprene and the main by-products changes slightly with variation of the HPA content. The 33PW sample shows a high selectivity for MCPD and MDHP due to the presence of acid sites with medium strength (Fig. 2). A marginal increase in the selectivity towards isoprene with a decrease of $H_3PW_{12}O_{40}$ loading from 20 to 5 wt% relates to a decrease in the rate of by-product formation due to the lower concentration of acid sites on the samples with low HPA loading.

As compared with the bulk HPA in terms of isoprene yield, supported $H_3PW_{12}O_{40}$ catalysts show higher yields of isoprene with good selectivity. The best catalytic performance was observed over the 20PW catalyst, which shows an isoprene yield of 47%. A further increase of HPA loading to 33 wt% does not result in an increase of isoprene yield because of the decrease in selectivity. Therefore, a 20 wt% loading of heteropolyacids on silica seems to be the most appropriate for investigating the effect of HPA type.

3.3.4 Effect of HPA structure. In further experiments, the role of HPA type was examined. The results of catalytic tests for different HPA catalysts in formaldehyde condensation with isobutene are shown in Table 3. The conversion of both formaldehyde and isobutene, as well as the yield of isoprene increase in the following order for the catalysts: $20SiMo < 20PMo < 20PW \approx 20SiW$, indicating that the tungsten based HPA catalysts are more active with respect to the molybde-num ones. Comparing the results of catalytic tests with the acidity measurements shows a clear correlation of formaldehyde conversion with the amount of acid sites determined by TPD-NH₃ (Table 1) over the catalysts studied. The differences in catalyst activity do not lead to any changes in the catalyst selectivity towards main products (Table 3).

These observations can be accounted for by the same type of active sites operating on all the catalysts, *i.e.* weak Brønsted acid sites.

Table 2 Effect of temperature of the reaction of formation you and isobutche over the 20PW catalyst (WHSV = 511, 105 = 4	Table 2	Effect of temperature on the reaction	of formaldehyde and	l isobutene over the	20PW catalyst (WHSV	$= 3 h^{-1}$, TOS $= 4 h$)
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Temperature,	Conversion of	Selectivity, mol%								
K	formaldehyde, %	Isoprene	Methylcyclopentadiene	3-Methylbutanal	4-Methyldihydropyranes	Trimethylcyclohexenes	СО	Other		
543	71.0	63.1	4.8	4.5	9.8	4.0	7.9	5.9		
553	73.8	62.9	4.9	4.4	9.7	3.9	7.9	6.3		
563	75.7	62.9	5.1	4.6	9.6	3.7	8.1	6.0		
573	76.9	59.5	5.7	5.1	10.9	4.1	8.2	6.5		
583	78.1	57.1	6.2	5.3	11.3	4.5	8.5	7.1		
593	85.5	48.5	8.6	5.8	15.5	4.9	8.8	7.9		

hyde, Isoprene 23.8	Methylcyclopentadiene	3-Methylbutanal	4-Methyldihydropyranes	Trimothylayolohoyonog			Isoprene
23.8			j al opjiales	rinneuryicyclonexenes	CO	Other	yield, %
	28.2	5.0	20.1	9.5	5.9	7.5	21.7
59.0	6.8	4.6	10.7	4.8	8.1	6.0	45.4
62.9	5.1	4.6	9.6	3.7	8.1	6.0	47.6
63.8	5.0	4.4	9.3	3.7	7.8	6.0	34.2
64.2	5.1	4.5	9.1	3.6	7.7	5.8	26.5
62.9	5.9	4.4	10.0	3.5	7.9	5.4	47.2
61.0	4.1	5.2	8.9	2.0	12.1	6.7	33.4
62.9	3.8	5.4	8.2	2.1	12.5	5.1	17.7
	62.9 63.8 64.2 62.9 61.0 62.9	62.9 5.1 63.8 5.0 64.2 5.1 62.9 5.9 61.0 4.1 62.9 3.8	62.9 5.1 4.6 63.8 5.0 4.4 64.2 5.1 4.5 62.9 5.9 4.4 61.0 4.1 5.2 62.9 3.8 5.4	62.9 5.1 4.6 5.6 63.8 5.0 4.4 9.3 64.2 5.1 4.5 9.1 62.9 5.9 4.4 10.0 61.0 4.1 5.2 8.9 62.9 3.8 5.4 8.2	62.9 5.1 4.6 9.6 5.7 63.8 5.0 4.4 9.3 3.7 64.2 5.1 4.5 9.1 3.6 62.9 5.9 4.4 10.0 3.5 61.0 4.1 5.2 8.9 2.0 62.9 3.8 5.4 8.2 2.1	62.9 5.1 4.0 9.0 5.7 8.1 63.8 5.0 4.4 9.3 3.7 7.8 64.2 5.1 4.5 9.1 3.6 7.7 62.9 5.9 4.4 10.0 3.5 7.9 61.0 4.1 5.2 8.9 2.0 12.1 62.9 3.8 5.4 8.2 2.1 12.5	62.95.14.09.05.78.16.063.85.04.49.33.77.86.064.25.14.59.13.67.75.862.95.94.410.03.57.95.461.04.15.28.92.012.16.762.93.85.48.22.112.55.1

Table 3 Reaction of formaldehyde and isobutene over HPA catalysts (T = 563 K, WHSV = 3 h⁻¹, TOS = 4 h)

3.3.5 Deactivation of the HPA catalysts. To analyze the deactivation of the different HPA catalysts, the isoprene yields plotted *versus* time on stream are shown in Fig. 8. All the catalysts show an induction period during the first 50 minutes of the experiment. The origin of this induction period was discussed in detail in our previous communication¹⁴ and is explained by the accumulation of active carbonaceous species on the catalyst surface. These carbonaceous deposits attached to the Brønsted acid sites of the catalysts give "working" active sites, which are responsible for isoprene formation.¹⁴ This point is very important since it shows that catalyst performance is significantly influenced by two features, which are interconnected between each other, namely, by i) the nature and the amount of acid sites and ii) the nature and the amount of coke deposits.

After the induction period the behavior of the catalysts depends on the type of HPA and its concentration (Fig. 8). It has to be noted that during the deactivation after first 2 h selectivity does not change significantly and loss of isoprene yield is due to the decrease in conversion.

Fig. 8a shows the isoprene yield *versus* time on stream for the PW samples with different HPA loadings. An increase in $H_3PW_{12}O_{40}$ content results in an increase in isoprene yields but does not change of the deactivation rate: all the catalysts studied demonstrate similar deactivation curve slopes. Thus, it can be concluded that HPA loading does not affect catalyst deactivation. The deactivation curves observed over different HPA catalysts are shown in Fig. 8b. Tungsten based catalysts 20PW and 20SiW exhibit a similar dependence of isoprene yield *versus* time on stream. The molybdenum based catalysts demonstrated faster deactivation with respect to the tungsten based catalysts and lower total isoprene yield. This different behavior can be explained by at least two reasons: i) a different amount of Brønsted acid sites and ii) a different nature of coke accumulated over the Mo and W based catalysts. To gain a deeper insight into the origin of such catalytic behavior, the amount and nature of coke deposits were analyzed for deactivated catalysts.

3.3.6 Study of deactivated catalysts. The deactivated catalysts were studied after 6 h on stream using low temperature nitrogen adsorption, ¹³C MAS NMR and TG techniques. Low temperature N_2 adsorption isotherms of the 20PW catalyst taken before and after deactivation are presented in Fig. 9. The results point to a slight decrease in the pore volume of the material due to coke deposition. The similar shape of the adsorption–desorption curves for fresh and deactivated samples points to a uniform distribution of coke on the surface.

The results of TG analysis of deactivated catalysts are shown in Fig. 10 and Table 1. All the tungsten catalysts show a major weight loss within the temperature range of 650–750 K which suggests that the nature of coke deposits is similar over all the catalysts studied. For the molybdenum HPAs coke oxidation occurs within a significantly lower temperature range of



Fig. 8 The yield of isoprene versus time on stream over supported HPA catalysts.



Fig. 9 N_2 adsorption-desorption isotherms for fresh and deactivated 20PW catalysts.

550–650 K which could be due to the pronounced oxidizing properties of Mo heteropolyacids.^{16–18} Besides that the amount of coke accumulated on the molybdenum HPAs was significantly lower than in the case of tungsten containing catalysts.

Analysis of the results presented in Fig. 8 and 10 and Tables 1 and 3 suggests that the amount of coke deposits calculated per gram of catalyst correlates with formaldehyde conversion and isoprene yield. Despite the highest amount of coke being accumulated on the surfaces of 20PW, 33PW and 20SiW, these catalysts show the highest activity in the condensation of formaldehyde and isobutene. This observation strongly supports the suggestion of the key role of carbonaceous deposits in the selective synthesis of isoprene from isobutene and formaldehyde over solid acid catalysts.¹⁵

¹³C MAS NMR spectra of deactivated 20HPA catalysts are shown in Fig. 11a. All the spectra display the presence of two broad features in the ranges of 12–50 ppm and 115–150 ppm corresponding to different carbon atoms in carbonaceous deposits. Besides this, the Mo-based catalysts show a narrow NMR line at ca. 61 ppm. While the resonances in the range of 12-50 ppm can be assigned to aliphatic saturated carbon atoms, the lines in the range of 115-150 can be attributed to olefinic carbon atoms. The signal at 61 ppm is most probably due to O-containing carbonaceous deposits. Our previous in situ ¹³C MAS NMR study of isobutene and formaldehvde interaction over niobium oxide catalyst14 has demonstrated that NMR lines in the region of 60-80 ppm can be attributed to surface alkoxides, ethers, esters or acetals. These O-containing carbonaceous deposits were shown to form as the initial surface species, which are further decomposed into alkenes leading to branched long chain oligomeric carbonaceous deposits. The active coke species were shown to be composed of C12-C20 branched unsaturated hydrocarbons, which are protonated on the acidic sites. These species were demonstrated to be responsible for the interaction with formaldehyde and isobutene via an addition-cleavage mechanism leading to selective isoprene formation.¹⁴

The analysis of carbonaceous deposits observed over Mo and W based catalysts suggests that the former gives a high contribution of O-containing light coke, which does not lead to isoprene formation. On the contrary, the latter mostly produces branched unsaturated carbonaceous deposits, which favour selective isoprene synthesis. These observations could be due to the lower acidity of the Mo catalysts (Fig. 3), which is not enough for the transformation of O-containing coke precursors into olefinic coke responsible for isoprene synthesis. This conclusion is supported by the comparison of the data obtained over the 20SiMo and 5PW catalysts. Indeed, the analysis of NH₃ TPD (Fig. 2), ¹³C MAS NMR (Fig. 11) and catalytic data (Fig. 8) points to the similar acidity, type of carbonaceous deposits and isoprene yields observed over these two catalysts. Since no difference in catalyst acid strength was found, it can be concluded that the amount of Brønsted acid sites influences the nature of coke deposits and therefore the activity of the HPA based catalysts. The presence of different types of coke deposits on the catalysts could be associated with the kinetics of coke precursor transformation



Fig. 10 TG curves of temperature programmed oxidation of the deactivated catalysts.



Fig. 11 ¹³C MAS NMR spectra of deactivated HPA catalysts. Spinning sidebands are marked with asterisks.

into active coke over the catalysts with different amounts of acid sites. A high concentration of acid sites on a catalyst (33PW, 20PW and 20SiW) leads to faster elimination of oxygen from coke precursors giving C=C bonds of unsaturated hydrocarbons with respect to the catalysts with a low amount of acid sites (5PW, 20PMo, 20SiMo).

Summarizing these data, the catalytic performance of the HPA catalysts depends on the amount of Brønsted acid sites which influence the nature of carbonaceous deposits formed during the reaction. A low concentration of acid sites cannot promote the conversion of coke precursors into olefinic hydrocarbons, which are responsible for the formation of "working" active sites yielding isoprene.

4. Conclusions

Tungsten phosphorus, tungsten silica, molybdenum phosphorus and molybdenum silica heteropolyacids with Keggintype structure supported over amorphous silica are shown to be efficient catalysts of isoprene synthesis from formaldehyde and isobutene. The main reaction pathway involves condensation of formaldehyde with isobutene leading to isoprene as a major product. Besides isoprene, the formation of small amounts of 3-methylbutanal, methylcyclopentadiene, methyl dihydropyranes, CO and heavy by-products is detected. All HPA based catalysts exhibit high selectivity towards isoprene.

Based on the relationship between the content of weak Brønsted sites determined by TPD-NH₃ and FTIR of adsorbed pyridine, the amount and type of carbonaceous deposits analyzed by ¹³C MAS NMR spectroscopy and TGA and the catalytic data, it was concluded that the generation of "working" active sites over HPA catalysts involves the formation of unsaturated branched surface species over weak Brønsted sites. These active carbonaceous species protonated on acidic sites are responsible for the interaction with formaldehyde and isobutene *via* an addition–cleavage mechanism leading to selective isoprene formation. The amount of such sites on the catalyst is governed by the amount of weak Brønsted acid sites with mild acidity, which are formed by the interaction of strong protonic sites of heteropolyacids with silanol groups of the silica support.

The reactivity of supported heteropolyacid catalysts is shown to increase in the following order: $H_4SiMo_{12}O_{40} < H_3PMo_{12}O_{40} < H_4SiW_{12}O_{40} \approx H_3PW_{12}O_{40}$. Besides that, the variation of HPA content from 5 to 33 wt% is also found to the increase their reactivity. The lower activity of Mo based catalysts and the catalysts with low HPA content is attributed to lower content of weak Brønsted sites over these materials, which is not enough for the transformation of O-containing coke precursors into olefinic coke responsible for isoprene synthesis. A low amount of weak Brønsted acid sites in the case of Mo based catalysts is associated with partial HPA decomposition during catalyst activation.

The best catalyst performance is observed over the catalyst with 20 wt% $H_3PW_{12}O_{40}$, which shows isoprene yields of 48% with a selectivity of 63% and is characterized by a high content of weak Brønsted sites. A further increase of HPA loading to 33 wt% leads to the formation of acid sites with medium acidity, which decreases the catalyst selectivity.

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