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Isomerization of 1-butene on supported and unsupported metal–oxygen cluster compounds (heteropoly oxometalates)

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On 12-tungstophosphoric acid (HPW) supported on silica, 1-butene is isomerized to cis- and trans-2-butene at 100°C and higher while a temperature of 150°C is required to form isobutene. While the conversion remains at 80–90% regardless of the loading of HPW on the support and the reaction temperature, the selectivity to isobutene reaches a maximum of 33% at a loading of 23% HPW/SiO_2 and 300–350°C. Small quantities of C_n ($n = 3, \ldots, 8$) species are also formed. These results together with those from ammonia poisoning, temperature-programmed desorption of ammonia, ^1H MAS NMR and infrared spectroscopy show that HPW/SiO_2 possesses sites of strength as high as or higher than those on HZSM-5, that such sites are required for the skeletal isomerization process and that both mono- and bimolecular processes are occurring on the catalyst. The absence of dependence of conversion of 1-butene and selectivities to cis- and trans-2-butene on loading and reaction temperature can best be rationalized on the basis of a rapid attainment of an equilibrium between the aforementioned three species and sec-butyl carbenium ions from which pool the energy barrier to the primary butyl carbenium and hence to isobutene is surmounted, given appropriate conditions.

Keywords: 1-butene; isomerization; isobutene; 12-tungstophosphoric acid

1. Introduction

After four decades the heterogeneously catalyzed isomerization of 1-butene continues to attract the attention of researchers in catalysis [1–55]. A predicted future oversupply of 1-butene coupled with its use as a precursor to methyl *t*-butyl ether have contributed to a recent surge in interest in this topic. In addition, requirements for acidic catalysts which are environmentally benign have encouraged workers to seek reactions which can be employed to provide assessments of the acidity of heterogeneous catalysts. The isomerization of 1-butene has recently been studied on a wide variety of catalysts including various oxides [1,3,5,9,10], aluminophosphates [4,8] and zeolites [2,6,7].

The isomerization of 1-butene can occur via the positional isomerization to cis- and trans-2-butene or the skeletal isomerization to isobutene, with the sites of higher acidic strength being required for the latter process. Cheng and Ponec have shown that the selective isomerization of butene to isobutene can occur by either a monomolecular mechanism requiring Lewis acid sites or a bimolecular mechanism involving Brønsted acid sites [9,10]. Although, with a Brønsted acid, the formation of secondary butylic carbenium ions from 1-butene has been frequently postulated, Cheng and Ponec suggest as more probable a carbenium-like bimolecular mechanism in which 1-butene is first dimerized into octenes which isomerize skeletally more easily than butenes [9,10]. Subsequently, these dimeric products crack to yield smaller hydrocarbons including isobutene.

The present work examines the isomerization of 1-butene on various heteropoly acids, but particularly 12-tungstophosphoric acid supported on silica.

2. Experimental

12-tungstophosphoric acid (HPW) and butenes were obtained from BDH and Praxair, respectively. The ammonium salt, NH_4PW was prepared from reagent grade purity $(NH_4)_2CO_3$ and HPW with NH_4^+/H^+ molar ratio of 1.0. The solution of $(NH_4)_2CO_3$ was added dropwise during 1 h at ambient temperature to a stirred aqueous solution containing the appropriate quantity of HPW dissolved in distilled water. The suspension was stirred for an additional 2 h at ambient temperature following addition of the cation source. The salt was heated over a water bath to near-dryness and dried in air at 110°C for 4 h.

The supported catalysts were prepared by wet impregnation of fumed silica (Cab-O-Sil, grade M-5) with aqueous solutions of HPW. Ten grams of the support were impregnated with 20 ml of an aqueous solution of HPW of appropriate concentration. The slurries were dried in the same method as above.

The catalytic reaction was carried out in a small flow system with a glass tube reactor filled with catalyst sample blocked at two ends by quartz wool. 200 mg of sample was used, except when otherwise mentioned. The

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catalysts were pre-treated in situ in helium flow (20 ml/min) at 350°C for 2 h prior to exposure to a mixture of 10% 1-butene in helium obtained from Praxair. "Initial" activity was measured at 10 min after introduction of the reactant mixture. The reactant and products were analyzed with a HP 5890 gas chromatograph equipped with a TCD and a Carbopack C column of 2 m × 1/8″ o.d. The selectivity was calculated on a products basis. No conversion of 1-butene was observed with an empty reactor in the range of temperatures employed in the present work.

FTIR spectra from 4000 to 1250 cm^{-1} were recorded at 4 cm^{-1} resolution on a Bomem MB-series Fourier transform infrared spectrometer. Spectral accumulation for 20 scans was performed. About 30 mg of sample was pressed to form a self-supporting disc of 13 mm diameter and placed in a glass IR cell connected to a conventional vacuum system, allowing the sample pretreatment to be performed under dynamic vacuum at 400°C for 1 h, followed by exposure to butenes.

Solid state NMR spectra were recorded on an AMX500 spectrometer operating at 500.14 MHz for ^1H and at 202.46 MHz for ^{31}P. Samples were packed in 4 mm o.d. rotors and spun at ~ 5 000 Hz.

3. Results

Preliminary experiments with 1-butene at 250°C were performed on unsupported and silica-supported 12-tungstophosphoric acid (HPW/SiO_2) as well as ammonium 12-tungstophosphate. All catalysts produced high (80–90%) conversions of 1-butene but only HPW/SiO_2 yielded appreciable quantities of isobutene. Consequently, the present report will consider only the results obtained with the latter catalyst.

A number of experiments were carried out to investigate the effect of loading on the conversion and product selectivities (fig. 1). The conversion changes relatively little with increase in the loading, although it is evident that the conversions obtained with the smallest loading, at any of the four reaction temperatures examined, are somewhat smaller than those obtained at the higher two loadings. In contrast, the selectivities to isobutene show marked differences with loading (fig. 1). At all four temperatures, the selectivities to isobutene increase with loading to a maximum at 23% and decrease for a further increase in loading to 29%. The highest selectivities to isobutene (33%) are obtained at 300–350°C on 23% HPW/SiO_2. Separate experiments in which 1-butene was passed over the silica support without the catalyst showed that the conversions were low (less than 40% at 300°C) and no isobutene was formed.

The effect of reaction temperature on the conversion and selectivities from 1-butene on 17% HPW/SiO_2 (after 10 min time-on-stream) is shown in fig. 2. It is of particular interest to note that the selectivity to isobutene reaches a maximum at the same temperature 300°C at which the selectivities to cis- and trans-2-butene reach minima. Further, the selectivity to the polymerized forms of butene also reach a maximum at this temperature.

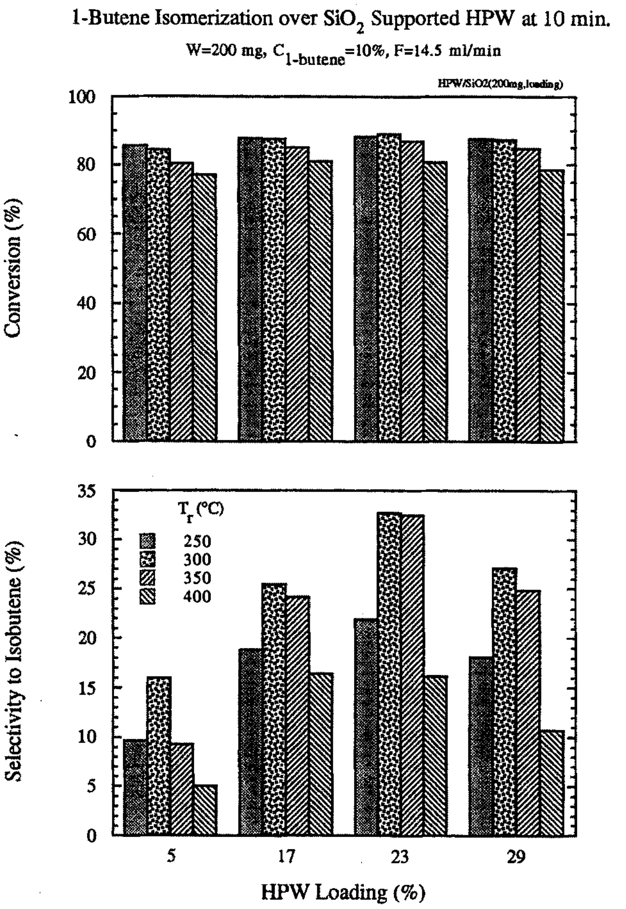


Fig. 1. Conversion of 1-butene and selectivity to isobutene for four loadings of HPW on SiO_2.

The period of time during which the reactant is in contact with the catalyst has, not surprisingly, a significant effect on the observations (fig. 3). Changes in the contact time are achieved by holding the flow rate of the reactant gas fixed while varying the mass of the catalyst. The conversion increases slightly with contact time while the selectivities to cis- and trans-2-butene decrease and that to isobutene increases suggesting that the 2-butenes are the primary products while the isobutene is a secondary product, apparently forming from the 2-butenes.

Results for various times-on-stream are shown in fig. 4. The selectivities to the 2-butenes increase with time-on-stream while those to isobutene and the polymeric forms decrease. The deactivation process evidently results in the loss of the sites which are active for the production of isobutene.

Exposure of the catalyst to ammonia prior to utilization of the catalyst in 1-butene isomerization produces little or no change in the conversion of 1-butene and the selectivities to the 2-butenes (fig. 5). In contrast, the

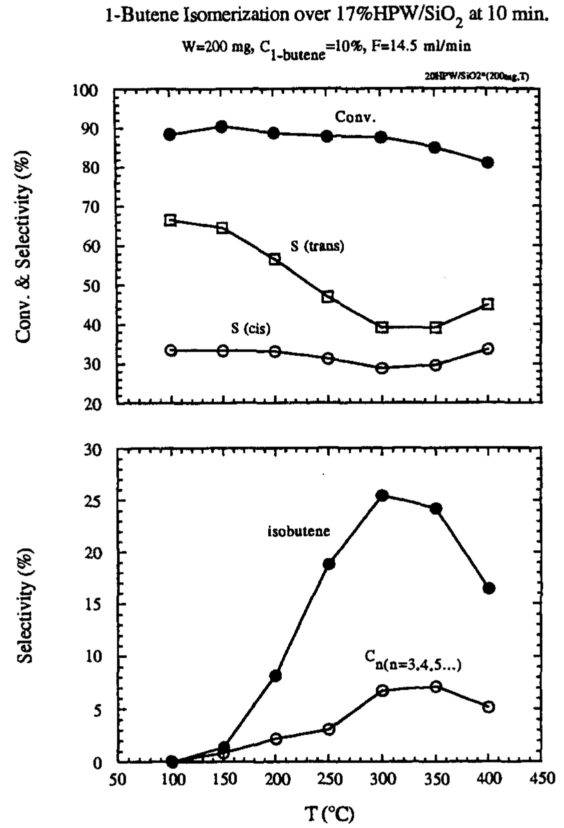


Fig. 2. Conversion and selectivities at various reaction temperatures.

selectivity to isobutene decreases precipitously with the first introduction of ammonia.

The results of temperature-programmed desorption measurements of NH_3 from HPW/SiO_2 are shown in fig. 6 a–f, together with that for 15% HPW/SiO_2 which had not been previously exposed to NH_3 (fig. 6 g). With all samples pretreated with NH_3 a peak appears between 100 and 150°C which can be attributed to weakly bound NH_3. This peak shifts slightly to higher temperatures as the loading of HPW on the support increases. A peak between 400 and 500°C is attributed to loss of water (cf. fig. 6 g) formed from the extraction of oxygen atoms from the anion by products, while that at approximately 550°C, which is only a shoulder with 5 and 9% HPW/SiO_2, results from the desorption of strongly bound NH_3.

Chemical shifts obtained from ^1H MAS NMR for

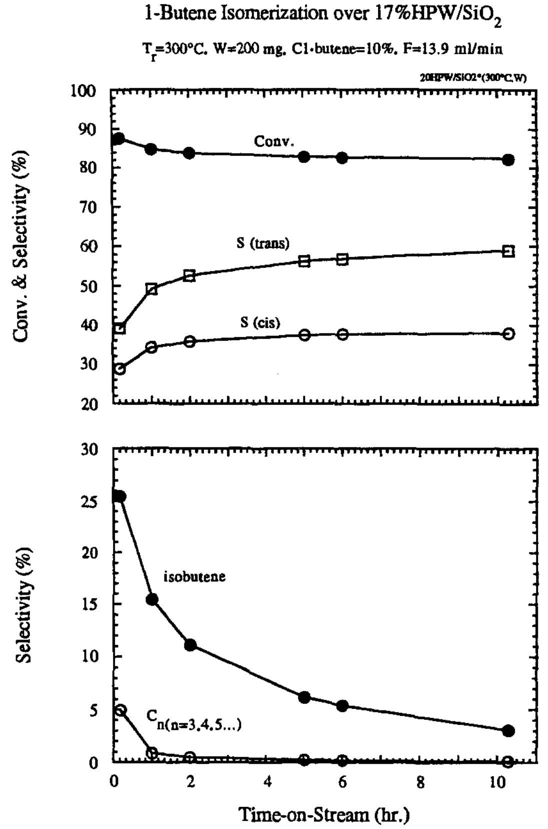


Fig. 4. Effect of time-on-stream on conversion and selectivities at 300°C.

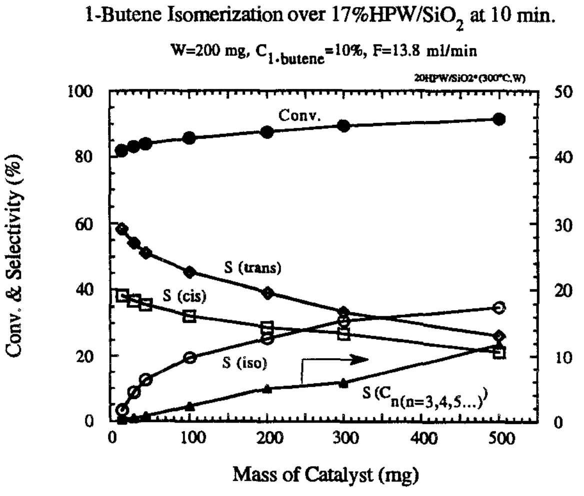


Fig. 3. Effect of residence time on conversion and selectivities.

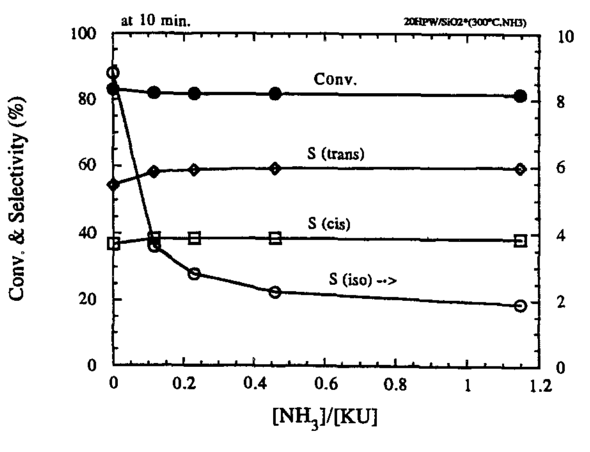


Fig. 5. Effect of poisoning by NH_3 prior to 1-butene reaction.

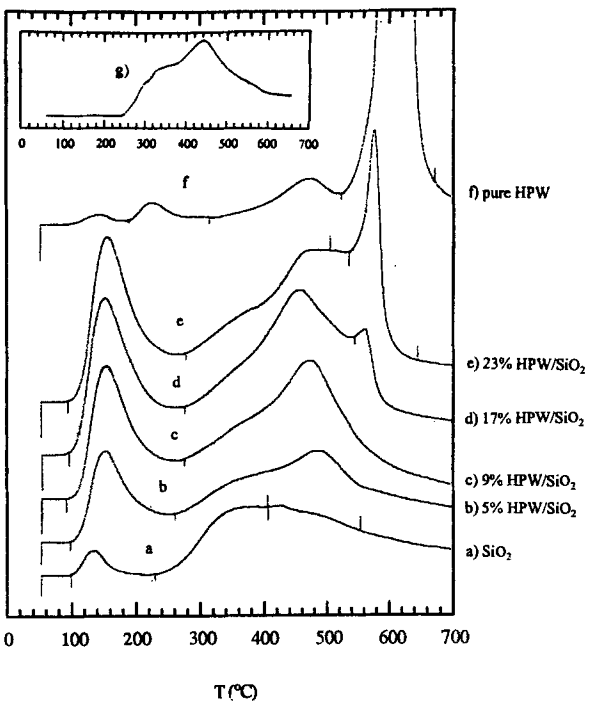


Fig. 6. Temperature programmed desorption of ammonia from (a) SiO_2, (b) 5% HPW/SiO_2, (c) 9% HPW/SiO_2, (d) 17% HPW/SiO_2, (e) 23% HPW/SiO_2, (f) pure HPW and (g) TPD of 15% HPW/SiO_2 not previously exposed to NH_3. $F(He) = 20$ ml/min. $dT/dt = 12$°C. After pretreatment in situ in helium flow at 200°C for 2 h, 3 × 10 ml of NH_3 was injected at 56°C followed by flushing at 56°C for 1 h.

four supported HPW/SiO_2 samples as well as pure HPW are shown in fig. 7. The continuous increase in the chemical shift as the loading increases is indicative of the changing environment of the proton and the acidic strengths.

^1H MAS NMR spectra are shown in fig. 8 for two loadings of HPW on SiO_2, both before and after exposure to 1-butene at 300°C. With each of the two samples, prior to exposure to 1-butene, a single relatively sharp peak is observed, with the 17% HPW/SiO_2 having a significantly higher chemical shift than that observed for the 5% HPW/SiO_2. After exposure to 1-butene, the peaks for each sample showed a shoulder and with each sample, the chemical shifts of the main peaks had decreased in magnitude.

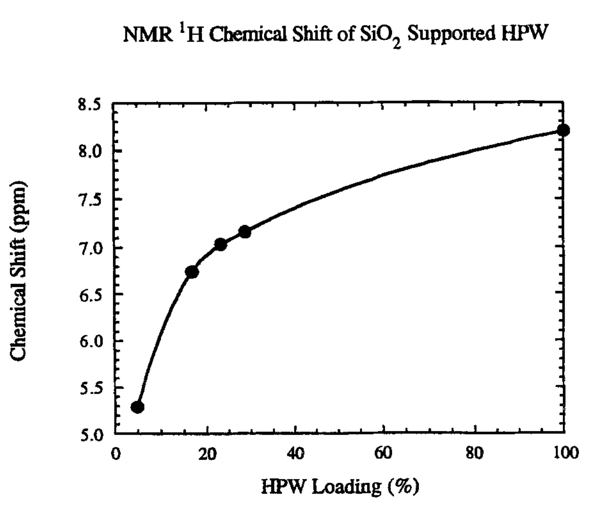


Fig. 7. ^1H MAS NMR chemical shifts for four loadings of HPW on SiO_2.

Infrared spectra of HPW before and after exposure to 1-butene displayed the series of bands in the region from 1100 to 800 cm^{-1} which are characteristic of the anions of Keggin structure (not shown). Infrared spectra of 13% HPW/SiO_2, obtained after exposure of the sample to 1-butene at room temperature show bands at 2962, 2933, 2875 and 2857 cm^{-1} which are attributed to asymmetric CH_3 stretching, asymmetric CH_2 stretching, symmetric CH_3 stretching and symmetric CH_2 stretching [56–58] (fig. 9). In gaseous 1-butene, three overlapping bands are evident at approximately 3080 cm^{-1} which have been attributed to the C–H asymmetric stretching vibrations in the $=CH_2$ group and consequently are indicative of the presence of olefinic groups [56,59]. Since these bands are not present in the spectra of the catalyst previously exposed to 1-butene, it is evident that olefinic groups are absent.

4. Discussion

Double-bond isomerization of 1-butene to cis- and trans-2-butene is evidently a facile process. This occurs at the lowest temperature employed in the present work (100°C) and shows little or no dependence on the loading of HPW on SiO_2 or the time during which the catalyst is in contact with the reactant.

In contrast, the formation of isobutene is strongly dependent on the loading, reaching a maximum of approximately 33% selectivity at 300–350°C and 23% HPW/SiO_2. Interestingly, a similar trend with catalyst loading was found for the partial oxidation of methane [60] and the oxidative dehydrogenation of ethane [61] on silica-supported metal–oxygen cluster compounds. Earlier work employing laser Raman spectroscopy (LRS), X-ray photoelectron spectroscopy and ^{31}P NMR spectroscopy 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% [62]. For loadings between this and 25%, aggregates begin to form, while at higher loadings particles of the acid are present. The results of both LRS and ^{31}P NMR spectroscopy show that the thermal stability of the highly dispersed heteropoly acid is enhanced as a result of the strong interaction between the supported material and the support [62].

Although a carbenium ion mechanism has frequently been invoked for the isomerization of 1-butene [15,16,18], Gielgens et al. [3,4] have recently noted that the formation of a primary carbenium ion is highly improbable [63,64] and that a bimolecular mechanism

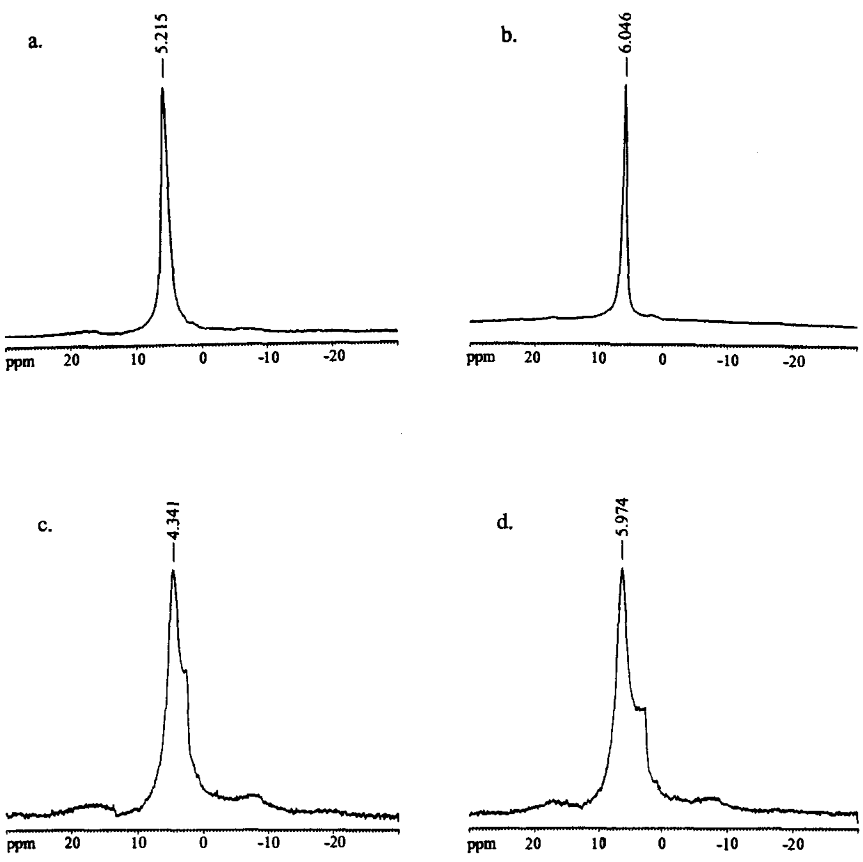
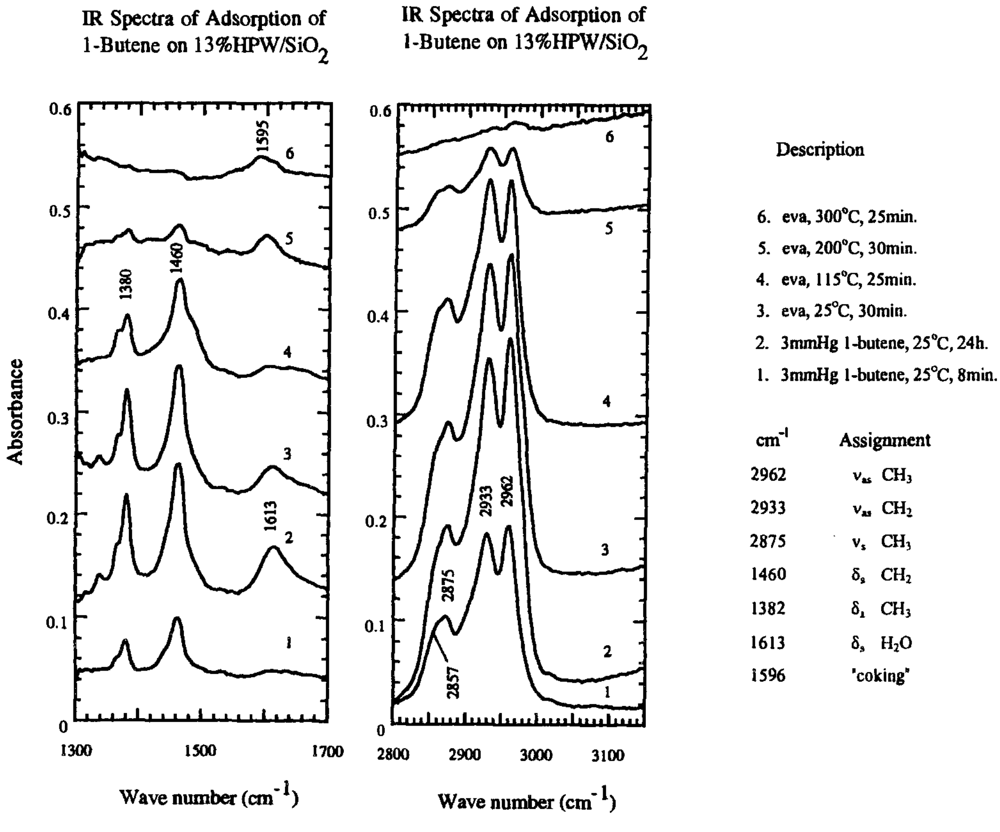


Fig. 8. ^{1}H MAS NMR spectra of 5% (a, c) and 17% (b, d) HPW/SiO$_2$ before (a, b) and after (c, d) exposure to 1-butene at 300°C for 2 h.



cm^{-1}	Assignment
2962	ν_{as} CH$_3$
2933	ν_{as} CH$_2$
2875	ν_s CH$_3$
1460	δ_s CH$_2$
1382	δ_s CH$_3$
1613	δ_s H$_2$O
1596	'coking'

Fig. 9. Infrared spectra of 13% HPW/SiO$_2$ after exposure to 1-butene.

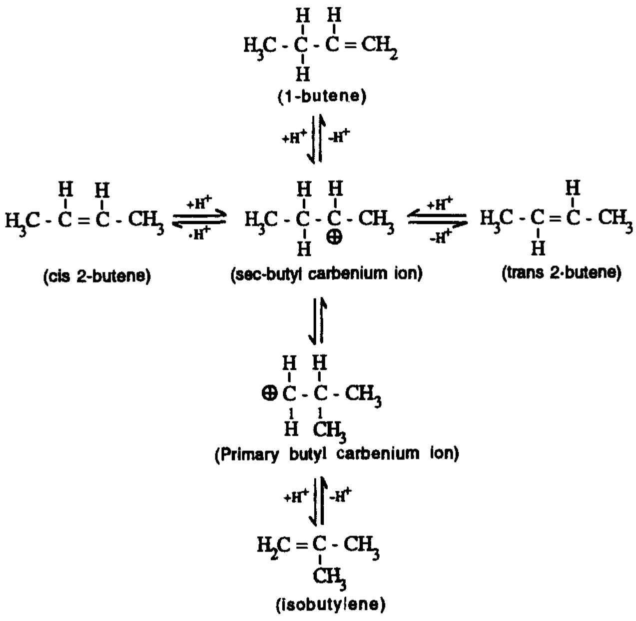


Fig. 10. Mechanistic scheme for 1-butene isomerization.

may be operative [65–67]. In their work with a series of oxides, both supported and unsupported, Cheng et al. [9,10] find evidence for the bimolecular mechanism but with the concomitant formation of products such as those containing three and five carbon atoms, but conclude that a monomolecular mechanism is dominant with their catalysts. In their most recent work on the isomerization on crystalline aluminophosphates, Gielgens et al. [3,4] find that metal-substituted aluminophosphates-11 (Me-$AlPO_4$-11) are active, selective and stable catalysts for the skeletal isomerization of 1-butene while the Me-$AlPO_4$-5 solids are not effective catalysts. They attribute the activity to a weakly acidic OH-group which may be placed near a Lewis acid site.

The observation that the selectivities to the cis- and trans-2-butenes decrease with increasing temperature while that to isobutene increases, the latter achieving a maximum while the former reach minima, suggests that the 2-butenes are precursors to isobutene. This conclusion is further supported by the results from experiments at different contact times. As the contact time increases, the selectivities to the 2-butenes decrease while that to isobutene increases, indicating that the former species are primary products while isobutene is a secondary product. An alternative interpretation which is equally consistent with these results may be proposed. Earlier photoacoustic FTIR studies have shown that the acidity of 12-tungstophosphoric acid can be attributed to Brønsted acid sites with little or no evidence of Lewis acid sites in these solids [68]. A common secondary carbenium ion may then be formed from 1-butene, cis- and trans-2-butene and an equilibrium established between these four species (fig. 10). Although the conversion of this secondary carbenium ion to a primary species is difficult [63,64], given the appropriate combination of circumstances, it is not impossible. As the temperature is increased and in the presence of appropriate properties of the surface, such as strong Brønsted acidic sites, the secondary to primary carbenium ion conversion can occur, through the usually invoked cyclopropane transition state, followed by loss of a proton to form isobutene. The secondary carbenium ions can be formed from the 2-butenes as well as from 1-butene by processes which will be fast in comparison with that in which the primary carbenium ions are generated. Thus, as the reaction temperature increases and the secondary carbenium ions are converted to primary species, the original four species equilibrium will be shifted away from 1-butene and the 2-butenes. The relative absence of dependence of the conversion on changes in the loading and reaction temperatures is consistent with the aforementioned explanation.

It is clear from the isomerization studies on the catalysts partially poisoned with NH_3 that the sites of highest acid strength are required for the formation of isobutene. It is also evident from the results of TPD experiments, that the quantity of NH_3 which is most tightly bound to the catalyst increases with the loading of the catalyst on the support. Since increasing values of the chemical shift δ_H have been shown to relate to increasing values of the acid strength [69], the ^1H MAS NMR spectra provide further evidence for the increase in the acidic strength with loading of the catalyst.

A number of additional processes are evidently occurring in the present work. The observation of C_3, C_4, C_5, …, C_8 species, although each with relatively small selectivities, suggest, as noted by Cheng et al. [9,10], that bimolecular processes may be occurring. Any octenes formed could crack into a variety of products including isobutene or form polymeric complexes which ultimately block the surface through the formation of coke. The accumulation of species possessing a band at 1590 cm^{-1} in the infrared spectra which is not removed on evacuation at 300°C suggests that the deactivation of the catalyst can be attributed to the formation of what is considered to be conventional coke on the surface of the catalyst.

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