J. Chem. Soc., Faraday Trans. 1, 1981, **77**, 3107-3117

Effect of Pretreatment on the Acidity of Heteropoly Compounds in Butene Isomerization

BY TSUNEO MATSUDA*, MASAHIRO SATO, TOMOAKI KANNO, HIROSHI MIURA AND KAZUO SUGIYAMA

Faculty of Engineering, Saitama University, 338 Urawa, Saitama, Japan

Received 26th January, 1981

On a variety of heteropoly compounds as catalysts the isomerization of but-1-ene and *cis*-but-2-ene was performed with the aim of examining the relationship between the acidic properties of the compounds and the method of pretreatment. Neither of the central atoms, P and Si, in the anions in these compounds affected the isomerization activity of but-1-ene, but the counter-cations and MoO_6 or WO_6 octahedra surrounding the central atom did affect the activity.

The *cis*-but-2-ene to *trans*-but-2-ene ratio was greater than 3 on the heteropolymolybdate catalysts pretreated at temperatures lower than 150 °C, and decreased with increasing pretreatment temperature until reaching a value of 1. In *cis*-but-2-ene isomerization Cu, Ni, Co and Mn salts of the heteropoly molybdates pretreated at 300 °C showed an increase in the ratio of *trans*-but-2-ene to but-1-ene, which corresponds to the formation of strongly acidic sites, while Ba and Sr salts did not show a pronounced increase in the ratio. A linear correlation between this ratio and the electronegativity of the salt counter-cation was seen in the pretreatment at 300 °C; the strongly acidic property is produced by the interaction of the counter-cation with the structural water, which is eliminated in the high-temperature range (200-250 °C) used in d.t.a.

But-2-enes containing deuterium were produced in the but-1-ene isomerization on the catalysts pretreated with D_2O, indicating that the structural water also correlated with the formation of acidic sites on the catalysts.

The use of heteropoly compounds in catalysis has been developed extensively; these uses include the oxidation of methacrolein to methacrylic acid,[1] the polymerization of benzyl alcohol,[2] the alcoholysis of epoxide,[3] the epoxidation of olefins[4] *etc.*[5] Considerable research into the catalytic properties of these compounds has also been reported recently.[6-9] There has also been a review of the preparations and properties of the compounds.[10] However, much research into their reaction mechanisms and catalytic properties is still needed.

The heteropoly compounds used in this study have the general formula $M_n[XN_{12}O_{40}]\cdot xH_2O$ where M is a counter-cation, X is a central P or Si atom, N is either molybdenum or tungsten and $n = 1$-3, corresponding to the valence of the counter-cation. x is the number of structural water molecules. The structure of the heteropoly anion, $[XN_{12}O_{40}]^{-3}$, in the compounds consists of a P or Si atom located at the centre of a tetrahedron, XO_4, which is surrounded by octahedra of MoO_6 or WO_6.[11] The roles of the central atoms and the structural water molecules in reactions where the compounds are used as catalysts have not been studied well. The heteropoly compounds have much structural water, which is easily removed by heat treatment in a number of stages.

The water appears to be associated with the development of acidic sites,[12] but which stage of water removal is related to which acidic site is still not clear. In the present study the correlation of acidity with pretreatment (heat treatment in a He stream) was examined in connection with the results of infrared spectroscopy, differential thermal analysis (d.t.a.), temperature-programmed desorption (t.p.d.), and but-1-ene and

cis-but-2-ene isomerization. The role of water was examined further with D_2O as the structural water. The heteropoly compounds have both acidic properties and oxidation activity.[13, 14] This study, however, was mainly concerned with the acidic properties.

EXPERIMENTAL

MATERIALS

Heteropoly compounds used as catalysts were prepared by literature methods.[13, 15, 16] The preparations are briefly described below. Dodecamolybdophosphoric acid, $H_3[PMo_{12}O_{40}]\cdot 14H_2O$ (I) was prepared from MoO_3 and H_3PO_4. Its salts were also prepared from (I) and carbonates of metals. Dodecatungstophosphoric acid, $H_3[PW_{12}O_{40}]$ was prepared from Na_2WO_4, Na_2HPO_4 and concentrated hydrochloric acid. Dodecamolybdo (or tungsto) silicic acid and its salts were prepared from sodium molybdate (or tungstate) and sodium silicate, and by the method similar to that used in the preparation of dodecamolybdophosphoric salts. The substituted compounds of molybdenum with vanadium, 11-, 10- and 9-molybdo-1-2- and 3-vanadophosphoric acids ($H_3[PMo_{11}VO_{40}]$, $H_3[PMo_{10}V_2O_{40}]$ and $H_3[PMo_9V_3O_{40}]$) were prepared according to a method described in the literature.[17] Once prepared, the catalyst samples were characterized with respect to elemental analysis (standard wet method), i.r.[18] and d.t.a.[16]

Commercial butenes (but-1-ene and *cis*-but-2-ene) were obtained from Kanto Kagaku Co., Inc. Their impurities were below 0.1% according to gas-chromatographic analysis. D_2O (Merck Sharp and Dohme, Canada) contained more than 99.7 atom % D. Reagents used in the reactions and in the synthesis of catalysts were all special grade from Wako Junyaku Co., Inc. They were used without further purification.

PROCEDURES

Isomerization of butenes was performed in a glass-tube reactor (5 mm i.d., 30 cm long) using a pulse method, with helium as the carrier gas. A 0.1-0.3 g sample of the catalyst was placed in the reactor and pretreated in a stream of dry He (20 $cm^3\ min^{-1}$) for 1 h at various temperatures *in situ* before the reaction. After the temperature of the catalyst bed was reduced to 80 °C, the reaction temperature, the feed of reactant was begun with a pulse of 0.25 cm^3. The reaction mixtures in both the isomerization of butenes and the dehydration of isopropyl alcohol were analysed by gas chromatography on a column of propylene carbonate (4 m at 0 °C) and polyethylene glycol 4000 (3 m at 100 °C), respectively. Analysis of the isomerization products containing deuterium was made with a mass spectrometer (Varian NEVA NAG-110). Temperature-programmed desorption (t.p.d.) of adsorbed ammonia consisted of a step-wise heating procedure (5 °C min^{-1}) under flowing N_2 or evacuation from room temperature to 450 °C. Brönsted and Lewis acids were determined from the infrared spectra (Jasco model E-3) of pyridine adsorbed for 1 h under its vapour pressure at room temperature and then evacuated for 30 min at 120 °C. Before the adsorption of pyridine powdered KBr was pressed into a thin disc of 1.5 cm diameter. A few drops of aqueous solution of the heteropoly compounds were placed on the disc and mounted in a quartz glass cell equipped with KBr windows and then evacuated for 1 h at various pretreatment temperatures. In an effort to examine the role of the structural water the catalyst containing D_2O was prepared as follows. The catalyst (0.2 g) was treated in a helium stream for 1 h at 300 °C because the water could be almost completely removed at that temperature; this was confirmed by d.t.a. After cooling the catalyst to room temperature, D_2O (*ca.* 30 mm^3) was gradually introduced. After treating it again at 300 °C in He, almost the same amount of D_2O as before was also introduced onto the catalyst, thus providing a catalyst containing D_2O as almost all the structural water. The catalyst was pretreated at 150 or 300 °C in He, followed by the isomerization of but-1-ene at 80 °C.

RESULTS AND DISCUSSION

The role of the central atoms in the but-1-ene isomerization was first examined. As shown in fig. 1 both central atoms (P and Si) did not affect the activity, because

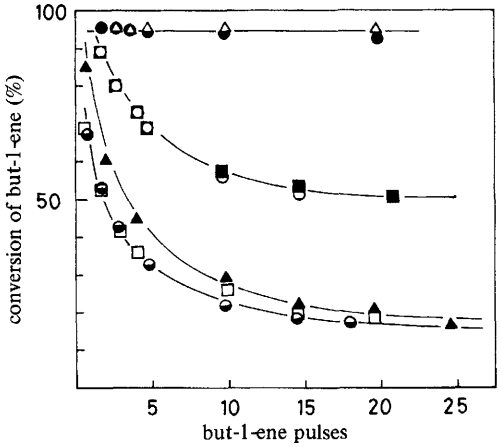

FIG. 1.—Effect of central atoms and of pretreatment temperature on but-1-ene isomerization. Pretreatment temperature 200 °C, catalyst 0.3 g. ●, $H_3[PW_{12}O_{40}]$; △, $H_3[SiW_{12}O_{40}]$; ○, $H_3[PMo_{12}O_{40}]$; ■, $H_3[SiMo_{12}O_{40}]$; ▲, $Co_3[SiMo_{12}O_{40}]_2$ (pretreatment temperature 200 °C); □, $Co_2[SiMo_{12}O_{40}]_2$ (pretreatment temperature 300 °C); ◒, $Co_3[PMo_{12}O_{40}]$ (pretreatment temperature 300 °C). The amount of structural water is abbreviated in the formulae of the catalysts cited above.

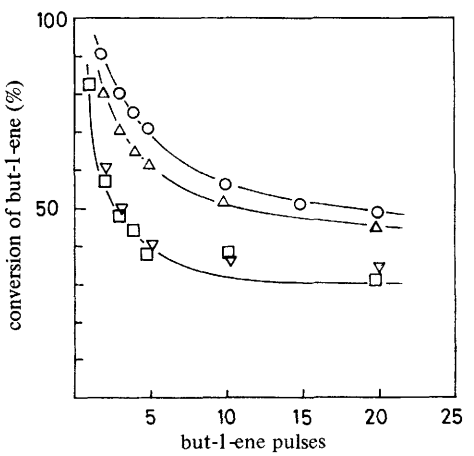

FIG. 2.—Isomerization of but-1-ene on molybdovanadophosphate catalysts. Pretreatment temperature 200 °C, catalyst 0.3 g. ○, $H_3[PMo_{12}O_{40}]$; △, $H_3[PMo_{11}VO_{40}]$; ▽, $H_3[PMo_{10}V_2O_{40}]$; □, $H_3[PMo_9V30_{40}]$.

the relation between the conversion of but-1-ene and the number of pulses can be drawn with only one curve at the same pretreatment temperature. The behaviour of but-1-ene isomerization is clearly different on the catalysts containing Mo or W. This demonstrates that the MoO_6 or WO_6 octahedra surrounding the tetrahedron of PO_4 or SiO_4 affect the catalytic or acidic sites on which the isomerization of but-1-ene proceeds.[19] When one in twelve of the molybdenum atoms in the heteropoly anion was displaced by vanadium, the activity decreased as shown in fig. 2. On the displacement of more than two, however, the decrease in the activity ceased. The vanadium atom should decrease the concentration of active or acidic sites and thus

does not lead to an increase in activity. The *cis*-but-2-ene to *trans*-but-2-ene ratio (*cis*/*trans*) was *ca.* 1.2 for all catalysts containing vanadium. This indicates that the number of acidic sites on the surface is not changed by the number of vanadium atoms substituted for molybdenum.

Since the central atom is surrounded by four tetrahedral oxygen atoms and further by twelve MoO_6 or WO_6 octahedra which share corners or edges (or both) with it, the catalytic action of the atom may be shielded by the octahedra, showing no difference in isomerization activity on changing the central atom. Heteropoly tungstic acids did not show a decline in the activity with the number of pulses, as did the heteropoly molybdic acids. The difference in this reaction behaviour is still not clear, but the cause may be that the former is more stable than the latter.[20] The *cis*/*trans* ratio for the reaction on the heteropolymolybdates gradually approaches 1 from its high ratio on increasing the pretreatment temperature to 300 °C, as shown in fig. 3, while in the reaction on the heteropolytungstates the ratio attained a constant

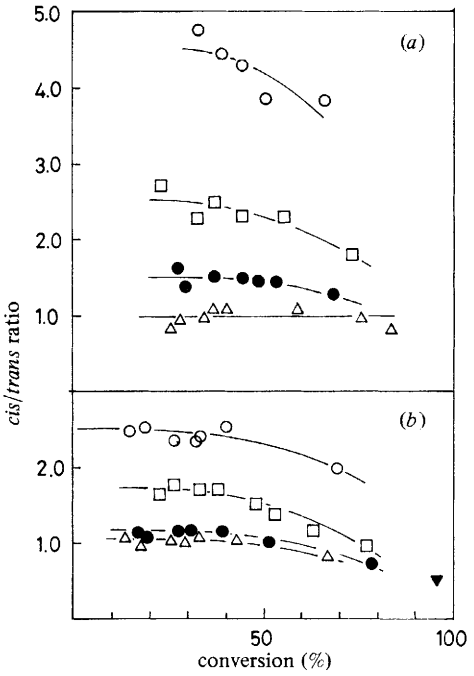

FIG. 3.—Isomerization of but-1-ene on Ni- and Co-heteropolymolybdate catalysts showing the relation between *cis*- to *trans*-but-2-ene ratio and pretreatment temperature. (*a*) $Ni_3[PMo_{12}O_{40}]_2$, catalyst 0.3 g: ○, 80; □, 130; ●, 180; △, 300 °C. (*b*) $Co_3[PMo_{12}O_{40}]_2$, catalyst 0.3 g: ○, 100; □, 140; ●, 190; △, 300 °C; ▼, $H_3[PW_{12}O_{40}]$, catalyst 0.2 g, pretreatment temperature 200 °C.

value of *ca.* 0.5, which was nearly an equilibrium value, owing to their high activity. The value of 1 for the ratio indicates that the acid sites responsible for the catalytic activity are protonic in nature, *i.e.* the reaction proceeds *via* a carbonium ion mechanism.[19, 21] Such a high ratio obtained on Ni and Co salts treated at temperatures below 150 °C (as shown in fig. 3) can be also obtained on such basic solid catalysts as MgO, CaO and Al_2O_3.[22] Consequently the high ratio was considered at first to be responsible for the basic nature of the catalysts, which will be gradually diminished

with increasing temperature of the pretreatment. In order to poison the basic sites on the catalysts pretreated at a lower temperature the adsorption of such acidic compounds as acetic acid was carried out, but there was almost no adsorption, indicating that the concentration of basic sites was very low. It was known that in the dehydration of isopropyl alcohol acetone is produced by the cooperation of both acidic and basic sites on the catalyst.[23] In the dehydration on the Ni-heteropolymolybdate catalyst acetone and propylene were also produced, although the conversion to acetone was very low. It is therefore considered that basic sites exist on the catalyst to some extent. On the catalyst treated with acetic acid both activity and selectivity to acetone decreased slightly as shown in fig. 4. It is clear that acetic

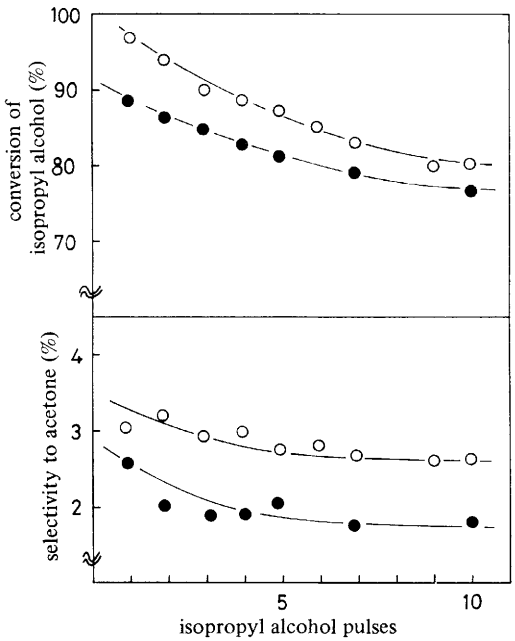

FIG. 4.—Dehydration of isopropyl alcohol. Pretreatment temperature 150 °C, catalyst 0.2 g: ●, poisoned with acetic acid, 10 mm³; ○, unpoisoned.

acid will poison the catalyst to some extent. The isomerization of but-1-ene, however, on the same poisoned catalyst showed almost the same results as the unpoisoned catalyst (see fig. 5), *i.e.* the concentration of basic sites may be so small that the effect on but-1-ene isomerization is negligible. It is therefore difficult to consider that the basic sites were responsible for the high *cis/trans* ratio on the catalysts pretreated at low temperatures. The following consideration seems rational. There may exist no strongly acidic sites on the catalysts pretreated at low temperature, which could selectively give the *trans* isomer as discussed later. On the other hand, heteropoly-tungstates have stronger acidic properties and higher activities than heteropolymolybdate.[24] This property may be favourable for the formation of the *trans* isomer, which will be responsible for the *cis/trans* ratio of 0.5 (see fig. 3). The catalysts pretreated at low temperature were weakly acidic and low in activity, which may be favourable for the formation of the *cis* isomer, thus producing the high *cis/trans* isomer ratio. With increasing pretreatment temperature the amount of active

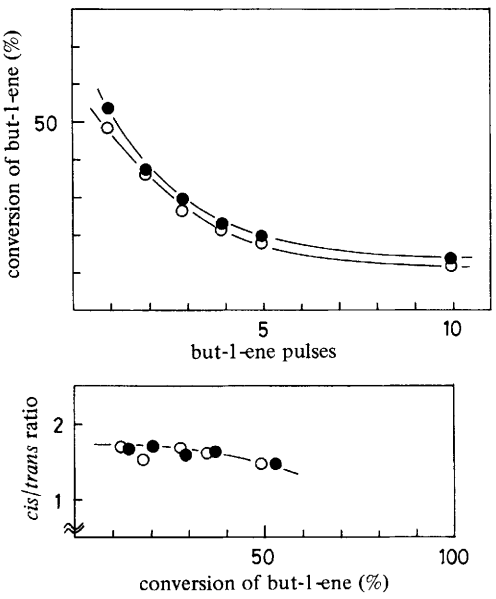

FIG. 5.—Isomerization of but-1-ene on the Ni-hetropolymolybdate catalyst adsorbed with acetic acid showing the variation *cis*- to *trans*-but-2-ene ratio with conversion.

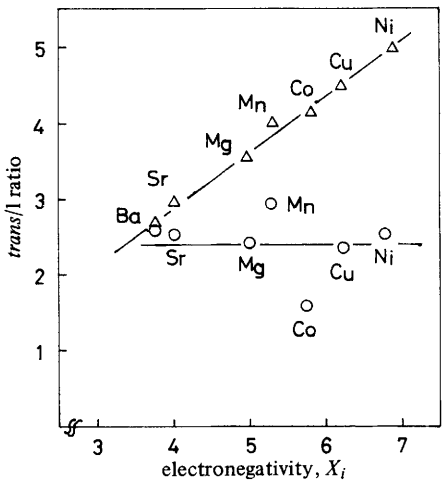

FIG. 6.—Relation between *trans*-but-2-ene/but-1-ene ratio and the electronegativity of the counter-cations in *cis*-but-2-ene isomerization: △, pretreatment at 300 °C; ○, pretreatment at 150 °C.

or acidic sites increases to attain a maximum at 150-200 °C, showing the highest activity.[25] On further increasing the temperature the amount of the acidic sites will be diminished, while the site will be converted to one that is strongly acidic; this was confirmed by *cis*-but-2-ene isomerization as follows. For the reaction on a variety of heteropolymolybdates, the relation between electronegativity[26] of the counter-cations substituted by metals and the *trans*-but-2-ene to but-1-ene ratio (*trans*/1) is plotted

in fig. 6. A linear correlation was obtained on the catalysts pretreated at 300 °C, but no correlation exists for those pretreated at 150 °C. In the isomerization on Cu-, Ni- and Co-heteropolymolybdates the relative value of the *trans*/1 ratio increased remarkably. This may be due to the formation of strongly acidic sites, in comparison with the results of *cis*-but-2-ene isomerization on metal sulphates.[27] Ba and Sr salts, however, exhibited almost no increase in the *trans*/1 ratio. The acid sites will be formed by the interaction between the counter-cations and the structural water; the cation brings about the polarization of the water by the following scheme

$$M_n[PMo_{12}O_{40}]\cdot H_2O \rightarrow [MOH^-]\ H^+[PMo_{12}O_{40}]$$

(in this example only one molecule of water and molybdophosphate anion is shown). The higher the electronegativity of the cations, the stronger their tendency to attract the OH^- anion, thus producing a strongly acidic site by an increase in the protonic nature of H^+. In both the Ba and Sr salts thus produced, MOH may be so strong in the basic sites that the polarization of H^+ will be low or MOH will strongly attract H^+, so that no formation of the strongly acidic sites may occur at either pretreatment temperature.

Pyridine vapour was adsorbed on the nickel heteropolymolybdate pretreated at both 150 and 300 °C. The results of infrared measurements are shown in fig. 7.

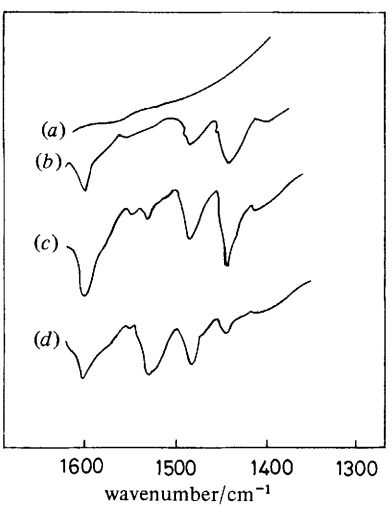

FIG. 7.—Infrared spectra of the adsorbed pyridine on $Ni_3[PMo_{12}O_{40}]_2$: (*a*) background, (*b*) pretreated at 150 °C, (*c*) 200 °C and (*d*) 300 °C.

Absorptions assigned to Lewis-acidic sites (1450 cm^{-1}) and Brönsted-(protonic) acid sites (1540 cm^{-1}) were found on the Ni salt pretreated at > 200 °C. Only Lewis-acidic sites were found following the pretreatment at 150 °C, but the number of sites decreased on increasing the pretreatment temperature and the number of protonic acid sites increased. Much of the structural water still remains on the catalyst pretreated at 150 °C and it may inhibit the adsorption of pyridine on the protonic acid sites; we considered that the protonic acid sites could not be detected despite their existence. The *cis*/*trans* ratio in but-1-ene isomerization attains 2 on the Lewis-acid sites.[27] Both the Ni salt pretreated at 180 °C and Co salt pretreated at 140 °C (see fig. 3) exhibited a ratio between 1 and 2, since both Lewis- and protonic acid sites are considered to exist on these catalysts. The Lewis-acidic site may exist on the counter-cation to attract

an electron pair and on increasing the pretreatment temperature it may interact with the structural water to be converted to the protonic acid sites.

On the catalysts containing structural water substituted by D_2O the isomerization of but-1-ene was performed. The results of the analysis of but-2-ene obtained are shown in fig. 8. A relatively high ratio of [$^2H_1$]butene ($= k_{57}$) to [$^2H_0$]butene ($= k_{56}$) was

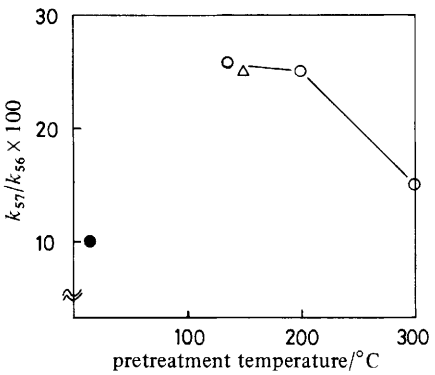

FIG. 8.—Isomerization of but-1-ene on the catalysts treated with D_2O, showing the variation of k_{57}/k_{56} with pretreatment temperature: ●, background; ○, $Ni_3[PMo_{12}O_{40}]$; △, $Co_3[PMo_{12}O_{40}]_2$.

found on the catalysts pretreated at 150 °C; here k_{57} and k_{56} indicate the peak heights of molecular weight 57 and 56, respectively, in the mass-spectrometric measurement. The ratio was low on the catalysts pretreated at 300 °C. The high ratio in the former is due to the larger concentration of the protonic acid sites than in the latter. In these reactions butenes substituted with two deuterium atoms could not be found. It was confirmed that the structural water is connected with the formation of the acidic site.

Differential thermal analysis of the heteropolymolybdates (except heteropoly acids) shows two main peaks of desorbed water; one appears at around 100 °C and the other from 200 to 250 °C. These results agree well with results in the literature.[16] The former may be physically absorbed water. The water desorbed at the higher temperature may be strongly bound to the heteropoly compounds or may exist in the bulk of the compounds and, when it is eliminated by the heat treatment at 300 °C, the strongly acidic sites will be formed by the interaction of the counter-cation with desorbed water. The nature of the acidic sites will also convert from Lewis-acidic to protonic by the interaction, which was confirmed by infrared measurements as already described.

T.p.d. analysis of ammonia adsorbed on Ba, Co and Cu heteropolymolybdate catalysts was carried out. The results are shown in fig. 9(*a*) and (*b*). The Ba salts pretreated at 150 and 300 °C, showed a desorbed peak at 365 °C in either case and there was no shift in the desorbed peak on the catalyst pretreated at 300 °C, indicating no formation of strongly acidic sites. The above three catalysts showed a desorbed peak at *ca.* 420 °C in every case. The heteropolymolybdates are less stable at temperatures higher than 400 °C;[16] this instability was also confirmed by d.t.a. The exothermic peak which could be ascribed to the decomposition was found at *ca.* 420 °C in the catalysts examined in this study. Therefore, for the peak at 420 °C it is doubtful whether the desorbed ammonia definitely comes from the acidic site or not. The Co and Cu salts, on the other hand, did not show a desorbed peak at 365 °C; this indicates that both Co and Cu salts have stronger acidic sites than the Ba salt. Since the Co and Cu salts pretreated at 150 and 300 °C showed only one peak desorbed at 420 °C,

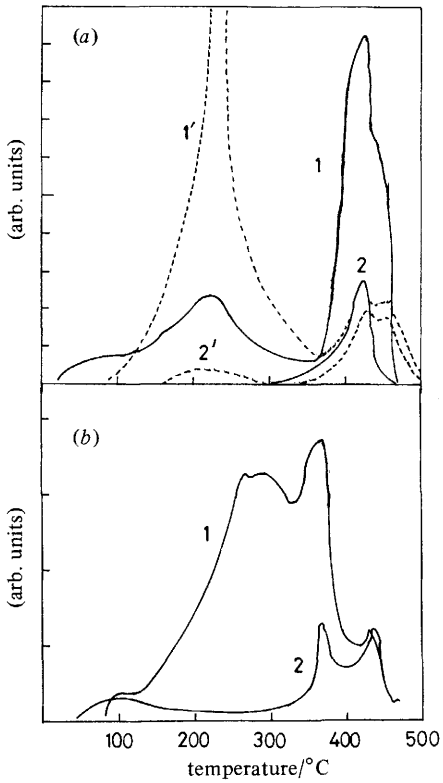

FIG. 9.—Temperature-programmed desorption diagrams (adsorbate ammonia gas): (*a*) (——) $Cu_3[PMo_{12}O_{40}]_2$, (-----) $Co_3[PMo_{12}O_{40}]$; (*b*) $Ba_3[PMo_{12}O_{40}]$. 1, 1′, pretreated at 150 °C; 2, 2′, pretreated at 300 °C.

the formation of the strongly acidic sites by the pretreatment at 300 °C could not be confirmed by the t.p.d. method. The peak desorbed at *ca.* 200 °C may be due to structural water, because the peak could not be found in the catalysts pretreated at 300 °C and the t.p.d analysis of the catalysts themselves (no adsorbed ammonia) also showed the desorption peak at *ca.* 200 °C. Ammonia will penetrate so deeply into the bulk of the heteropoly compounds[28] that it cannot easily be desorbed in the flowing atmosphere of nitrogen. Consequently the desorption method under evacuating conditions seems to be favourable. As shown in fig. 10, the desorbed peaks at near 110 and 100 °C in the evacuation method were found on the Ni salt catalysts pretreated at 300 and 200 °C. Thus, in this method ammonia can be desorbed at a lower temperature. The difference in the pretreatment temperatures by 100 °C produced a shift in the desorbed peak of *ca.* 10 °C, thus producing strongly acidic sites in the pretreatment at the higher temperature. In this method no desorption peak could found by heating to 350 °C.

One can largely separate the structural water into two parts as already mentioned for d.t.a.; the one binding weakly and existing in a shallow site within the bulk and the other binding strongly and existing in a deeper position in the bulk. They are both concerned with the formation of acidic sites, the latter especially relating to that of the strongly acidic sites. In the measurement of acidity by the adsorption method it

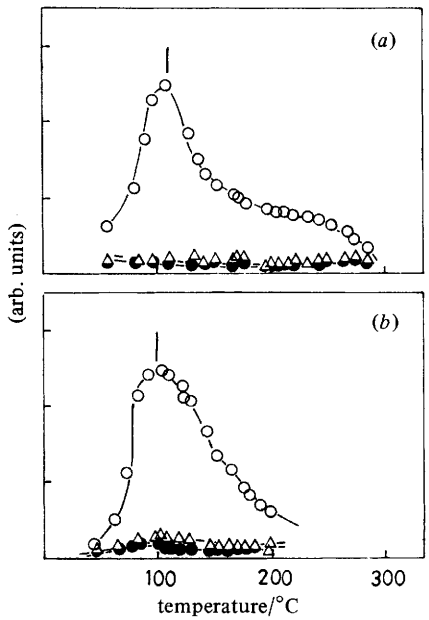

FIG. 10.—Temperature-programmed desorption diagrams measured by the evacuation method (adsorbate ammonia gas, catalyst $Ni_3[PMo_{12}O_{40}]$): (*a*) pretreatment temperature 300 °C; (*b*) pretreatment temperature 200 °C. ○, Desorbed curve of molecular weight of 17 due to NH_3; △, Desorbed curve of molecular weight of 18 due to H_2O; ●, Desorbed curve of molecular weight of 28 due to N_2.

is reported that adsorbates such as ammonia or pyridine will penetrate into the bulk of the heteropoly compounds.[28] Thus, since the bulk is considered to participate in adsorption and subsequent reactions, it appears to be very difficult to measure the acidity of the compounds correctly. It is also difficult to apply the titration method of indicators because the heteropoly compounds (except the tungstates) are coloured.

The surface area of heteropolymolybdic acid increases on pretreatment by more than 10 times,[7] but some salts do not increase so much as the acid or are unchanged. The cause of the change in surface area is still obscure, although the structural water may perhaps take part in it. This problem requires further investigation.

[1] T. Ohara, *Shokubai*, 1979, **19**, 157.
[2] K. Nomiya, T. Ueno and M. Miwa, *Bull. Chem. Soc. Jpn*, 1980, **53**, 827.
[3] Y. Izumi and K. Hayashi, *Chem. Lett.*, 1980, 787.
[4] M. N. Sheng and J. G. Zajeceh, *Adv. Chem. Ser.*, 1968, **57**, 418.
[5] For alkylation: R. T. Sebulsky and A. M Henke, *Ind. Eng. Chem., Process Des. Dev.*, 1971, **10**, 272. For the preparation of saturated carbonyl compounds: *Brit. Pat.*, 1965, 990639.
[6] M. Ohtake and T. Onoda, *Shokubai*, 1975, **17**, 13, 1976, **18**, 169.
[7] M. Misono, Y. Konishi, M. Furuta and Y. Yoneda, *Chem. Lett.*, 1978. 709.
[8] M. Furuta, K. Sakata, M. Misono and Y. Yoneda, *Chem. Lett.*, 1979, 31.
[9] H. Tsuneki, H. Niiyama and E. Echigoya, *Chem. Lett.*, 1978, 645.
[10] G. A. Tsigdinos, *Topics in Current Chemistry* (Springer, Berlin, 1978), vol. 76.
[11] G. A. Tsigdinos, *Topics in Current Chemistry* (Springer, Berlin, 1978), vol. 76, pp. 15–17.
[12] H. Niiyama, Y. Saito and E. Echigoya, *Proc. 7th Int. Congr. Catalysis*, Tokyo, 1980, reprint C13.
[13] G. A. Tsigdinos, *Molybdenum Chemicals, Bulletins Cdb-12a* (Climax Molybdenum Co., 1969).
[14] M. Ai, *Shokubai*, 1980, **22**, 13.

[15] E. O. North and W. Haney, *Inorganic Synthesis* (McGraw Hill, New York, 1939), vol. 1, pp. 127 and 132.
[16] G. A. Tsigdinos, *Ind. Eng. Chem., Process Des. Dev.*, 1974, **13**, 267.
[17] G. A. Tsigdinos and I. Hallada, *Inorg. Chem.*, 1968, **7**, 437.
[18] C. Rocchicclobi-Deltcheff, R. Thouvenot and R. Franck, *Spectrochim. Acta, Part A*, 1976, **32**, 587.
[19] K. Tanabe, *Shokubai no Hataraki* (*Functions of Catalysts*), (Kodansha, Tokyo, 1974), p. 19.
[20] G. A. Tsigdinos, *Topics in Current Chemistry* (Springer, Berlin, 1978), vol. 76, p. 12.
[21] J. W. Hightower and W. K. Hall, *Chem. Eng. Progr., Symp. Ser.* 1967, **63**, 122.
[22] H. Hattori, N. Yoshii and K. Tanabe, *Proc. 5th Int. Congr. Catalysis*, Palm Beach, 1973, reprint no. 10.
[23] M. Ai, *Bull. Jpn Petrol. Inst.*, 1976, **18**, 50.
[24] M. Ohtake and T. Onoda, *Shokubai*, 1975, **17**, 13P.
[25] T. Matsuda, H. Miura, K. Sugiyama and M. Sato, 44*th Catalysis Congr. Japan*, Fukuoka, 1979, reprint 4R 12.
[26] M. Misono, E. Ochiai, Y. Saito and Y. Yoneda. *J. Inorg. Nucl. Chem.*, 1967, **29**, 2635.
[27] M. Misono, Y. Saito and Y. Yoneda, *J. Catal.*, 1967, **9**, 135.
[28] M. Misono, K. Sakata and Y. Yoneda, *Proc. 7th Int. Contr. Catalysis*, Tokyo, 1980, reprint B27.

(PAPER 1/113)