

Review Paper

ACID-BASE PROPERTIES OF H_3PO_4 AND PHOSPHATE CATALYSTS

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Summary

Phosphates are a newly emerging type of catalysts for hydrocarbon conversion processes. Recent studies on phosphoric acid, boron phosphate and aluminium phosphate catalysts are reviewed with a view to understanding their surface acid-base properties.

1. Introduction

The possible uses of phosphoric acid (H_3PO_4) and its salts with metals as catalysts for various reactions have been explored since the early 1960s. The earliest review dealing with the versatility of these materials for the catalysis of a variety of reactions appeared in 1968 [1]. Their marked stability and therefore the possibility that they may serve as suitable supports [2] for metal catalysts have also been reported. In 1978, Moffat [3] critically evaluated all the available information on the methods of preparation and characterization and on the reactions catalysed by phosphates. It is evident from his review that orthophosphates, particularly boron phosphate (BPO_4) and aluminium phosphate ($AlPO_4$), have found extensive use as catalysts in various hydrocarbon conversion processes. Since then there have been many reports on both fundamental and applied studies relating to catalysis by H_3PO_4 and boron or aluminium phosphates. These studies mainly deal with the preparation, surface properties, texture, adsorption characteristics and the catalytic activity for various reactions of these systems. The purpose of this article is to review briefly all the available new information to enable an understanding of the surface acid-base properties of these catalysts.

2. H_3PO_4

H_3PO_4 is a stable crystalline solid (melting point, $42.35\text{ }^\circ\text{C}$) and is used as a catalyst in its molten state or in a supported form over various inert matrices. The pure acid and its crystalline hydrates have tetrahedral PO_4 groups connected by hydrogen bonds [4]. Many industrially important reactions such as hydrolysis, dehydration, polymerization and alkylation occur on these catalysts [1].

The high activity of this catalyst for the direct hydrolysis of alkenes has led to many patents [5, 6]. In the direct hydrolysis of ethylene the activity of the H_3PO_4 catalyst showed a time-dependent behaviour, *i.e.* the catalyst showed a maximum activity only after 28 h [5]. A rate equation including the effect of time has been derived and a mathematical model based on this equation has been proposed with parameters whose variation allows the life of the catalyst to be increased [7]. However, an initial induction period of 250 - 300 h for the hydration of ethylene over $\text{H}_3\text{PO}_4\text{-SiO}_2$ gel has been reported [8]. This behaviour has been explained using a model which proposes that the deep surface layers of H_3PO_4 are the active phase. As H_3PO_4 has been shown to be a good catalyst for hydrolysis, it is expected to show a high activity for dehydration. The dehydration of *sec*-butyl alcohol proceeds [9] with a 75% - 90% conversion and the activation energy (97.8 kJ mol^{-1}) is of the same order of magnitude as that for similar reactions on boron phosphate ($62.3\text{ - }123.7\text{ kJ mol}^{-1}$) [10]. This indicates the presence of Brønsted acid sites in H_3PO_4 similar to those which have been proved to be the active sites in boron phosphate.

H_3PO_4 exhibits a good activity for alkylation reactions. Alkylation of phenols with $\text{C}_4\text{ - C}_9$ alkanes leads to 4-alkyl phenols as the major product [11]. This reaction is found to occur at temperatures as low as $60\text{ }^\circ\text{C}$. Benzylolation of *o*-, *m*- and *p*-cresols [12] is achieved by benzyl alcohol and the different isomers of benzylated compounds formed as products showed that the active sites are heterogeneous on the surface. Generally, in any alkylation reaction, *O*-alkylation (via the formation of alkoxide ions through the abstraction of protons by the Lewis base sites on the surface) leading to the formation of ethers is found to occur initially by a Langmuir-Hinshelwood mechanism [13]. A further rearrangement from the *O*-alkyl product to the *C*-alkyl product occurs, depending on the presence of an electrophilic surface which polarizes the O-C bond.

Thus H_3PO_4 has both acidic and basic sites and the exact nature of these sites and an accurate model are yet to be clearly established. Only typical representative examples of the large number of catalytic studies of H_3PO_4 are considered.

3. Boron phosphate

Moffat and coworkers have carried out extensive work on boron phosphate catalysts. Moffat has reported the results obtained on both stoichio-

metric and various non-stoichiometric boron phosphates with various boron-to-phosphorus ratios. Studies on the method of preparation of these catalysts [14] and of the characterization of the surfaces with probe molecules such as nitrogen [14], ammonia [14], water vapour [15], krypton [16] and argon [17] have shown the presence of various acid-base sites on the catalyst surfaces. In particular, the adsorption and desorption of water have been analysed by various techniques such as IR [18], temperature-programmed desorption [19] and scanning electron microscopy [20]. Various pretreatment conditions [21] have been used for the following reasons.

(i) Water is a product in one of the main reactions promoted by these catalysts, namely dehydration.

(ii) The surface hydroxyl groups are believed to be the primary reaction sites for the observed catalytic activity.

In small amounts, water is found to modify the surface slightly and, in large amounts, it affects both the surface and the bulk properties drastically [22]. IR and temperature-programmed desorption studies [18, 19] on the adsorption of water have shown the presence of various types of surface hydroxyl groups, involving either individual phosphorus and boron ions or a combination of both. Electron spin resonance spectral studies [23] of adsorbed perylene, diphenylethylene and tetraphenylethylene have shown the absence of water in preheated evacuated catalysts. It has also been deduced that the catalyst may be a mixture of phosphorus pentoxide and boron trioxide. IR spectral studies of these surface species [24] have shown that the surface contains more Lewis acid sites than Brønsted acid sites. IR spectra of adsorbed ammonia [25] have revealed the presence of ammonium ions and of both molecularly and dissociatively adsorbed ammonia on boron phosphate. These results are similar to the observations made on aluminosilicates, indicating the presence of similar types of acid-base sites on these two catalysts. A systematic study of the activity of boron phosphates to catalyse various reactions, such as the decomposition reactions of formic acid [26], ethyl alcohol [27] and propyl alcohol [10] and the oxidation of iodide ions [28], has led to the following conclusions.

(i) The activity depends on the phosphorus-to-boron ratio.

(ii) The surface acid-base properties and therefore the resultant activity are strongly dependent on the pretreatment temperature.

(iii) Changes in the pretreatment conditions allow a variation in the type of water present on the surface.

All these studies have been critically considered in the review by Moffat [3]. Various methods of preparation have led to different catalyst samples and each one of them has been found to be useful for a specific industrial process. Tartarelli *et al.* [29] have reviewed the available patent literature on the manufacture and the catalytic activity of boron phosphate catalysts.

Recent studies on boron phosphate catalysts have added valuable information on the nature of the catalysts. This is briefly reviewed in the following sections.

3.1. Preparation and characterization

Various methods of preparation of boron phosphate have been described by Kubasov and coworkers [30, 31] for carrying out specific reactions. The catalyst prepared from an equimolar mixture of phosphoric anhydride and orthoboric acid was active for the hydration of ethylene, whereas the catalyst prepared from equimolar amounts of orthoboric acid and H_3PO_4 in a basic medium was found to be active for the dehydration of *n*-butyl alcohol. Boron phosphate has been shown to have a polymorphous silica structure and thermal treatment studies [32] have shown that the cristobalite phase is the stable phase. Other properties such as the thermal expansion, the transition temperature and the lattice constants have also been studied. Boron phosphate is also found to form a solid solution with aluminium phosphate in a β -cristobalite structure [33]. A range of catalysts with boron-to-phosphorus ratios ranging from 0.4 to 1.6 has been prepared by Haber and Szybalska [34] and the surface acid-base properties have been evaluated by adsorption and reaction studies (see Sections 3.2 and 3.3 respectively). A patent has also been obtained on the preparation of boron-phosphate-based catalysts from mineral oxides for hydrorefining purposes [35].

3.2. Adsorption studies

HD has been used as a probe molecule to study the surface of boron phosphate [36 - 38]. The kinetics of D_2 pick-up by the surface are studied by analysing H_2 , D_2 and HD in the gas phase, and the energy of activation as a function of the surface coverage has been calculated. These studies have shown that the surface contains heterogeneous sites most of which adsorb D_2 exclusively and the rest are capable of hydrogen exchange. The IR spectra of adsorbed molecules such as pyridine, ammonia, methyl cyanide and hydrogen chloride have been reported [34, 39]. The appearance of bands at 1455 and 1620 cm^{-1} as a result of pyridine adsorption indicates electron acceptor centres on the surface, while bands due to protonated pyridine were absent. IR bands due to molecular ammonia as well as to ammonium ions were observed on adsorption of ammonia, revealing the presence of both Lewis and Brønsted acid sites on the surface. The IR spectra of adsorbed species such as pyridine, 2,6-dimethylpyridine and 2,6-di-*tert*-butylpyridine on boron phosphate catalysts (both stoichiometric and non-stoichiometric) have shown a predominant presence of Lewis acid sites when the phosphorus-to-boron ratio is less than unity. The steric inhibition for strong adsorption is deduced from the fact that pyridine can displace both 2,6-dimethylpyridine and 2,6-di-*tert*-butylpyridine from the adsorbed state; 2,6-di-*tert*-butylpyridine is the more readily replaced [40]. Studies of adsorption of various alkenes on non-stoichiometric boron phosphates have shown that the tertiary carbonium ion is the common adsorbed species for all the alkenes. The tertiary carbonium ion has been suggested as the intermediate in the oligomerization of these alkenes [41].

3.3. Catalytic reaction studies

The dehydration of dimethylbutan-2-ol [42] and *tert*-butyl alcohol [43] on boron phosphate leads to a variety of products, indicating the presence of Brønsted acid sites of various strengths. The activity and selectivity are very sensitive to the pretreatment temperature. The maximum activity is obtained when the pretreatment temperature is 100 - 150 °C at which water molecules attached to the surface by hydrogen bonds and physisorbed water molecules are removed. When the pretreatment temperature is higher than 150 °C, there is a decrease in activity, indicating the desorption of water which is responsible for the Brønsted acidity in these catalysts. Studies of the compositional variations have shown that dehydration is more favourable in catalysts for which the phosphorus-to-boron ratio is greater than unity. Dehydration of primary, secondary and tertiary alcohols has been shown to take place by an E2 bimolecular elimination mechanism [44]. This is deduced on the basis of the increase in the basicity of the catalyst during the reaction. The presence of different types of hydroxyl groups on boron phosphate catalysts supported on SiO₂ gel is due to a disordered structure. This may be the reason that these systems promote the dehydration of various alcohols and the hydrolysis of alkenes [45].

The isomerization of cyclohexanone oxime to ϵ -caprolactam, which requires the presence of a Lewis acid site, is reported to take place on boron phosphate catalysts with an 84% - 100% conversion [46]. This type of Beckmann rearrangement is found to occur only when the phosphorus-to-boron ratio is less than unity. Haber and Szybalska [34] have also arrived at the same conclusion that solids with phosphorus-to-boron ratios greater than unity promote reactions requiring Brønsted acid sites, namely the dehydration of ethanol and cumene cracking, while reactions such as the Beckmann rearrangement which require Lewis acid sites do not take place. As expected, when the phosphorus-to-boron ratio is less than unity, the catalyst shows a high activity for the Beckmann rearrangement type of reactions, and the dehydration and cumene cracking type of reactions which require Brønsted acid sites do not occur.

Supported boron phosphate catalysts have been shown to promote the polymerization of 1-alkenes [47]. In fact, the polymerization of naphtha fractions is found to occur on boron phosphate at a rate comparable with that on aluminosilicate [48]. Oligomerization of *cis*-2-butene occurs on boron phosphate without the migration of the double bond [49]. However, the catalyst calcined at 1173 K completely lost its activity.

Boron phosphate catalysts are very useful in syntheses. They have been recognized as good catalysts for the following reactions: the synthesis of phenolic nitriles [50], which are important intermediates in the preparation of herbicidal compounds; the formation of tetrahydrofuran [51] by the cyclization of 1,4-butanediol; the manufacture of isoprene from 2-methylbutanol [52] and 4,4-dimethyl-1,3-dioxane [53]; the conversion of adipic acid to adiponitrile [54, 55].

Recently, there have been reports [56, 57] on the formation of salts of borophosphate anions with metals such as zinc, magnesium and lead. The

boron salt of one heteropoly acid, namely 12-tungstophosphoric acid, has been shown to have considerable activity for the conversion of methanol into higher hydrocarbons [58]. However, the potential of boron phosphates as catalysts for various reactions has yet to be evaluated.

4. Aluminium phosphate

Aluminium phosphate has the characteristics of a catalyst and a catalyst support as well as of an adsorbent [2]. Rhodium and nickel catalysts supported on aluminium phosphate have been reported by Campelo *et al.* [59, 60]. They have compared the activity of Ni/SiO₂, Ni/Al₂O₃ and Ni/AlPO₄ and reported that the specific catalytic activity for hydrogenation of 1-hexene depends on the nature of the support. The preparation of aluminium phosphate from aluminium salts and H₃PO₄ has recently been reported by Gallace and Moffat [61, 62]. Aluminium phosphate has been found to catalyse almost all the reactions catalysed by boron phosphate, but with a lower activity [3]. The acid-base properties of aluminium phosphate have been studied in detail by Krzywicki *et al.* [63] by means of titrations in non-aqueous media, thermogravimetric studies and electron spin resonance spectral studies of adsorbed species. They have also reported [64] that aluminium phosphate can promote the Prins reaction (the preparation of isoprene from isobutylene and formaldehyde) which requires strongly acidic sites. Studies of the decomposition of N₂O on aluminium phosphate have shown the presence of one-electron donor sites on these surfaces [65].

5. Concluding remarks

There are also certain transition metal phosphates which have been reported as catalysts for hydrocarbon conversion reactions. However, they are not as widely used as H₃PO₄ or boron and aluminium phosphates because of efficiency and cost considerations. More intrinsic studies on the electronic structure of these surfaces will be helpful to maximize the utility of phosphates as catalysts. The acid-base properties and the electronic structure of aluminosilicate catalysts [66] have been studied using theoretical cluster model calculations. The molecular structural properties, such as the position of the molecular energy levels, the electronic charge distribution, the bond indices and the single-bond energy, evaluated by these calculations have been found to be reasonably consistent. On the basis of the values calculated for these parameters, it has been possible to predict the surface properties with reasonable accuracy. In addition, since orthophosphates exist with crystal structures similar to those of aluminosilicates, such model calculations can also be expected to provide useful information on the nature of the surface acid-base sites. This will allow their catalytic behaviour to be predicted. We have attempted such semiempirical quantum mechanical calculations on

typical phosphate clusters using complete neglect of differential overlap/2 calculations to evaluate the changes in the surface acid-base properties of phosphates as a result of the adsorption of water. Similar extensive studies can be expected to reveal the specific sites involved in catalytic reactions on these catalysts.

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