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A Comparative Catalytic Study of Stoichiometric Metal Phosphates

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The stoichiometric orthophosphates of aluminum, calcium, chromium, iron, cobalt, nickel, and bismuth were prepared and their activities in the isomerization of 2,3-dimethylbut-1-ene (231), 2,3-dimethylbut-2-ene (232), and 3,3-dimethylbut-1-ene (331) have been measured. The activities of these catalysts for the isomerization 231 $\rightleftarrows$ 232 were correlated with the acidity as estimated from the adsorption of ammonia and with the partial charges of the phosphate oxygen atoms.

INTRODUCTION

The catalytic properties of phosphates, both stoichiometric and nonstoichiometric, have recently been reviewed (*1*). Although considerable work has been done on catalysts containing phosphorus, relatively few reports of studies of the effect of the cation or metal in such materials have appeared. Earlier, a number of orthophosphates were evaluated for their activity in the dehydration of isopropyl alcohol (*2*). Somewhat more recently, the isomerization of propylene oxide was carried out on phosphates of lithium (and with sodium and potassium), aluminum, magnesium, and calcium (*3*). The activity of phosphates has also been determined with the oxidative dehydroaromatization of propylene (*4*). In the present work the stoichiometric phosphates of aluminum, calcium, chromium, iron, cobalt, nickel, and bismuth are prepared and a number of properties are examined. The isomerization of dimethylbutenes is employed as a test reaction for catalytic activity.

EXPERIMENTAL

Catalysts. The stoichiometric metal phosphates were prepared by precipitation reactions in aqueous solution (*5*). Each of the phosphates, with the exception of aluminum and bismuth, was prepared by two methods. An aqueous solution of a salt of the metal cation and either an aqueous solution of disodium hydrogen phosphate (method 1) or phosphoric acid (method 2) were employed. Aluminum phosphate was prepared by one of the methods of Kearby (*6*).

Materials. Aluminum chloride, bismuth trichloride, calcium chloride, chromium nitrate, cobalt chloride, and nickel nitrate were obtained as "Baker Analyzed" from J. T. Baker Chemical Co. Ferric chloride was purchased from Pennwalt Corp. Di-ammonium hydrogen orthophosphate was obtained as "Analytical" from BDH Chemicals. Molybdic acid was obtained as 85%, powder, A.C.S. certified from Matheson, Coleman and Bell. Phosphoric acid, 85% certified A.C.S., was purchased from Fisher Scientific Co. 2,3-Dimethylbut-1-ene (99.9%) and 2,3-dimethylbut-2-ene (99%) were obtained from Chemical Samples Co. and 3,3-dimethylbut-1-ene (95%) was purchased from Aldrich Chemical Co. All chemicals were used as received.

Methods. The catalysts were heated under 10^{-3} Torr at 150°C for 24 hr prior to use. A microcatalytic pulse reactor was employed for all activity measurements at 150°C. A 6-ft column of 35% propylene carbonate on Chromosorb P (80/100 mesh) was

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used at room temperature for the chromatographic analysis. Preliminary experiments were employed to establish suitable reaction operating conditions as 120 ml/min helium flow rate and catalyst mass of 50 mg to minimize secondary reactions and eliminate mass transfer problems. With this relatively small mass of catalyst it is considered that any errors due to packing differences between catalyst samples will be minimized. Experimental reproducibility in the reactor studies was approximately 1%. Mass balances were correct to 5–10%. The BET (N_2) surface areas were measured at liquid nitrogen temperatures with a Cahn electrobalance attached to a standard vacuum system. Quantities of ammonia and carbon dioxide chemisorbed were obtained with a quartz spring at room temperature by first exposing the evacuated sample to pressures of the adsorbate, followed by evacuation to remove the physically adsorbed gas. The increase in weight measured after pumping was taken as the amount chemisorbed.

RESULTS

The surface areas of the various phosphates as prepared by the two methods and after heating are summarized in Fig. 1 except for the cobalt phosphate catalyst prepared by method 2 which had a negligible surface area. With all the catalysts except that containing iron the surface areas obtained from both methods of preparation are similar. In the case of iron, the surface areas from the two preparations are 13.1 and 96.8 m²/g. Aluminum phosphate has the highest surface area of those phosphates examined, and there is an overall trend to smaller surface areas as the atomic number of the metal or cation increases. However, iron phosphate, as prepared by method 2, has a significantly higher area than the remaining solids, except for aluminum.

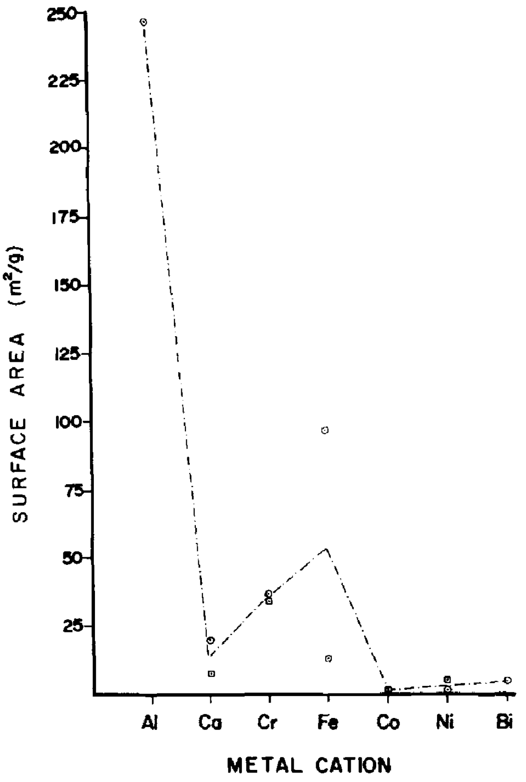


FIG. 1. Surface area of phosphates (phosphates prepared by method 1, ⊡, and by method 2, ⊙).

The activity per unit mass of the metal phosphates in the isomerization of the dimethylbutenes 231, 232, and 331 at 150°C is summarized in Fig. 2. With the exception of chromium phosphate, the metal phosphates are nearly inactive in the isomerization of 331. The activity of chromium phosphate from preparation method 1 is higher in the 331 isomerization than is that from method 2. It should be noted that the molar ratios of 231/232 produced from 331 are 0.24 and 0.13, from preparations 1 and 2, respectively, of chromium phosphate. The equilibrium ratio is 0.36 at 150°C.

All of the phosphates, with the exception of bismuth, show activity in the isomerization of 231. Aluminum, chromium, and iron phosphate prepared by method 2 produce approximately equilibrium concentrations of 231 and 232. On calcium phosphate 22% conversion of 231 is obtained from preparation 2, but no conversion from preparation 1. With cobalt and nickel phosphates the products from preparation 1 are found to be more active than those from method 2. About 45% of 231 is converted to 232 on the

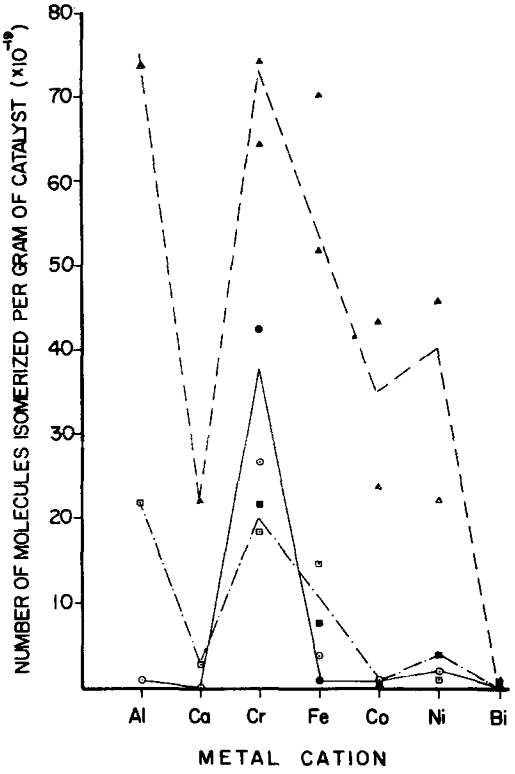


FIG. 2. Number of molecules isomerized per gram of catalyst (reactant: 331, ⊙; 231, △; 232, ⊡). Solid symbols: preparation method 1; open symbols: preparation method 2.

cobalt and nickel phosphates prepared by method 1 while only 22% conversion is observed on the products from method 2. In all cases, negligible amounts of 331 were produced.

In the isomerization of 232, aluminum phosphate and both chromium phosphates show the highest activity. With these catalysts the product compositions are close to the equilibrium values. The two iron phosphate products also show some activity with that from method 2 being more active than that from method 1. The remaining phosphates show little or no activity for the isomerization of 232.

The quantities of ammonia chemisorbed on the various catalysts are shown on both a unit mass and a unit area basis in Fig. 3. Per unit mass, aluminum, iron, and chromium catalysts chemisorb the largest amounts of ammonia, while on a unit area basis, cobalt and bismuth chemisorb the largest quantities.

The aluminum, calcium, chromium, and bismuth catalysts chemisorb negligible quantities of carbon dioxide. However, the iron, cobalt, and nickel catalysts chemisorbed small but significant quantities of carbon dioxide, namely, 1.4, 41.0, and 29.0 $(\times 10^{+17})$ molecules/m^2 of catalyst, respectively.

DISCUSSION

The isomerization of the dimethylbutenes, 231, 232, and 331, is usually considered as occurring through a carbonium ion mechanism on acidic catalysts (*7*), although a concomitant allylic process has been suggested for γ-alumina activated at 723°K (*8*). The carbonium ion mechanism may be represented as shown in Scheme 1. With the carbonium ion mechanism, a secondary carbonium ion forms from 331. Since secondary carbonium ions are less stable than the tertiary ions, the secondary ion will re-

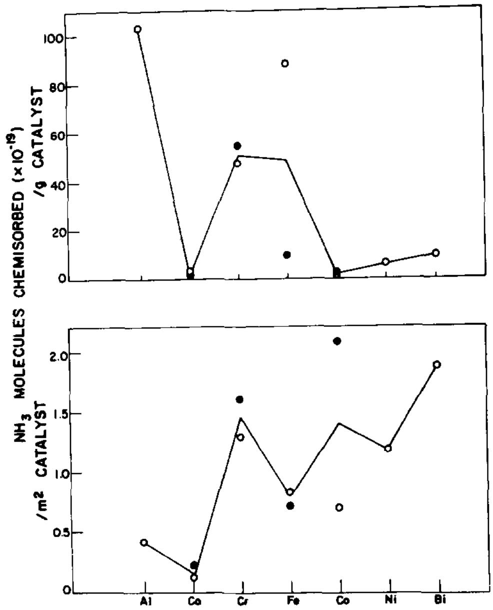
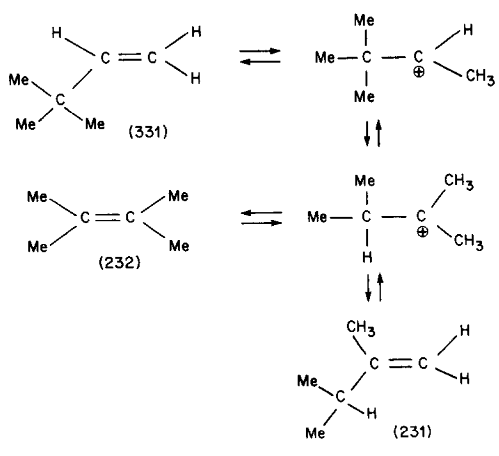


FIG. 3. Number of NH_3 molecules chemisorbed per g and per m^2 of catalyst. Solid and open symbols: preparation methods 1 and 2, respectively.



SCHEME 1

quire more energy to be formed and thus will occur less readily. If the secondary species forms, a 1,2-methyl-hydrogen shift would be required to produce the more stable tertiary species. Since the tertiary species should form directly from either 231 or 232, it is apparent that the 231 ⇄ 232 isomerization should occur more readily than the isomerization of 331.

The extent of the isomerization of each of 231, 232, and 331 shown in Fig. 2 provides support for this mechanism. 231 isomerizes more readily than either of the two isomeric forms, while the isomerization of 331 is practically zero. There is however one interesting exception which occurs with chromium phosphate. With this phosphate the isomerization of 231, as with the other catalysts, occurs to the largest extent of the three isomeric forms, while the isomerization of 331 occurs more readily than that of 232, unlike the observations with any of the remaining catalysts. Although it is not possible from the present evidence to provide an explanation for this result, it is possible that more than one mechanism may be occurring in this case.

With the present catalysts, the quantity of 231 and 232 isomerized can be related to the amount of ammonia chemisorbed, both expressed per unit mass (Fig. 4). As the amount of ammonia chemisorbed increases, the amounts of either isomer which is converted increase. The quantity of 231 isomerized to 232 displays a rather steep increase for relatively small amounts of ammonia chemisorbed, and then levels off at an isomerization of approximately 70–75%, a value close to the equilibrium composition for 231 and 232. The isomerization of 232 shows a more gradual increase with the quantity of ammonia chemisorbed, reaching a nearly constant value of approximately 20% for catalysts which chemisorb more than 40 × 10^{19} molecules of NH_3 per gram. This dependence of the isomerization on the number of acidic sites on the catalyst provides further evidence in support of the carbonium ion mechanism.

It is interesting to attempt to relate the activity of these catalysts to a bulk property of the solid. It has been shown that the activity can be correlated with the acidity and thus a relation between the acidity and some property of the metal phosphates is required. It is presumed that the Brønsted acidity will be associated with the anion, rather than the cation, and in particular the oxygen atoms of the phosphate ion, and the electronic density of such oxygen atoms. However, such charge density will be influenced by the nature of the cation, and the

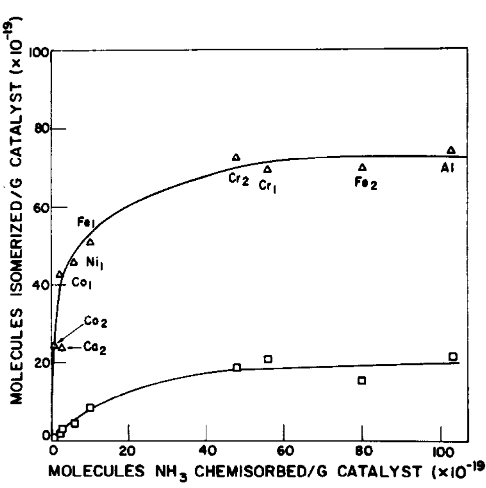


FIG. 4. Molecules isomerized per g of catalyst versus molecules of NH_3 chemisorbed per g of catalyst (231, △; 232, □).

solid-state structure of the metal phosphate.

Sanderson (*9*) has developed a simple semiempirical method for estimating the partial charge on an atom in a compound:

$$\text{Partial charge} = \frac{\Delta\chi}{\Delta\chi(1)}$$

where $\Delta\chi$ refers to the change in electronegativity of an atom in becoming part of a compound, and $\Delta\chi(1)$ is the corresponding change in gaining or losing one electron. The latter term can be related to the electronegativity, χ, of the isolated atom by

$$\Delta\chi(1) = 2.08\,\chi^{1/2}.$$

The principle of electronegativity equalization (*10*) is employed in the calculation of $\Delta\chi$. The acidity of the catalyst should presumably increase as the partial charge on the oxygen atom in the phosphate decreases.

Although approximate, an inverse relationship between the quantity of ammonia chemisorbed/area and the partial change on the phosphate oxygen atom is evident from Fig. 5. A straight line has been tentatively drawn to represent the correlation. It is of interest to note that two of the phosphates yielding the equilibrium composition of 231 and 232 under the reaction conditions, namely, those of aluminum and iron, chemisorb smaller quantities of ammonia than would have been expected from Fig. 5. This may tentatively be interpreted as evidence for the existence of a more compressed distribution of acidic strengths on the surface of these catalysts.

It is evident from the present work that the catalytic activity of the solids investigated is dependent on the metal or cation present. This is not unexpected. There is little evidence, however, that the activity, at least with respect to the isomerization reactions, can be correlated with electronegativity as has been suggested previously (*2*). The inability of most of the present catalysts to isomerize 331 suggests that the active sites are not strongly acidic. However, only one activation temperature has been employed, and it is possible that the activity may be altered at higher activation temperatures. No conclusions concerning the nature of the acidic sites can be drawn from the present work.

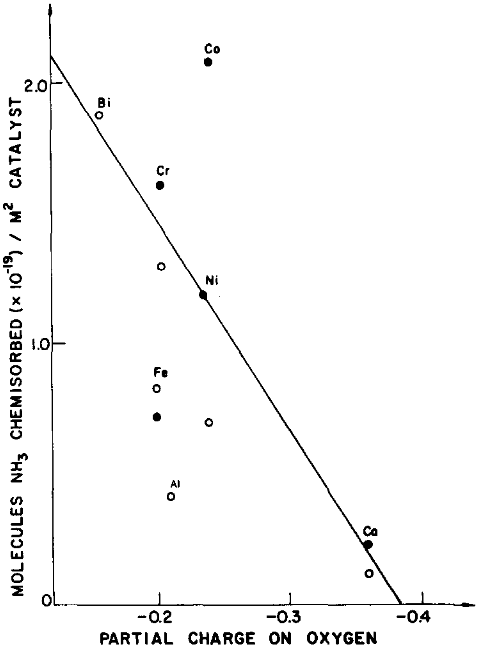


FIG. 5. Number of NH_3 molecules chemisorbed/m^2 and partial charge on the phosphate oxygen of the various catalysts. Solid and open symbols: preparation methods 1 and 2, respectively.

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