Catalysis Letters Vol. 81, No. 3–4, August 2002 (©2002)

A comparative study of the conversion of 2-methylpent-2-ene on 12-tungstophosphoric, 12-tungstosilicic and 12-molybdophosphoric acids: an acidity probe

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Received 14 December 2001; accepted 11 March 2002

The conversion of 2-methylpent-2-ene (2M2PE) is employed as a probe reaction to investigate the acidic properties of 12-tungstophosphoric acid for various loadings on silica, residence times, time-on-stream and reaction temperatures. The high selectivities to methyl shift products as compared with those to double-bond shifts indicate the presence of strong acid sites. Infrared spectra show that adsorbed 2M2PE exists as saturated species on the surface of HPW/SiO_2 with irreversibly adsorbed material forming conventional coke. Similar conversions of 2M2PE and selectivities to products are obtained with 12-tungstosilicic acid supported on SiO_2 while with 12-molybdophosphoric acid the conversions are markedly lower and the highest selectivities are found with products obtained from double-bond shifts, indicating the presence of relatively weak acidic sites. The results obtained from 2M2PE conversion on other acidic catalysts are compared with those from the supported heteropoly acids.

KEY WORDS: 2-methylpent-2-ene; tungstophosphoric acid; tungstosilicic acid; molybdophosphoric acid.

1. Introduction

The definition of acidic strengths of homogeneous aqueous systems is unambiguous and the measurement of these acidities is generally straightforward. In contrast, with solids and in particular the surfaces of solids, the topic is considerably more complex [1–5]. Solids of catalytic interest are generally isotropic both in the bulk and in their surfaces, and this geometric heterogeneity almost inevitably results in energetic heterogeneities, further complicating discussions of acidic strength.

A variety of methods for the measurement of the acidity of solid surfaces has been proposed and tested, from inverse gas chromatography to the adsorption of bases [1–5]. The acidity of various heteropoly acids in their solid forms has, for example, been evaluated from Hammett indicator titrations, temperature-programmed desorption, photoacoustic infrared spectroscopy and microcalorimetry [1,6]. While each of these methods has its advantages and disadvantages the relationship between the results obtained from these various techniques is difficult and often impossible to establish and their interpretation in terms of any unambiguous definition of acidity is as yet not forthcoming.

Catalysis practitioners are generally more concerned with the relative efficiency of a given solid in an acid-catalyzed process as opposed to information on the absolute values of acidic strength, however useful such data might be. With this in view, various probe reactions have been suggested by a number of workers [5]. A number of years ago Kramer, McVicker and Ziemiak advocated the use of 2-methylpent-2-ene (2M2PE) as a particularly useful reaction for probing the relative acidity of solids since the migration of alkyl groups relative to double-bond shifts should be strongly dependent on acidic strength [7–9].

The conversion of 2M2PE has been employed as a probe reaction with a number of catalysts, including ultrastable Y zeolites and amorphous silica–alumina [8], halided γ-Al_2O_3 and silica–alumina of various compositions [9], γ-Al_2O_3 and WO_3/r-Al_2O_3 [10], various SAPO-11 and MeAPSO-11 [11], Ga-substituted MCM-41 [12] and boron phosphate of various P/B ratios [13]. In the present work the conversion of 2M2PE has been investigated on 12-tungstophosphoric ($H_3PW_{12}O_{40}$, abbreviated as HPW), and compared with the results obtained with 12-tungstosilicic ($H_4SiW_{12}O_{40}$, abbreviated as HSiW) and 12-molybdophosphoric ($H_3PMO_{12}O_{40}$, abbreviated as HPMo) acids supported on silica.

2. Experimental

All methylpentenes and hexenes were purchased from Aldrich with purities of 96% or better. Dimethylbutenes (99%) were obtained from Chemical Supplies Co.

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1011-372X/02/0800-0199/0

The silica-supported catalysts were prepared by the incipient wetness technique. The acids were purified by dissolving in distilled water, filtering and evaporating to dryness. Silica (Davison grade 643, 200–425 mesh, 150 Å, 99+%) was purchased from Aldrich. The supported acids were dried in a vacuum oven (70 °C) for approximately 3 h before use.

The isomerization of 2M2PE was affected in a plug-flow microreactor with an on-line gas chromatograph (Hewlett-Packard 5890) fitted with a Carbopak C/0.19% picric acid or a 50 m PONA column and employing helium as a carrier gas. In some cases a GCMS system (HP5890, HPMS5970) was employed. Carbon mass balances were accurate to ±5%.

FTIR spectra from 4000 to 1250 cm^{-1} were recorded at 4 cm^{-1} resolution on a Bomem MB-series FTIR spectrometer. Spectral accumulation for 20 scans was performed.

3. Results and discussion

With HPW/SiO_2 and a reaction temperature of 300 °C the conversion of 2M2PE was relatively independent of loading with values ranging from 75 to 80% (figure 1). Products formed as a result of methyl shifts included 3-methyl-2-pentene (3M2PE), hexene, 2,3-dimethyl-2-butene (23DM2BE) and 3-methyl-1-pentene (3M1PE), in order of decreasing selectivities. Selectivities to these totalled 70–75%. Two isomers, 4-methyl-2-pentene (4M2PE) and 2-methyl-1-pentene (2M1PE), resulted from double-bond shifts. Although the selectivities to the principal products were relatively unchanged with loading, that to 23DM2BE showed a maximum at a loading of approximately 23%. A small but significant quantity of 3-methylpentane (3MPA), indicative of hydride transfer, was also observed.

With 23% HPW/SiO_2 catalysts the conversion increases up to 300 °C but remains constant for further increases in temperature up to 350 °C (figure 2). At a reaction temperature of 150 °C, 3M2PE, 2M1PE and 4M2PE are the dominant products with small or insignificant selectivities to the remaining products which were observed at 300 °C. With increase in temperature above 150 °C, selectivities to 3M2PE, 4M2PE, 3M1PE, 23DM2BE and hexene increase, while that to 2M1PE decreases slightly. The selectivities to 3M2PE, 2M1PE, 4M2PE and 3M1PE become virtually constant with increase in temperature above 250 °C, while that to hexene continues to increase. Although the former observation is suggestive of a system approaching equilibrium at these higher temperatures, at least with respect to pentene-based species, the latter observation indicates that equilibrium has not been achieved with respect to all reaction processes.

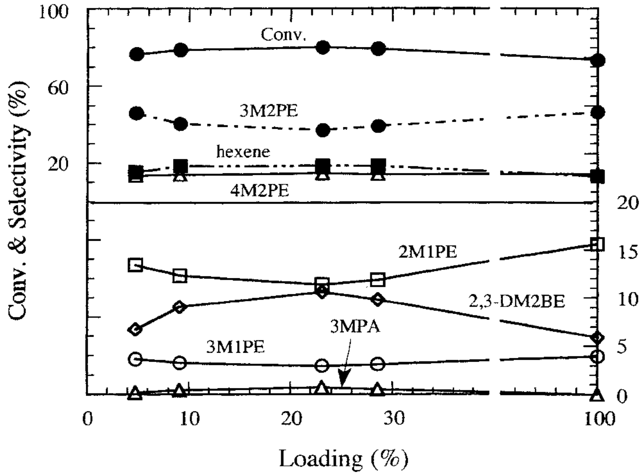

Figure 1. Conversion and selectivities from 2M2PE on HPW/SiO_2 at 300 °C for various loadings. $W = 30$ mg, $F = 14$ ml/min, 4.2% 2M2PE.

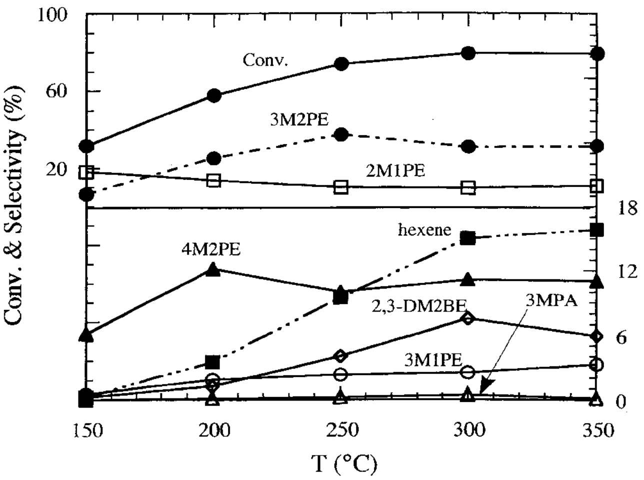

Figure 2. Conversion and selectivities from 2M2PE on 23% HPW/SiO_2 for various reaction temperatures. $W = 30$ mg, $F = 14$ ml/min, 4.2% 2M2PE.

With 23% HPW/SiO_2 at a reaction temperature of 300 °C the conversion increases, as expected, with increase in residence time (not shown). The selectivities to 3M2PE, 2M1PE and 3M1PE decrease with W/F, implying that these are primary products, while those to hexene and 2,3-DM2BE increase, as would be expected for secondary products. With the same catalyst and reaction temperature the conversion decreases from 80 to 60% over 5 h time-on-stream (not shown). The selectivities to 4M2PE, 2,3-DMBE, and 3MPA decrease, indicative of the irreversible consumption of protons.

For comparison purposes, $HPMo/SiO_2$ and $HSiW/SiO_2$ were also subjected to exposure by 2M2PE. The results are summarized in figure 3 for loadings of 20% on SiO_2 and a reaction temperature of 300 °C. It is clear that the conversions and selectivities for the two tungsten-containing catalysts are virtually identical with conversions of approximately 80% and highest selectivities to 3M2PE, 2M1PE, 4M2PE and hexene, as noted before. A small selectivity to 3MPA, as found with HPW/SiO_2, is again observed. In marked contrast the conversion on $HPMo/SiO_2$ under similar conditions

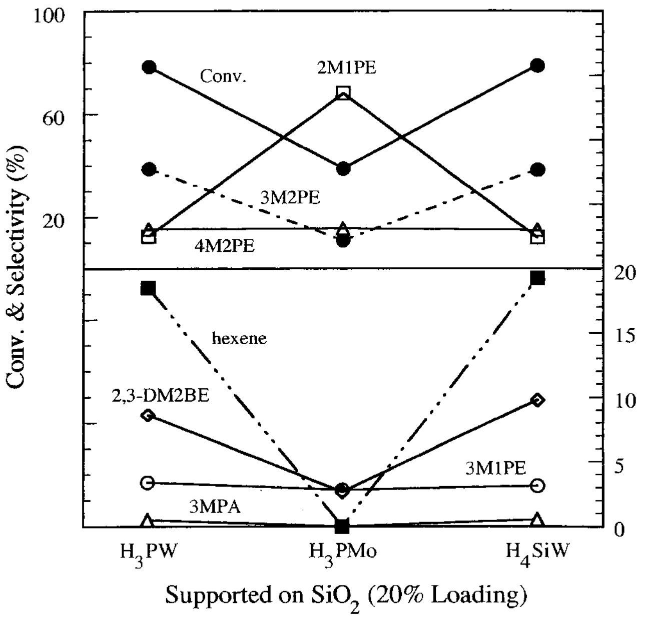

Figure 3. Conversion and selectivities from 2M2PE on 20% HPW/SiO_2, HPMo/SiO_2 and HSiW/SiO_2 at 300 °C. $W = 30$ mg, $F = 14$ ml/min, 4.2% 2M2PE.

is approximately half that observed with the tungsten-containing catalysts and the highest selectivity is found with 2M1PE, resulting from a double-bond shift. The products resulting from methyl shifts, namely 3M2PE, hexene and 23DM2BE, are substantially smaller on HPMo/SiO_2 than those on HPW/SiO_2 and HSiW/SiO_2, indicative of the relatively weaker Brønsted acid sites on HPMo/SiO_2. No 3MPA was observed.

IR spectra of 23% HPW/SiO_2 after exposure to 2M2PE are shown in figures 4 and 5. The spectra in figure 4 were obtained after exposure of the sample to 2M2PE vapor at room temperature followed by evacuation at elevated temperatures, while the spectra in figure 5 were measured after exposure of the sample to 2M2PE at various temperatures followed by evacuation at room temperature. On exposure of the sample to 2M2PE for 10 min at 25 °C followed by evacuation at the same temperature and for the same period of time, strong bands appear at 2962, 2933, 2875 and 2857 cm^{-1}, attributed to asymmetric CH_3 stretching, asymmetric CH_2 stretching, symmetric CH_3 stretching and symmetric CH_2 stretching, respectively (figure 4) [14–16]. No bands are observed in the region above 3000 cm^{-1}, indicating the absence of the $=CH_2$ (3080 cm^{-1}) and the $=CH-$ (3020 cm^{-1}) groups in the adsorbed 2M2PE, while the bands below 3000 cm^{-1} associated with saturated C–H groups are comparatively intense. It is of interest to note that, although evacuation at 200 °C markedly reduced the intensities of the aforementioned bands, evacuation at a temperature of 300 °C virtually eliminated all spectral evidence of the adsorbed species.

In the spectral region from 1350 to 1700 cm^{-1} three bands at 1370, 1380 and 1460 cm^{-1} are observed on exposure of the catalyst to 2M2PE for 10 min. As with the bands in the 2800–3100 cm^{-1} region these bands decrease in intensity with evacuation for 20 min at temperatures up to 200 °C and vanish at 300 °C.

The absence of bands above 3000 cm^{-1} is indicative of the absence of olefinic bonds, while the strong bands below this wave number attest to the presence of saturated groups in the adsorbed species from 2M2PE and are suggestive of the formation of carbocations. However, as Peri [17] has pointed out in his report on butene adsorbed on silica–alumina, the latter species

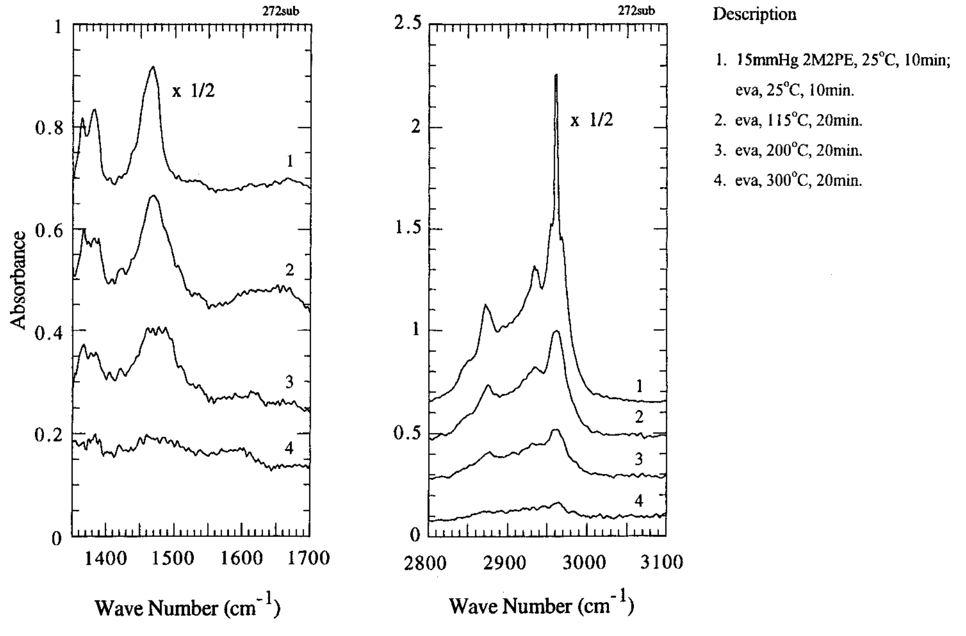

Figure 4. IR spectra of adsorbed 2M2PE on 23% HPW/SiO_2 for various evacuation temperatures.

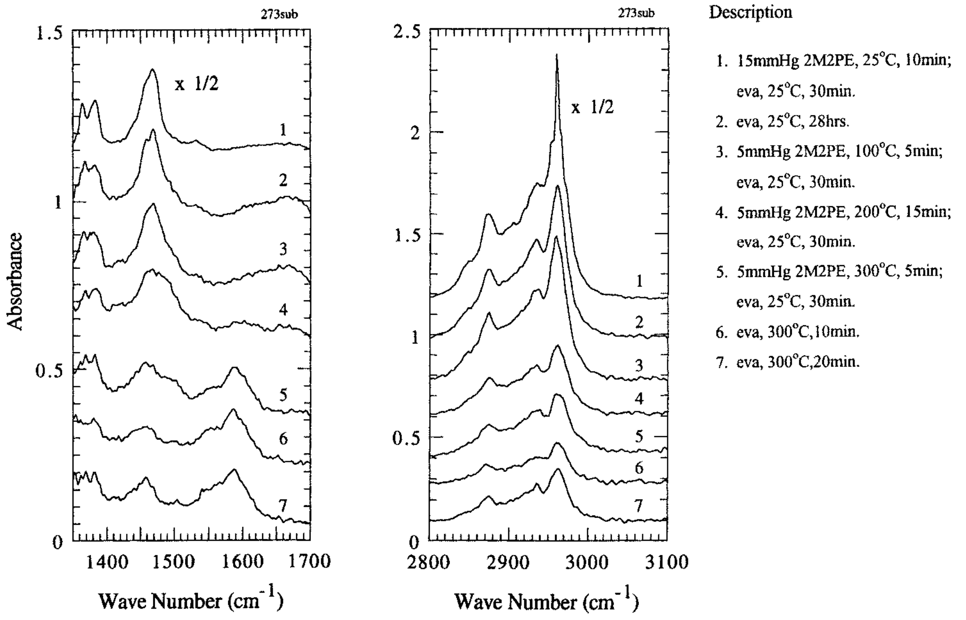

Figure 5. IR spectra of adsorbed 2M2PE on 23% HPW/SiO_2 for various exposure temperatures and evacuation duration of time.

probably exist transiently at levels too low to detect. PAS–FTIR studies have shown that gas-phase methanol interacts with the Brønsted acid sites on HPW to form CH_3^+, which are bound to the terminal oxygen atoms of the anion thus methylating the surface [18]. Since bands at 1460, 1375 and 1325 cm^{-1} have been attributed to W(O–C_3H_7)$_6$ [19], the strong bands at 1460 and 1380 cm^{-1} found with 2M2PE are suggestive of the alkylation of the terminal oxygen atoms of the anion.

The effect of exposure of the catalyst to 2M2PE at temperatures higher than 25 °C is shown in figure 5. Although the majority of the bands seen in figure 5 are similar to those seen in figure 4, a band at 1580 cm^{-1} forms after exposure to 2M2PE at 300 °C followed by evacuation at 25 °C and intensifies with evacuation at 300 °C. This band can be attributed to the formation of irreversibly chemisorbed 2M2PE, polymerized species formed from it or conventional coke [20].

It is clear that the tungsten-containing acids have stronger Brønsted acid sites than those on the acids containing molybdenum. It is tempting, in view of the spectroscopic results, to suggest that the conversion process on the former acids involves the interconversion of alkoxy species into intermediates and/or the existence of these as relatively free, stable alkyl cations as intermediates on the catalyst surface such as tentatively proposed by Kramer *et al.* for ultrastable Y zeolites [8]. The formation of butene in selectivities as high as 75% from isobutane on HPW/SiO_2 provides further support for this contention [21]. In contrast, with the molybdenum-containing acid the selectivities to products formed from methyl shifts are considerably smaller than those on either HPW/SiO_2 or HSiW/SiO_2 and further no butane was formed from isobutane [21], corresponding to the observation of Kramer *et al.* on amorphous silica–alumina [9], who again contend that alkoxy intermediates play a role but that free secondary cations are either absent or present in low concentrations. It is of interest to note that earlier calculations have shown that the magnitude of the negative charge on the terminal oxygen anions of HPMo is substantially higher than that on HPW, consistent with the restricted movement of any alkyl cations or protons bound to these atoms in the former acid [22]. Under the assumption that the protons in the heteropoly acids are bound to the terminal oxygen atoms of the heteropoly anions primarily by Coulombic forces, the mobility of the protons and hence their acidic strengths would be inversely related to the magnitude of the negative charges on these oxygen atoms. The lower magnitude of negative charges calculated for those terminal oxygen atoms in tungsten-containing heteropoly acids is indicative of a higher mobility of protons and hence a higher acidic strength than found with the molybdenum-containing anions where the aforementioned magnitude is lower. Such theoretical predications are evidently in accord with the results found in the present work.

Finally, it is of some interest to compare the results obtained in this work with those found with various solid acids (table 1). Note that reaction conditions may not be identical for entries in the table. Not surprisingly, while the 3M2PE/4M2PE ratio for γ-Al_2O_3 is small, chloriding increases the ratio by a factor of 10 and fluoriding by fifty-fold. Of the various phosphates, SAPO-11 and BPO_4 have the highest ratio values at 1.5 and 2.8, respectively. The molybdenum-containing heteropoly acid has a ratio similar to that of Ni- and MnHPSO-11 while the tungsten-containing heteropoly

Table 1
Comparison of the conversion of 2M2PE and selectivities to products on various catalysts

	Conversion	3M2PE/4M2PE[a]	T[b]	Reference
γ-Al$_2$O$_3$	28.5	0.04	250	10
CoAPSO-11	33.8	0.11	200	11
FeAPSO-11	34.4	0.15	200	11
Ultrastable Y	–	0.25	200	8
1.5% Cl–γ-Al$_2$O$_3$	–	0.45	250	9
20% HPMo/SiO$_2$	4.0	0.70	300	[c]
15% SiO$_2$–Al$_2$O$_3$	–	0.76	250	9
NiAPSO-11	42.8	0.83	200	11
MnAPSO-11	42.6	0.83	200	11
10% WO$_3$/r–Al$_2$O$_3$	48.1	0.89	250	10
SAPO-11	55.7	1.50	200	11
20% HPW/SiO$_2$	60.0	2.10	200	[c]
1.5% F–γ-Al$_2$O$_3$	–	2.48	250	9
20% HPW/SiO$_2$	80.0	2.80	300	[c]
20% HSiW/SiO$_2$	80.0	2.80	300	[c]
BPO$_4$ (1.4 P/B)	60.0	2.80	200	13

[a] Ratio of 3-methyl-2-pentene/4-methyl-2-pentene.
[b] Reaction temperature (°C) (note that other reaction conditions may differ).
[c] This work.

acids have values similar to that found with BPO$_4$ of high P/B ratio. It should be noted that, in the heteropoly acids, the protons are intrinsic to the structure (*e.g.* H$_3$PW$_{12}$O$_{40}$), whereas in boron phosphate (BPO$_4$) the protons serve as charge-balancing species on the surface oxygen atoms.

Acknowledgments

The financial support of the Natural Sciences and Engineering Research Council of Canada through Operating, Equipment and Industrially Oriented Research Grants, the Province of Ontario through its University Research Incentive Fund and Imperial Oil through the Environmental Science and Technology Alliance Canada is gratefully acknowledged.

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