Ring-expansion of methylcyclopentane to cyclohexane and ring-contraction of cyclohexane to methylcyclopentane on silica-supported 12-tungstophosphoric acid and stoichiometric and nonstoichiometric microporous silver 12-tungstophosphate

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Methylcyclopentane is ring-expanded to cyclohexane and cyclohexane is ring-contracted to methylcyclopentane on 12-tungstophosphoric acid (HPW) supported on silica and on stoichiometric microporous silver 12-tungstophosphate. The conversions of the two reactants increase with the loading of HPW on SiO_2 while achieving significantly higher values on silver 12-tungstophosphate which pass through a maximum as the Ag/H^+ preparative ratio increases. The ring-expansion and ring-contraction processes on the supported HPW and the microporous AgPW are catalyzed by the acidic protons in the solid acid and the residual protons in the silver salt.

Keywords: heteropoly, 12-tungstophosphoric acid, silver 12-tungstophosphate, cyclohexane, methylcyclopentane, ring-expansion, ring-contraction

1. Introduction

Metal–oxygen cluster compounds (heteropoly oxometalates) are found with a wide variety of elemental compositions and structures [1,2]. Those most commonly studied for their catalytic properties have anions of Keggin structure, in the present work of stoichiometry $PW_{12}O_{40}^{3-}$, in which a central PO_4 tetrahedron is enveloped by and shares oxygen atoms with twelve octahedra with tungsten atoms at their approximate centres and oxygen atoms at their vertices [3]. If the charge of the anion is balanced by protons a solid acid results, 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$, abbreviated as HPW). Although this has a low surface area ($<10\ m^2\,g^{-1}$) [4] photoacoustic (PAS) FTIR experiments have shown that polar molecules such as ammonia can penetrate into the bulk structure, but not into the anion, to interact with both peripheral and interior protons [5]. The differential heats of adsorption of ammonia on HPW as obtained from microcalorimetry are, up to 3 molecules of ammonia per anion, approximately $150\ kJ\,mol^{-1}$, placing this solid in the superacid category [6–8]. Since nonpolar molecules do not penetrate into the bulk of the solid and the surface areas are low it is convenient to support the solid acids on a high area solid such as silica [9].

Substitution of monovalent cations, such as those of the alkali metals, for one or more of the protons, has been found to increase the surface area as well as generate a microporous structure [10]. Recent work has shown that production of the high surface area, microporous solids is not restricted to elements of the 1A group of the Periodic Table as monovalent cations but can be extended to those of the 1B and 3A groups as well, including salts formed from Ag^+ [11].

In addition, PAS FTIR experiments have shown that the aforementioned salts, when prepared with stoichiometric quantities of the preparative reagents, nevertheless contain residual protons, the quantities of which are dependent upon the cation/proton ratios employed in the preparation [5]. Not surprisingly the morphological properties of the salts prepared from the monovalent cations are also dependent upon the preparative cation/proton ratios [10d,11,12] so that, for example, the surface areas and micropore volumes of the silver salt of HPW (abbreviated as AgPW) increase with cation/proton ratio while the mean micropore radius remains relatively unchanged.

Recent work has examined the dehydration of the 1-, 2- and *tert*-butyl alcohols on the stoichiometric and nonstoichiometric compositions of microporous AgPW [13]. In the present work, the ring-contraction of cyclohexane (CY) to methylcyclopentane (MCP) and ring-expansion of methylcyclopentane to cyclohexane are studied on silica-supported 12-tungstophosphoric acid and stoichiometric and nonstoichiometric microporous silver 12-tungstophosphate. Ring-opening processes which generate linear or branched molecules are catalyzed by noble metals but ring-expansion reactions are usually considered to require the presence of both metallic and acidic sites [14,15]. However, Farcasiu

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and coworkers have shown that methylcyclopentane isomerizes to cyclohexane on sulfated zirconia catalysts at temperatures as low as 65 °C [16,17]. The present work demonstrates that the aforementioned two processes can occur on silica-supported 12-tungstophosphoric acid and stoichiometric silver 12-tungstophosphate and examines the dependence of such processes on the properties of the supported HPW and the surface and morphological properties of AgPW of various stoichiometric and nonstoichiometric compositions.

2. Experimental

The silica-supported catalysts were prepared by the incipient wetness method. 12-tungstophosphoric (BDH) acid was purified by dissolving the solid in distilled water, filtering the solution, followed by evaporation to dryness. Silica (Davison grade 643, 200–425 mesh, 150 Å, 99+%) was supplied by Aldrich. The HPW/SiO_2 was dried in a vacuum oven (70 °C) for approximately 3 h before use.

The stoichiometric and nonstoichiometric silver salts of HPW were prepared by precipitation, as described in detail previously [11]. An aqueous solution of silver nitrate (BDH) was slowly added, with stirring, to a solution of HPW at room temperature, followed by filtering. The solid was dried overnight under vacuum at room temperature. AgPW samples with preparative Ag/H ratios of 0.50, 0.85, 1.0, 1.15 and 1.50 were synthesized for this work.

The reactions were performed in a plug-flow microreactor with an on-line gas chromatograph (Hewlett Packard 5880 Å) fitted with a 1% SP1000, 60/80 Carbopak B column operated isothermally at 135 °C. A constant temperature saturator was employed to introduce MCP (Aldrich 98%) and CY (Baker Analyzed), both of which were used as received, into the feedstream. The catalyst was held in place between quartz wool plugs in a quartz reaction tube. The reactor temperature was measured with a thermocouple held near the upper surface of the catalyst. Carbon mass balances were accurate to ±5%.

Infrared spectra were recorded on a Bomem MB-100 FTIR spectrometer. Powder X-ray diffraction employed a Siemens D500 diffractometer using Cu Kα radiation and a graphite monochromator, at 30 mA and 40 kV. ^{1}H MAS NMR spectra were obtained with a Bruker AMX-500 with an external reference of benzene, at room temperature and spinning rate of 7 kHz. Prior to the ^{1}H MAS NMR measurements the samples were heated to 120 °C for 1.5 h, allowed to cool to room temperature under vacuum for 1.5 h and stored in a desiccator. The mass of the sample placed in the zirconia holder was obtained prior to each measurement.

The BET surface areas and micropore distributions were obtained by appropriate analysis of nitrogen adsorption–desorption isotherms [11,13].

3. Results

The surface areas of HPW/SiO_2 are listed in table 1 and those of AgPW, along with the micropore volumes (V_{MP}) and mean micropore radii (r_{MP}), are contained in table 2. The retention of the Keggin structure of the anion as the protons are replaced by the silver cations was confirmed from infrared spectra and powder X-ray diffraction patterns (not shown). The surface area of HPW/SiO_2 decreased with loading (table 1), the surface area and micropore volumes of the AgPW samples increased with the Ag/H ratio up to 1.00 while the mean micropore radius remained constant (table 2). The numbers of protons remaining in the AgPW samples for the various preparative ratios are shown in table 3. As noted in the introduction and consistent with the earlier PAS studies [5], nonvanishing number of protons remain for stoichiometric preparative ratios and higher although, not surprisingly, these numbers decrease as the preparative Ag/H ratio increases. Residual protons are found in compositions with preparative ratios at least as high as 1.15.

Maximum conversions of CY and MCP on silica, processed as it would have been during the impregnation step but in the absence of HPW, were negligible up to 500 °C.

Table 1
Surface areas of HPW/SiO_2.[a]

Loading (wt%)	A_s ($m^2\,g^{-1}$)
0.0	195.5
4.7	179.4
9.1	154.1
23	122.1
50	94.3
70	55.0
100	5.7

[a] N_2 adsorption, 77 K, BET.

Table 2
Morphological properties of the stoichiometric and nonstoichiometric silver salts of 12-tungstophosphoric acid.

Property	Preparative stoichiometry[a]				
	0.50	0.85	1.0	1.15	1.50
A_s ($m^2\,g^{-1}$)	77.6	86.2	100.9	101.4	100.5
V_{MP} ($ml\,g^{-1}$)	0.027	0.031	0.037	0.037	0.035
r_{MP} (Å)	8.0	7.8	7.9	7.8	7.7

[a] Preparative cation/proton ratio.

Table 3
Protons in silver 12-tungstophosphate.

Preparative Ag/H^+ ratio	From ^{1}H MAS NMR[a]
0.50	0.94
0.85	1.78
1.00	1.27
1.15	1.26
1.50	1.14

[a] From integration of peaks.

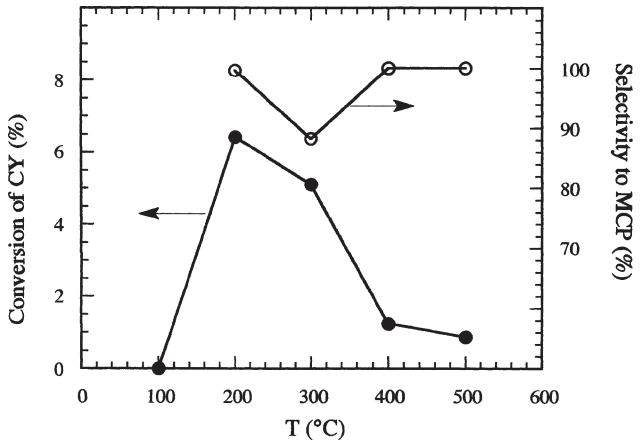

Figure 1. Conversion of cyclohexane and selectivity to methylcyclopentane on 20% HPW/SiO_2. $F = 11$ ml min^{-1}, $W = 200$ mg.

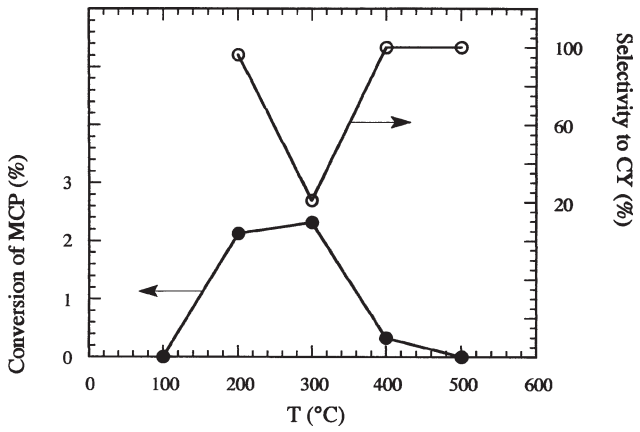

Figure 2. Conversion of methylcyclopentane and selectivity to cyclohexane on 20% HPW/SiO_2. Reaction conditions as in figure 1.

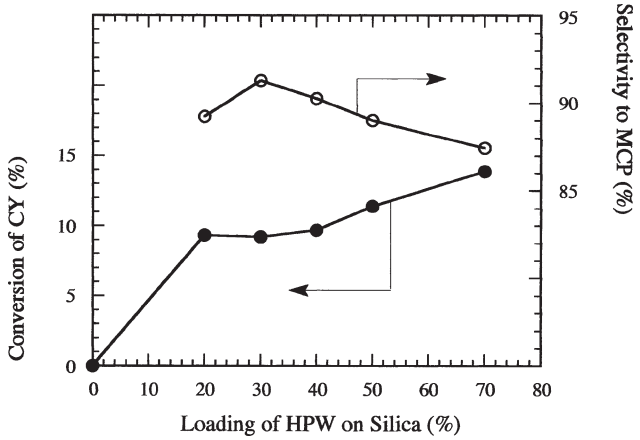

Figure 3. Conversion of cyclohexane and selectivity to methylcyclopentane on HPW/SiO_2 at 300 °C. Reactions conditions as in figure 1.

The conversions of CY and MCP on 20% HPW/SiO_2 were insignificant at room temperature and 100 °C but were significant at 200 °C (figures 1 and 2), reaching maximum values at 200 and 300 °C for CY and MCP, respectively. It should be noted that, where conversions are very small and approaching zero, the selectivities are subject to considerable imprecision. At 400 °C the conversions of CY and MCP were small relative to those observed at 200 and 300 °C. At a reaction temperature of 300 °C, the conversion of CY was approximately 10% on 20% HPW/SiO_2 but increased relatively little as the loading was further increased (figure 3). The selectivity to MCP from CY was virtually constant at 90% for 20% HPW/SiO_2 and higher loadings. The conversion of MCP was significantly lower than that of CY at 300 °C for all loadings and the selectivities to CY were lower and more variable with changes in loading (figure 4).

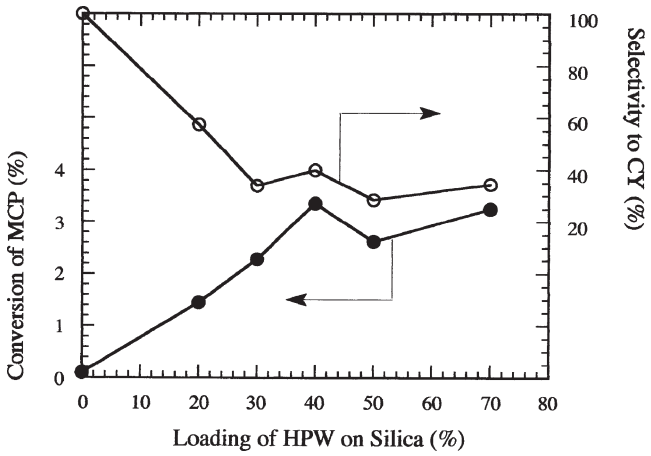

Figure 4. Conversion of methylcyclopentane and selectivity to cyclohexane on HPW/SiO_2 at 300 °C. Reaction conditions as in figure 1.

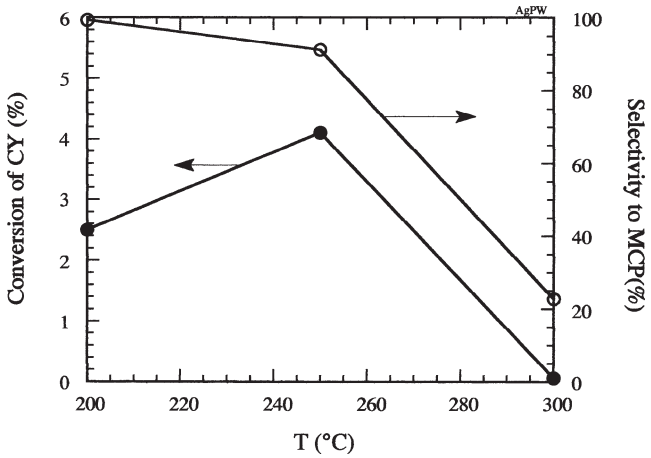

Figure 5. Conversion of CY and selectivity to MCP versus reaction temperature with AgPW(1.00). Helium flow bubbling through CY at 10 °C, $F = 10$ ml min^{-1}, $W = 200$ mg.

With AgPW(1.00) the conversion of CY increases with reaction temperature to a maximum of approximately 4% at 250 °C while the selectivity to MCP decreases precipitously for temperatures higher than 250 °C (figure 5). For a reaction temperature of 250 °C the conversion of CY increases to approximately 18% with increasing Ag/H preparative ratios from 0.85 to 1.30, and decreases to relatively small values as Ag/H is further increased to 1.60 (figure 6). In contrast, the selectivity to MCP remains at 82–90% for Ag/H ratios up to 1.80.

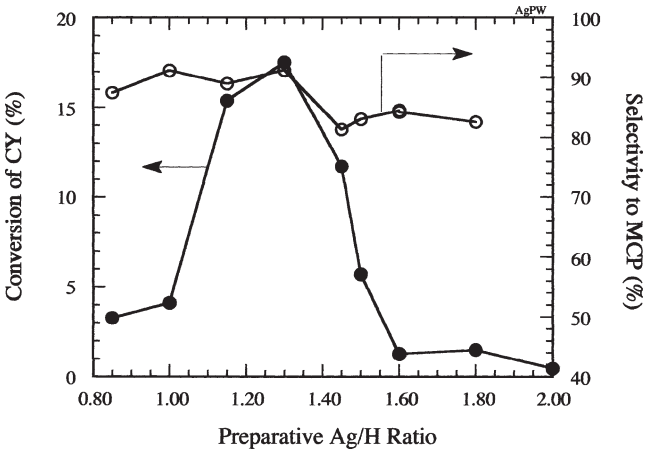

Figure 6. Conversion of CY and selectivity to MCP versus preparative Ag/H ratio at 250 °C. Helium flow bubbling through CY at 10 °C, $F = 10\ \mathrm{ml\,min^{-1}}$, $W = 200$ mg.

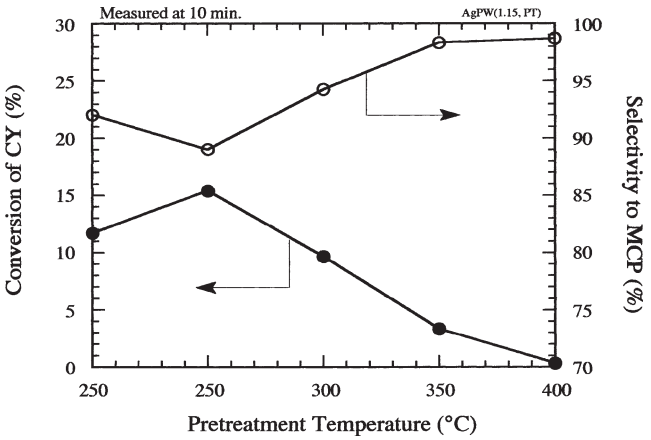

Figure 7. The effect of pretreatment temperature on the conversion of CY and selectivity to MCP. Sample: AgPW(1.15), reaction temperature 250 °C, helium flow bubbling through CY at 10 °C, $F = 10\ \mathrm{ml\,min^{-1}}$, $W = 200$ mg, pretreatment time 1 h, except for first point (see text).

The effect of increases in the pretreatment temperature is examined at a reaction temperature of 250 °C with the AgPW(1.15) sample (figure 7). For a sample raised from room temperature to 250 °C over a period of 30 min followed by exposure to CY, the conversion was approximately 12%. With a separate aliquot of the same sample raised to 250 °C as the previous but held at that temperature for 1 h, the conversion increased slightly to 15%. Further increases in the pretreatment temperature resulted in decreases in the conversion to negligible values at 400 °C. Concomitantly the selectivity to MCP decreased from approximately 92 to 89% followed by increases to values approaching 100% at 400 °C, although the errors in the measurement of selectivity at very small conversions are obviously not negligible.

With increases in the contact time at a reaction temperature of 250 °C and AgPW(1.15) the conversion of CY increases to a maximum of 15% and decreases slightly while the selectivity to MCP concomitantly decreases and ultimately increases (figure 8), implying

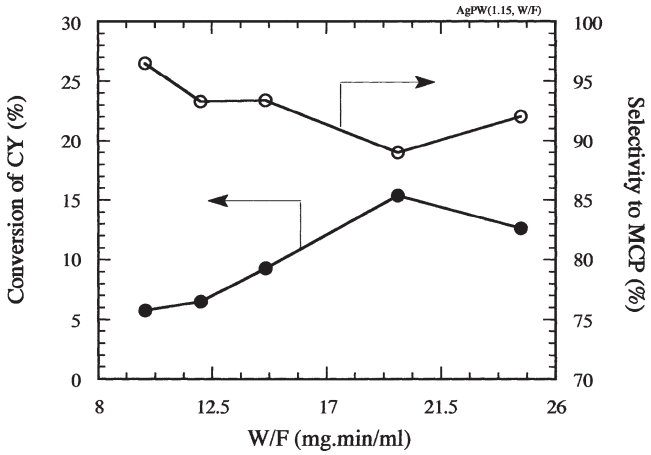

Figure 8. The effect of contact time (W/F) on the conversion of CY and selectivity to MCP. AgPW(1.15), reaction temperature 250 °C, helium flow bubbling through CY at 10 °C, $W = 200$ mg.

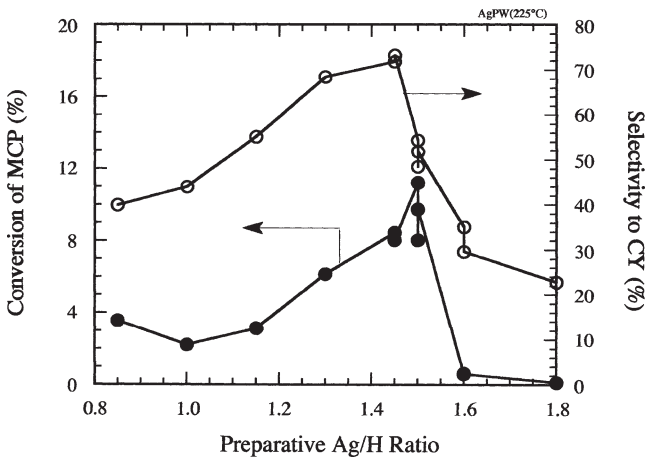

Figure 9. Conversion of MCP and selectivity to CY on AgPW for various preparative Ag/H ratios. Reaction temperature 225 °C, helium flow bubbling through MCP at 0 °C, $F = 10\ \mathrm{ml\,min^{-1}}$, $W = 200$ mg.

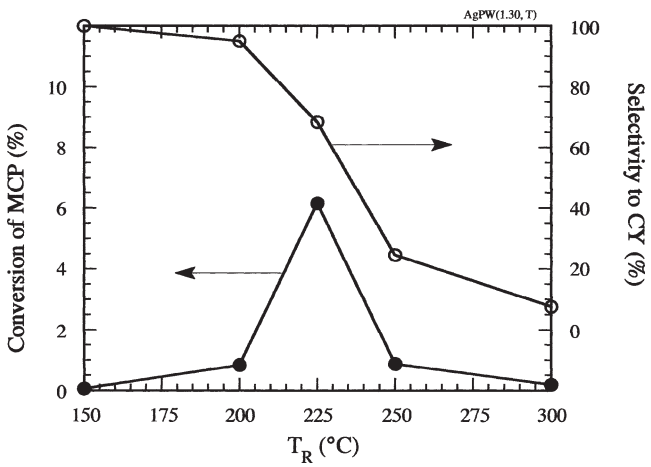

Figure 10. Conversion of MCP and selectivity to CY versus reaction temperature AgPW(1.30), helium flow bubbling through MCP at 0 °C, $F = 10\ \mathrm{ml\,min^{-1}}$, $W = 200$ mg.

that MCP is the primary product in the isomerization process.

With MCP as the reactant the conversion at 225 °C also passes through a maximum, but at an Ag/H preparative ratio of 1.50, although as evident from the reproducibility of the data the values of AgH at which the maximum is found are best indicated as 1.5 ± 0.1 (figure 9). The selectivities to CY increase, pass through a maximum of approximately 75% for an Ag/H ratio of 1.45 ± 0.1 and, with further increases in the latter, decrease up to 1.80. As noted in the preceding, the experimental errors in measurements for small conversions are not insignificant.

With the AgPW(1.30) sample the conversion of MCP, as with CY, passes through a maximum (≈6%) at a temperature of 225 °C somewhat lower than that observed with CY (figure 10). The selectivity to CY from MCP decreases continuously with increase in temperature.

4. Discussion

12-tungstophosphoric acid is known to possess strongly acidic sites which have differential heats of adsorption of ammonia which are sufficiently large to permit the classification of this material as a superacid [6–8]. Photoacoustic FTIR studies have shown that this acidity can be attributed to Brønsted acid sites with little or no evidence of Lewis acidity [5]. The surface area is, however, relatively low at less than 10 $m^2\,g^{-1}$ [4] so that, with nonpolar reactants, it is convenient to augment the surface area by use of a support such as silica as is employed in the present work [9].

Earlier studies of the isomerization of 1-butene on HPW/SiO_2 have shown that the formation of isobutene is strongly dependent on the loading with the selectivity to the skeletal isomerization product reaching a maximum for a loading of approximately 23% [9b]. TPD experiments with adsorbed NH_3 showed that the peak due to strongly bound NH_3, not evident for loadings of 5 and 9%, was extant with the 17% HPW/SiO_2. Furthermore, the ^1H MAS NMR chemical shift was 5.3 for the 5% sample but had increased to 6.8 for the 15% loading, to be compared with 8.2 for the pure acid.

Earlier work with laser Raman (LRS), X-ray photoelectron and ^{31}P NMR spectroscopies has shown that 12-molybdophosphoric acid can be deposited uniformly on the surface of silica in a highly dispersed form up to a loading of approximately 10 wt% and the strong interaction between the supported material and the silica apparently enhances the thermal stability of the acid [18]. With AgPW both the conversion of CY and of MCP are much more sharply dependent on the composition of the catalyst than was observed with HPW/SiO_2. The maxima in conversion for CY and for MCP are found at Ag/H values significantly higher than 1. The observation that the conversion of CY on AgPW(1.15) passes through a maximum for a pretreatment temperature of 250 °C and decreases for higher temperatures suggests that Brønsted acidic sites are

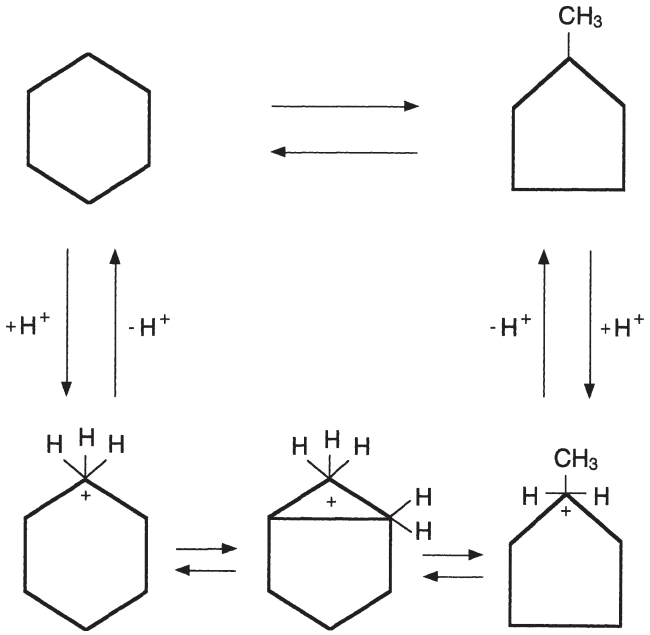

Figure 11. Postulated mechanisms for the ring-contraction of CY and the -expansion of MCP.

primarily responsible for the catalysis and these are diminishing in number with pretreatment at higher temperatures. Consequently, the most plausible mechanism for the ring-expansion and -contraction processes in the present work can be taken to involve the formation of carbocations with either CY or MCP and the aforementioned protons (figure 11).

Morphological factors could be responsible for the differences observed between the results for HPW/SiO_2 and the various AgPW compositions. However, the surface area of 23% HPW/SiO_2, for which the dispersion may be taken as optimal, is 122 $m^2\,g^{-1}$, not too dissimilar from that observed (101 ± 1 $m^2\,g^{-1}$) for the AgPW samples with preparative ratios between 1.0 and 1.5. In addition, the micropores in the AgPW samples, although not completely uniform in size, are sufficiently large to allow passage of both reactants and products. With AgPW of various compositions the surface area increases up to a preparative Ag/H ratio of 1.00 and remains relatively constant for further increases in this ratio. However, the conversions of either reactant remain at 3–4% for preparative Ag/H ratios up to and including 1.00.

The significant differences between the conversions with HPW/SiO_2 and the various AgPW compositions thus appear to be attributable to dissimilarities in the numbers of protons and/or their acidic strengths. However, since the number of protons remaining in the AgPW samples decreases continuously with increasing preparative Ag/H ratio while the conversions of the reactants each pass through a maximum, no direct correlation is evident. The maxima in the conversions are tentatively attributed to perturbations of the acidic strengths as a result of the presence of Ag^+ cations in the protonic environments and/or inaccessibility of a portion of the protons to the reactants [13].

The present report has demonstrated that ring-expansion and -contraction can occur on acidic solids such as the heteropoly oxometalates in the absence of a metallic component and further, that the activities of the microporous silver salt of HPW show unexpected dependencies on the preparative Ag/H ratios, which can be tentatively attributed to differences in the effective number of protons and their acidic strengths.

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