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Effect of water in the performance of the "solid phosphoric acid" catalyst for alkylation of benzene to cumene and for oligomerization of propene

Fabrizio Cavani, Gianni Girotti and Giuseppe Terzoni

Centro Catalizzatori EniChem Synthesis, via B. Luini 241, 20099 Sesto S. Giovanni (MI) (Italy)

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Abstract

The solid phosphoric acid catalyst has been utilized industrially for a long time for the synthesis of cumene by benzene alkylation, as well as for the oligomerization of propene to liquids utilized for gasoline blendings. This paper describes the effect of the water content in the feedstock on the catalytic performance of the solid phosphoric acid catalyst, both in terms of activity/selectivity and of the overall life. The water was found to affect the activity strongly in the case of the propene oligomerization, the highest activity was achieved in the case of complete hydrolysis of the P_2O_5/H_2O , constituting the active phase of the catalyst, to the *ortho*-phosphoric acid. In the case of the benzene alkylation, instead, complete hydrolysis led to a decrease in both the activity and the selectivity to alkylaromatics. However, the main influence of water was on catalyst lifetime: more than 200 ppm water in the feed led to a quick destruction of the catalyst, with loss of the mechanical properties. This phenomenon was found to be due to the hydrolysis of the main catalyst components, the silicon phosphates. A remarkable improvement in lifetime of the solid phosphoric acid catalyst was achieved by making the system more resistant to hydrolysis through a modification in the preparation procedure.

Keywords: benzene alkylation; cumene synthesis; phosphoric acid; propene oligomerization; silicon *ortho*-phosphate; silicon pyro-phosphate; solid phosphoric acid

INTRODUCTION

The synthesis of cumene, a very important intermediate in the petrochemical industry, is mainly carried out utilizing the heterogeneously catalyzed, fixed bed process developed in the 40's by UOP [1-5]. The catalyst is so-called solid phosphoric acid, consisting of a polyphosphoric acid impregnated over a natural diatomaceous earth (Kieselguhr) [6-9]. Another very important application of this type of catalyst is for the synthesis of propene oligomers [10-14], utilized as gasoline components, for the detergent industry and as raw

Correspondence to: D.G. Terzoni, Centro Catalizzatori EniChem Synthesis, via B. Luini 241, 20099 Sesto S. Giovanni (MI), Italy. Tel. (+39-2)2401451, fax. (+39-2)2620007.

materials in oxo-synthesis. The overall yearly consumption of this kind of catalysts can be estimated to be around 15000 tonnes.

The main advantage of this type of catalyst is related especially to its very low operating cost, which derives from both its low price and from its very high selectivity in the desired product (i.e. cumene). The main disadvantage, on the other hand, is related to the disposal of spent catalyst, which is not regenerable; pollution problems arise when disposing of large amounts of a strongly acidic material, containing phosphates and organic tars. For this reason, recently different kinds of catalysts, mainly zeolitic, have been proposed as alternative to the solid phosphoric acid catalyst [15-24]. The successful Mobil/Badger, H-ZSM-5-based, process for the synthesis of ethylbenzene is an example of the possibility of utilizing zeolitic materials in the field of aromatic alkylation [25].

Recently, a new process for ethylbenzene and cumene synthesis has been jointly announced by Unocal, Lummus and UOP, utilizing a zeolite-based catalyst for the synthesis of both ethylbenzene and cumene [15,26]. The zeolitic systems offer the advantage of being regenerable, not toxic and stable over a wide range of temperatures; moreover, in the case of the alkylation reactions, they are active in the transalkylation of the polyalkylated products, therefore giving the possibility of increasing, under particular conditions, the selectivity to cumene [23,27,28].

Despite all the mentioned advantages of zeolites, the traditional process based on the solid phosphoric acid catalyst, appears to be still advantageous, due above all to its lower cost and higher selectivity (more than 97%, compared to less than 90% for zeolites). Moreover, it is not possible to utilize the zeolitic catalysts in conventional reactors, due to the very different operating conditions.

The effect of reaction parameters on the solid phosphoric acid performance has been seldom described in the literature [5], and absolutely no recent data are available. In the case of cumene synthesis, the main parameters affecting the catalytic activity are the temperature of the reaction, the total pressure and the molar ratio between the benzene and propene; the latter parameter strongly affects the selectivity to cumene [5].

Another important parameter, that however has never been discussed in the literature, is the water content in feedstock, for both alkylation and oligomerization applications. The water content in the reactor inlet essentially depends on the moisture content of the fresh feedstock (therefore on its temperature and composition), on the presence of some pretreatments of the feedstock itself, on the amount of recycled feed, as well as on the amount of injected water in the feed stream. Anyway, a certain amount of water is necessary to maintain the Brønsted acidity of the catalyst [29]. Under typical industrial operation the water content in the reactor inlet can range from 200 to 1000 wt. ppm in the case of propene oligomerization, from 50 to 300 ppm in the case of cumene synthesis.

The plant operators know very well that the productivity of cumene, as well

as its purity, can vary when the water in the feedstock is not strictly controlled, thus when the moisture level in the feed fluctuates with time-on-stream (mainly because of modifications in the feed saturation). In addition, it is generally believed that the overall life of the catalyst can be improved by an accurate control of the water content.

Aim of the present work is to give a contribution to the understanding of the effect of the water content on the solid phosphoric acid catalyst behaviour, both in terms of activity/selectivity and of life. We intend to: (i) clarify the effect of water on the catalyst performance, and give an indication about the necessity to operate under strictly controlled operative conditions; (ii) reach a comprehension of the phenomena which lead to catalyst deactivation in presence of water. This has given us the basis for developing a new grade of the solid phosphoric acid catalyst, more resistant as regards these deactivation phenomena and therefore characterized by an improved life.

EXPERIMENTAL

The industrial preparation of the solid phosphoric acid catalyst is carried out by preliminary mixing of the Kieselguhr and of the polyphosphoric acid in the amount necessary to have a Si/P ratio close to 1/1. The obtained paste is thereafter extruded into small cylinders, whose dimensions depend on the kind of reactor in which it is utilized; for chamber reactors the size of the extrudate is 1 cm in length and 0.6 cm in diameter. For application in a multitubular reactor the average size is 0.6 cm in length and 0.5 cm in diameter. After extrusion the material is calcined at temperatures higher than 300°C. The time and maximum temperature of calcination are a versatile tool to modify the catalyst's physico-chemical and mechanical properties (titratable phosphoric acid, hydrolyzability, hardness). All the samples utilized in laboratory as well as pilot plant tests have been taken either from the industrial production, or when desiring unusual physical or chemical properties, were specifically designed and prepared in a laboratory unit.

The catalysts have been characterized by means of X-ray analysis (powder technique), utilizing a Philips instrument (Cu K α radiation).

The intrinsic acidity of the catalyst is characterized by titration of the fraction of the polyphosphoric acids that is leached when the catalyst is first ground into powder, and then submerged into room-temperature water for ten minutes. The aqueous solution, containing the leached phosphoric acids, is then titrated with 0.1 M NaOH. The titrated fraction will be hereafter designated as "free P₂O₅". When the sample is instead left in water for longer times, at either room temperature or at higher temperatures to accelerate the test, the silicon phosphates (mainly *ortho*-, Si₃(PO₄)₄, and *pyro*-, SiP₂O₇) that constitute the main catalyst components are slowly hydrolyzed, too, with release of silica and of phosphoric acid. The fraction of released phosphoric acid can be

titrated as above, at different time intervals (i.e. every day, when the measurement is prolonged for one week), and gives a measurement of the catalyst hydrolyzability.

Another test was developed, which gives a measurement of the compacting of the catalytic bed when an homogeneous pressure is exerted on it. 1 l Of catalyst is submerged in water, inside a reactor-like tube; a piston applies an axial pressure of 0.5 kg/cm^2 over it; the decrease of the bed height is measured as a function of time.

The bench-scale, laboratory unit for catalytic tests is constituted of a fixed bed, stainless steel reactor, containing 10 ml of catalyst; the reactor is placed inside an oven; an axial thermocouple inserted in the reactor is utilized for the measurement of axial gradients of temperature. Either pure propene or a mixture of benzene and propene (in the right relative amount) are fed from a cylinder kept at 30 atm ($1 \text{ atm} = 101.325 \text{ kPa}$) through a HPLC-type double piston reciprocating pump to the reactor. The reactor effluent is collected and analyzed by means of gas chromatography, utilizing a silicon oil DC 550, wide-bore column, with programmed temperature.

Pure propene, instead of an industrial-like propane/propene mixture, was utilized for reasons of convenience. This leads to an higher heat of reaction per unit of mass fed; however, short residence times were used, so as to keep the propene conversion lower than 30%. Such conditions, as well as some technical tricks utilized for the reactor construction, allowed a relative uniform temperature profile in the catalytic bed close to the inlet temperature (the maximum ΔT was always lower than 15°C).

A semi-pilot plant, containing 2 to 4 l of catalyst, was utilized for evaluation of the long-term catalytic performance and of pressure drop. The reactor consisted of a tube with the same diameter as the industrial one in multitubular reactors, but shorter in length (2 m). A bundle of thermocouples was located inside the catalytic bed, at different heights. Membrane pumps were utilized for feeding the reactants (benzene, propene). The reactor pressure was controlled by means of an automatic control loop, operating on a pneumatic valve. The heating was provided by electric resistances, and the heat of reaction was removed by means of a sand bath.

The water content in the stream was measured with an on-line moisture analyzer, from Panametrics.

RESULTS AND DISCUSSION

In order to get a better understanding of the role of water on the catalyst performance, we analyzed the catalyst activity/selectivity and the lifetime separately.

Catalyst activity and selectivity

The activity of the solid phosphoric acid catalyst is known to be related to its intrinsic acidity, thus to the amount and nature of the phosphoric acid spread over the support [3,6,9]. Phosphoric acid exists in different forms (*ortho*-, pyro-, tri- and polyphosphoric acids, with increasing degrees of condensation), the relative amounts depending on the P_2O_5 and water contents [30,31]. Fig. 1 shows the relative amounts of the different species, as a function of the water content in P_2O_5/H_2O mixtures [30,31].

The figure indicates that at relatively low water content the average degree of condensation of the acids is higher. In addition, it is known that the acid strength of the various phosphoric acids varies considerably [3,9]. Therefore, for catalysts characterized by the same overall amount of P_2O_5 , and by similar morphological and compositional features, the activity depends essentially on the P_2O_5/H_2O ratio on the catalyst surface.

An experimental evaluation of the phosphoric acids distribution in these catalysts is given by the titration of the "free P_2O_5 ", constituted of the acids with lower degree of condensation, such as the *ortho*- and pyro-phosphoric acids (the higher condensed acids take longer to be hydrolyzed and therefore can not be readily titrated), that are easily leached from the catalyst when it

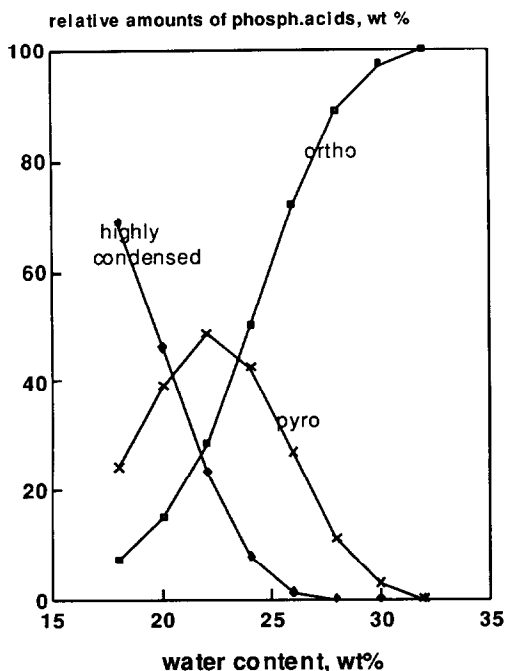


Fig. 1. Distribution of phosphoric acids as function of water content in P_2O_5/H_2O mixtures.

is submerged in water. Thus, the amount of "free P_2O_5 " can be taken as representative of the kind of acids distribution, for a fixed overall amount of P_2O_5 .

Fig. 2 shows the amounts of "free P_2O_5 " that are titrated as functions of the water content in the catalyst (the latter measured by weight loss at $600^\circ C$). The water content of the catalyst is essentially a function of the preparation procedure; in this case it was varied by modifying the time of calcination. Values ranging from 3 to 18 wt.-% of "free P_2O_5 " are titrated: the lower values are obtained in correspondence to the lowest water contents; in fact, as shown in Fig. 1, low concentrations of water give rise to a distribution where the acids are highly condensed, and therefore the amount of titratable phosphoric acid ("free P_2O_5 ") is low. On the other hand, the titration of relatively high amounts of phosphoric acid is an indication of the presence of low condensed acids, thus of a high level of catalyst hydration.

The hydration level of the solid phosphoric acid catalyst in the reaction environment, and thus the catalytic performance, clearly can be affected by the water content in the reactant phase. Fig. 3 plots the amount of titrated "free P_2O_5 " on the catalyst as a function of the water content in the reactant phase, measured under stationary conditions. The two curves refer to (i) the case of

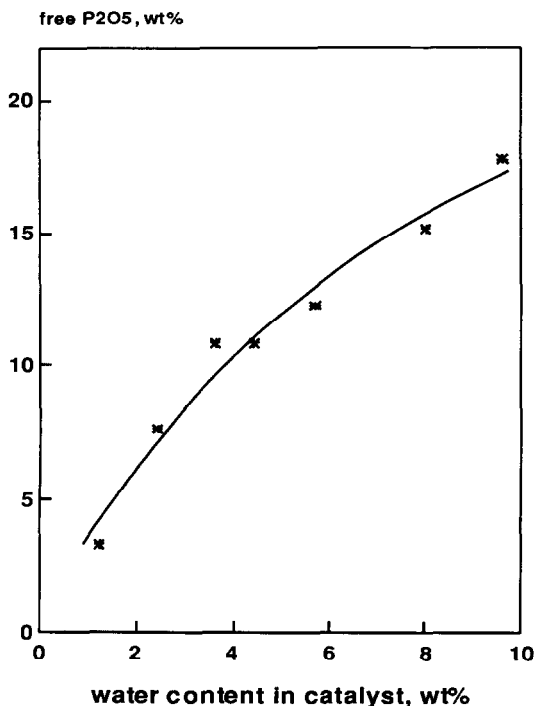


Fig. 2. Titrated amount of phosphoric acid ("free P_2O_5 ") as function of water content in the solid phosphoric acid catalyst.

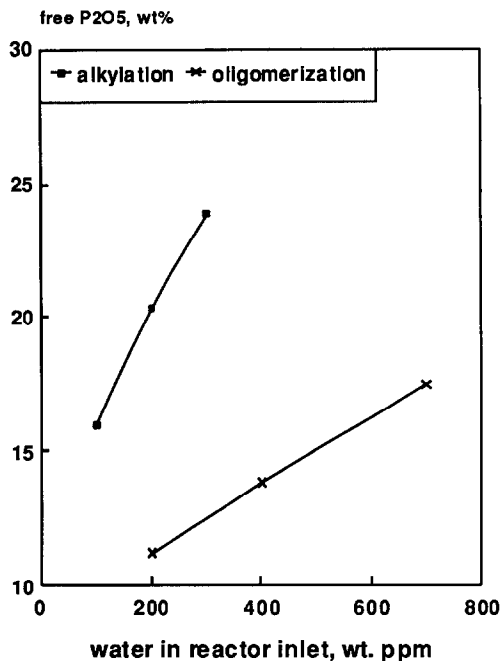


Fig. 3. Titrated amount of "free P₂O₅" in equilibrated catalyst as function of the water content in the feed stream, for cumene synthesis and for propene oligomerization; tests were carried out in a bench-scale reactor.

the alkylation of benzene with propene (inlet temperature 220°C, benzene/propene molar ratio 7, LHSV 2 h⁻¹, pressure 30 atm), and (ii) the case of the propene oligomerization (inlet temperature 180°C, LHSV 6 h⁻¹, feed of pure propene, pressure 30 atm). It is shown that the equilibrated amount of "free P₂O₅" on the catalyst is strongly dependent on the water content in feed. In agreement with the data of Figs. 1 and 2, the higher amount is titrated for higher concentrations of water in feed.

The different operating conditions utilized for the two reactions give rise to different equilibrium situations. This indicates that a partition equilibrium is established between the P₂O₅/H₂O mixture adsorbed on the catalyst surface and the reactant phase, possibly modifying the acids distribution on the catalyst. This equilibrium is also affected by the reaction conditions, such as temperature and nature of the reactant phase.

Fig. 4 shows the effect of the "free P₂O₅" amount (thus of the acids distribution) on the activity in propene oligomerization, and how the latter is modified with the time-on-stream, until steady state conditions. The three reported catalysts contain the same overall P₂O₅ content, but different amounts of water, and therefore different amounts of initial "free P₂O₅" (the value of titrated

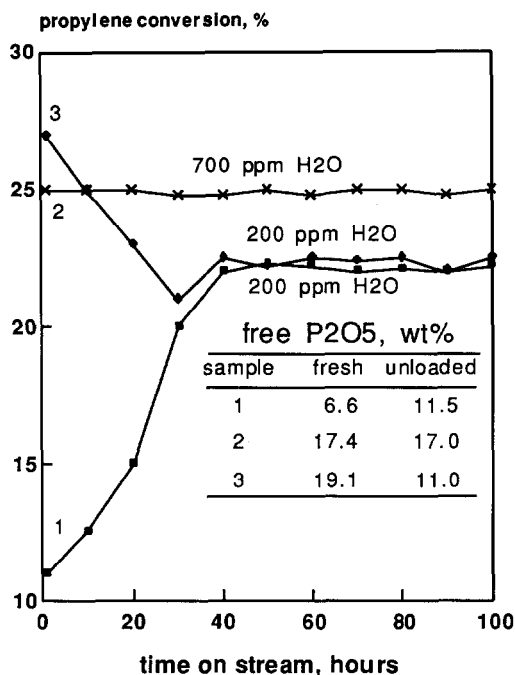


Fig. 4. Propene conversion at 180°C (inlet temperature) and at residence time 5 min (LHSV 12 h⁻¹), in a bench-scale reactor, as function of the time-on-stream, for three different catalysts; the table gives the titrated amount of "free P₂O₅" in the samples both before and after reaction. Two different levels of water were added in the stream (200 and 700 ppm).

acid is given in the table in Fig. 4, for both fresh and equilibrated catalysts). The tests were carried out with low values of residence time (around 5 min, LHSV 12 h⁻¹) in order to obtain low levels of propene conversion. The three samples were characterized by similar values of the surface area (around 3 m²/g).

Sample 1, characterized by a low amount of titratable phosphoric acid (6.6 wt.-% of "free P₂O₅"), initially displays the lowest activity, which, however, slowly increases along with the time-on-stream when feeding propene which contains 200 ppm of water. Correspondingly, the chemical analyses demonstrate that the acids distribution is remarkably changed during the non-stationary period: after 40 h, under stationary conditions, the titrated "free P₂O₅" is 11.5 wt.-%, thereafter remaining constant. Thus, the hydration level of the catalyst is increased, with a corresponding increase in the relative amount of the low condensed acid forms. In other words, this level of "free P₂O₅" corresponds to the equilibrium one when 200 ppm of water are present in the inlet stream, under the utilized reaction conditions.

Sample 2, characterized by an initial "free P₂O₅" amount of 17.4 wt.-% shows an initial activity much higher than that of sample 1. When feeding around 700 ppm of water, the catalyst maintains a constant activity since the very

beginning up to the end of the catalytic tests. Correspondingly, the unloaded catalyst, after 120 h of reaction, possesses an acidity very similar to the initial one (17.0 wt.-% of "free P_2O_5 "). Thus, with 700 ppm of water in the reactant phase, the distribution of the acids remains in this case substantially unaltered, being the two phases at equilibrium, and correspondingly the activity remains constant.

Finally, sample 3 is characterized by an initial titratable acid content of 19.1 wt.-%; the permanence in the reaction medium, under a propene feedstock containing 200 ppm of water, leads to a decrease in the activity with the time-on-stream. After approximately 35-40 h the propene conversion is stabilized, and the final amount of "free P_2O_5 " is 11.0 wt.-%, thus the same as for equilibrated sample 1. Moreover, sample 3 reaches the same activity as sample 1, in agreement with the similar amount of titrated phosphoric acid, thus with a similar acids distribution.

The data suggest that the catalyst reaches a stationary state after the period of time that is necessary to equilibrate with the water content in the reactant phase. During this non-stationary period, the catalyst's activity is modified, following the surface evolution. The equilibrium is reached under reaction through a modification in the distribution of the different species of phosphoric acid. With relatively high contents of water (such as in the case of the tests with 700 ppm of water) the most condensed acids are hydrolyzed, and the distribution is shifted towards the less condensed acids; the opposite occurs in dehydrated conditions (i.e. 200 ppm).

Fig. 5 shows the effect of the "free P_2O_5 " content on the initial propene conversion, in several catalysts. The data were collected at the very beginning of the catalytic tests, thus before the equilibration of the P_2O_5/H_2O mixture was attained. The aim of the tests was to find whether a simple quantitative relationship exists between the "free P_2O_5 " and the activity. The two curves in the figure correspond to two different groups of samples, characterized by different values of surface area (3 and 6 m^2/g , respectively); the value of surface area depends on the preparation procedure utilized. The maximum value of titrated acid is around 22%, corresponding to the complete hydrolysis of the polyphosphoric acids to *ortho*-phosphoric acid; thus, higher amounts of water in the catalyst do not lead to a further increase in the titrated amount of "free P_2O_5 ".

The highest activity is obtained for the maximum "free P_2O_5 " content (20 wt.-%). The presence of water contents higher than this latter value do not lead to further increase in the initial activity, but rather to a decrease. In fact, high water contents flood the catalyst (which is highly hydrophilic) by filling the pore volume and thus hindering the access of reactants to the active centres inside the pores. The trend is similar for the two groups of catalysts, with a relative maximum in activity around the 11 wt.-% of "free P_2O_5 ".

The data indicate that the activity is not simply proportional to the acid

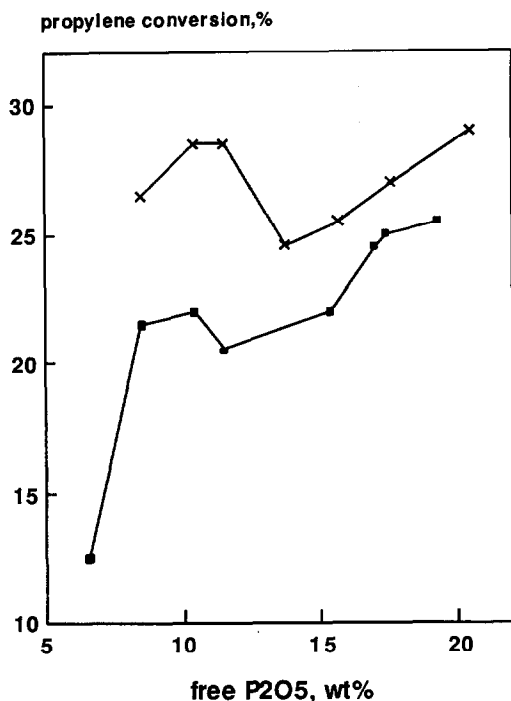


Fig. 5. Non-stationary propene conversion at 180°C (inlet temperature) as function of the initial amount of titrated “free P₂O₅” in fresh catalysts; set of catalysts with surface area 3 (■) m²/g; (×) 6 m²/g.

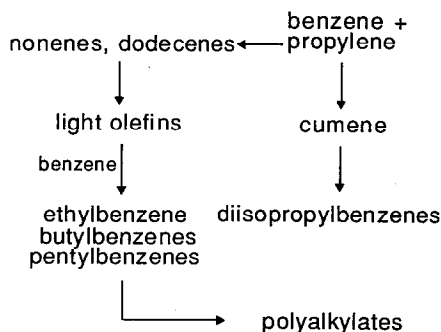
content. It can be reasonably hypothesized that the observed trend derives from the overlapping of two effects, coming from the combination of the two curves corresponding to the relative amounts of *ortho*- and pyro-phosphoric acids (see Fig. 1). In other words, in the range of low *ortho*-phosphoric content (thus of lower hydration level), the pyro-phosphoric acid mainly determines the activity of the catalyst, thus leading to the maximum in activity shown. With increasing water content, the *ortho* species becomes dominant, and becomes the determining species for the catalyst activity.

This can also explain the discordances found in the literature about the nature of the active acid species in the solid phosphoric acid catalysts [3,9]. Though it is generally agreed that the most active species are those with a lower degree of condensation, a direct correlation between any of these species and the activity has never been reported. Our data indicate that different kinds of phosphoric acids can contribute to activity, depending on the reaction conditions (temperature, water content in feed). Therefore, the catalyst's performance at steady state is mainly affected by the reaction conditions. The catalyst composition (i.e. the phosphoric acids distribution) affects the initial activity,

but within a few hours the distribution is modified according to the reactant phase composition, and the activity is varied until equilibrium is established.

Somewhat different is the case of benzene alkylation. Scheme 1 summarizes the network of reaction in the case of benzene alkylation with propene over the solid phosphoric acid catalysts. Propene can either oligomerize or alkylate benzene; the formed oligomers then in part crack, giving rise to different alkenes. The formed alkenes themselves can form alkylates other than cumene, mainly butylbenzenes. The main by-products are, however, polyalkylates, such as diisopropylbenzenes; some fraction of n-propylbenzene (around 100–200 ppm) is formed too.

Fig. 6 shows the effect of the water content (added in various concentrations to the pre-dried feedstock) in the feed stream on the activity and selectivity in cumene synthesis, under steady-state conditions. The levels of water concentrations utilized fall within the range of values typically measured in industrial reactors (100–300 ppm). In particular, the propene conversion and the selectivity to cumene are plotted against the amount of “free P_2O_5 ” titrated in equilibrated catalyst, corresponding to the different water contents in the feedstock. It is shown that the propene conversion decreases upon increasing the “free P_2O_5 ” amount above the 17%; this amount is reached, under stationary conditions, when approximately 100 ppm of water are contained in the feed stream (see Fig. 3). The activity trend, when compared to the one shown in Fig. 5, evidences a significant difference; the decreasing trend of activity with the “free P_2O_5 ” suggests that under these conditions the active acid form is different from that operating in the case of the oligomerization, and is possibly constituted of some highly condensed acid or, more likely, of the pyro-phosphoric acid. Fig. 6 shows, moreover, that the selectivity, too, is a function of the water content. In particular, the selectivity to cumene increases (around one percent point in the range examined), with respect to both the converted propene and benzene, while the overall selectivity to alkylaromatics with respect to the propene converted decreases slightly. The differences in selectivity



Scheme 1. Reaction network for benzene alkylation with propene.

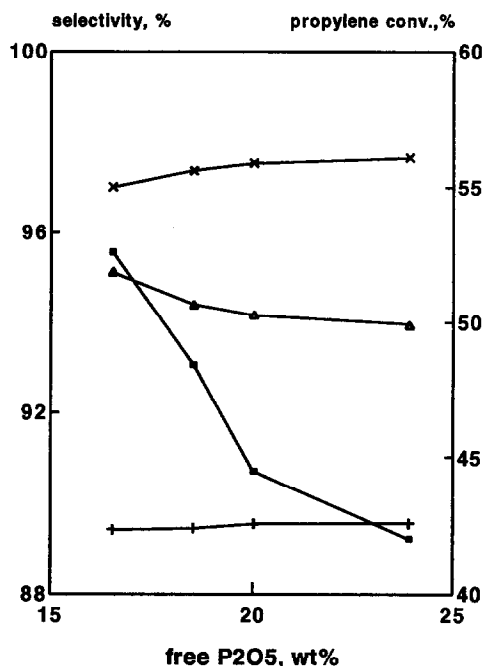


Fig. 6. Catalyst performance as a function of the equilibrated amount of "free P₂O₅" in the catalysts. The water content was varied in the feed stream. Temperature 220°C, benzene-to-propene molar ratio 7, residence time 30 min (LHSV 2 h⁻¹), pressure 30 atm. Conversion of propene (■), selectivity to cumene with respect to converted benzene (×), selectivity to cumene with respect to converted propene (+), selectivity to alkyaromatics with respect to converted propene (Δ).

in the examined range are small, but are remarkable from an industrial point of view.

The data indicate therefore that the increase in water content gives rise to a slight increase in the formation of propene oligomers (undesired by-products) with respect to the formation of alkyaromatics. On the other hand, among the various alkyaromatics, the formation of cumene is slightly favoured, with respect above all to diisopropylbenzene; this leads to the overall slight increase in cumene selectivity (with respect to the benzene converted). However, the oligomers are industrially more undesirable than the polyalkylates, due to the fact that most of the oligomers are constituted of nonenes, which are hard to separate by distillation from cumene, and therefore give rise to a worsening in the cumene bromine number. Polyalkylates, as well as other alkylates, are instead easily removed, and can be afterwards dealkylated or transalkylated to benzene or cumene.

Catalyst life

The lifetime of the solid phosphoric acid catalyst can vary remarkably, depending on the kind of utilization. Industrially, in the case of multi-tubular

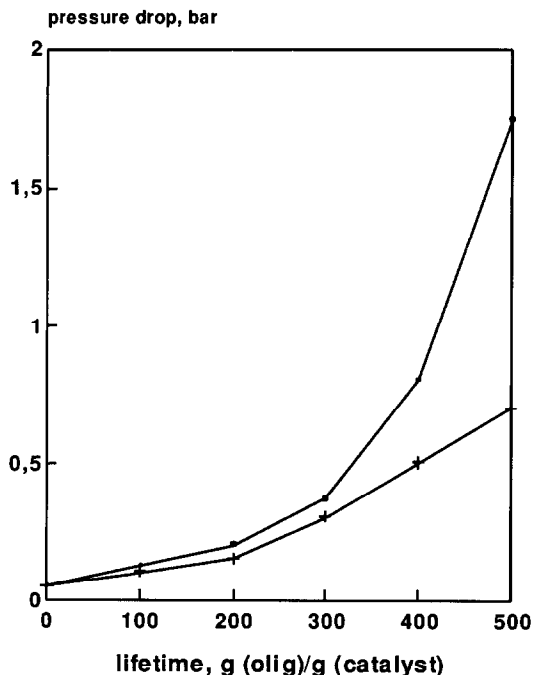


Fig. 7. Pressure drop in a semi-pilot plant as function of the lifetime, for 500 ppm (■) and 200 ppm (+) of water in feed. Inlet temperature 180°C.

oligomerization reactors, without recycle, typical values of lifetimes generally fall between three and six weeks. In chamber reactors, operating with partial recycle of lighter oligomers, the lifetime is usually longer, from five to eight months. Finally, in alkylation chamber reactors the catalyst generally lasts longer than one year.

Reasons for life ending of the catalyst can be several. In multitubular reactors, breaking up of the catalyst quickly leads to a decrease of the void space in the catalytic bed and to a strong increase in the pressure drop. A sort of mud is formed, constituted of a mixture of the destroyed catalyst and of leached phosphoric acids, with some amount of tars (organic heavy compounds) and coke. In the case of chamber reactors, instead, the catalyst unloading is usually due to a modification of the performance: in propene oligomerization to a considerably diminished activity, in benzene alkylation to an increased formation of by-products (oligomers, polyalkylates). The worsening of the performance is due to the formation of coke and tars inside the catalyst pore volume.

When operating in multitubular reactors, the resistance of the catalyst towards disintegration is therefore the most important feature that the catalyst must exhibit; improvements in lifetime of some weeks is a very successful re-

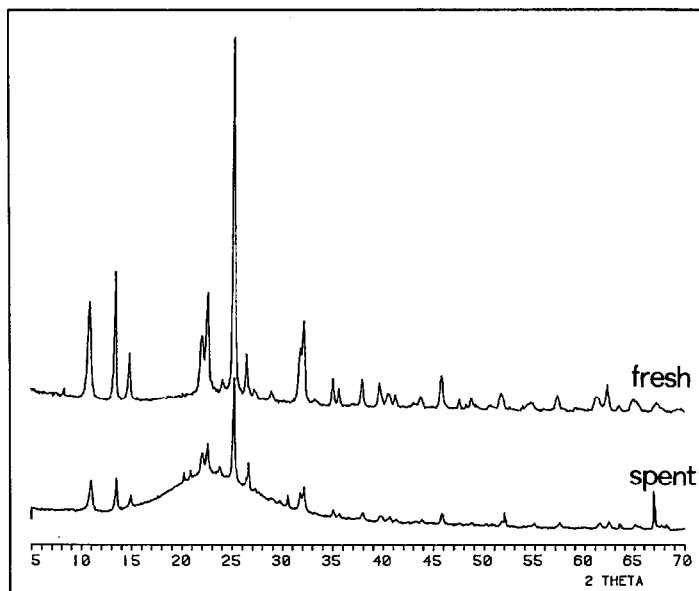


Fig. 8. X-ray diffraction spectrum of a fresh catalyst and of an unloaded one from an oligomerization reactor.

sult, and therefore a study of the mechanism leading to catalyst degradation is worthwhile, and can be very useful to improve the catalyst properties.

As an example of the behaviour of a conventional solid phosphoric acid catalyst in a multitubular reactor, Fig. 7 plots the pressure drop in a pilot plant (constituted of a tube with the same diameter as the industrial one, but shorter in length) as a function of the lifetime (measured as grams of oligomers produced per gram of catalyst). Two curves are drawn, corresponding to two different water levels in the feedstock.

It is shown that the water content in the feed can strongly affect the pressure drop in the tube; higher water levels lead to an higher rate of catalyst destruction, and therefore to a shorter lifetime. Operating with 200 ppm of water allows the pressure drop to be maintained at a low level for longer periods of time than does operating with 500 ppm.

Fig. 8 compares the X-ray diffraction spectra of a fresh solid phosphoric acid catalyst and of a spent catalyst (unloaded, corresponding to the higher pressure drop). The fresh catalyst is highly crystalline, showing the lines typical of $\text{Si}_3(\text{PO}_4)_4$; this is formed during catalyst preparation by reaction at high temperature between the SiO_2 (main component of kieselguhr) and P_2O_5 , and practically constitutes the support for the mixture $\text{H}_2\text{O}/\text{P}_2\text{O}_5$, the active phase [7,8]. A second catalyst component, formed by reaction between silica and P_2O_5 , is the silicon pyro-phosphate, SiP_2O_7 . The relative amounts of the silicon

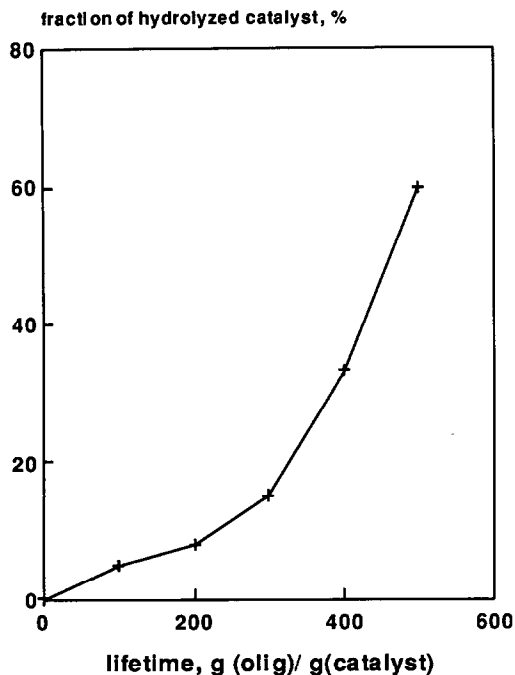


Fig. 9. Amount of hydrolyzed catalyst as function of lifetime for a catalyst from an oligomerization semi-pilot plant reactor. Inlet temperature 180°C.

ortho- and pyro-phosphates is known to be affected by the conditions of the calcination treatment [32].

The spent catalyst is instead much more amorphous; the destruction of the crystalline structure occurs because of the hydrolysis of the silicon phosphates, with release of phosphoric acid and silica.

Fig. 9 plots the amount of hydrolyzed silicon phosphates (calculated from the diffraction spectra of catalyst sampled at determined time intervals) as function of the lifetime, when feeding 500 ppm of water in the propene. It is shown that the permanence in the reaction environment produces a progressive destruction of the catalyst, thus of the silicon phosphates, therefore giving rise to the increase in the pressure drop. Clearly, the possibility of improving the catalyst lifetime is related to an improving of the catalyst resistance towards hydrolysis.

On account of the obtained results, we carried out some experiments aimed to improve the physico-chemical features of the catalyst for propene oligomerization in multitubular reactors. In particular, the attention was focused on obtaining a material which would hydrolyze more slowly in the presence of water, thus giving rise to a slower increase in the pressure drop.

Fig. 10 plots some results of the study; in particular, data are displayed con-

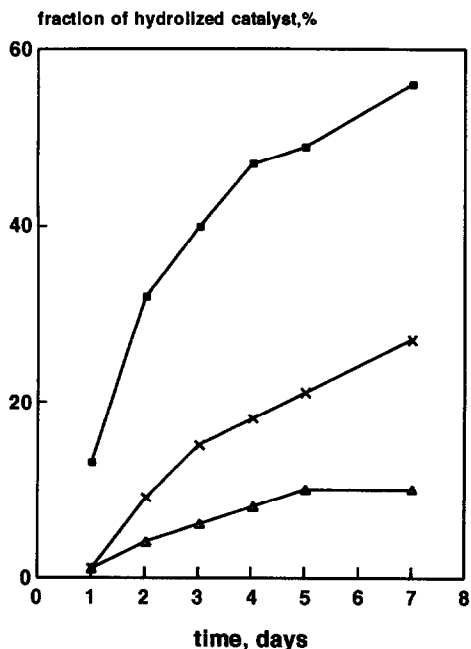


Fig. 10. Fraction of hydrolyzed catalyst as a function of the time of permanence in water at 20°C for three different grades of catalysts. Samples A (■), B (×), C (△).

cerning a laboratory test developed to evaluate the hydrolyzability of the catalysts (see the experimental section for the description of the test): the amount of hydrolyzed silicon phosphates, determined by titration of the released “free P_2O_5 ”, is reported as a function of time. The three reported samples were prepared utilizing increasing temperatures of calcination, and were characterized by different relative amounts of silicon *ortho*- and pyro-phosphates. It is shown that sample A hydrolyzes very quickly, while samples B and C release the phosphoric acid much slower, and are therefore more resistant towards the hydrolysis of the silicon phosphates that constitute the skeleton of the catalyst. Correspondingly, the X-ray analysis of the samples evidences a large fraction of hydrolyzed silicon phosphates in sample A, while sample C is substantially unaltered.

The improvement gained is clearly displayed in Fig. 11. The figure reports the results of a test which measures the decrease of the catalytic bed volume when applying a pressure over it. The decrease of the void space is obviously a consequence of the catalyst disintegration, occurring because of the silicon phosphates hydrolysis. The lower hydrolyzability of sample C corresponds to a less enhanced decrease of the bed volume.

The performance of sample C in the industrial reactor is compared with the one of sample B in Fig. 12. The figure shows the pressure drop along the cat-

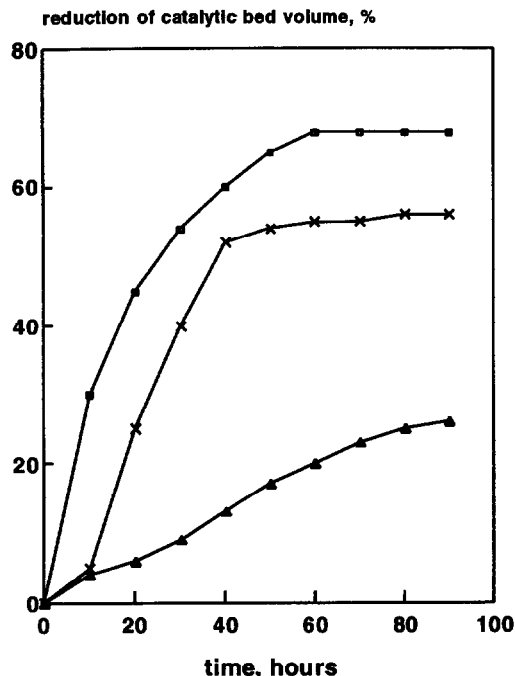


Fig. 11. Reduction of the catalytic bed volume as function of time when applying a compression over three different grades of catalysts. Samples A (■), B (×), C (△).

alytic bed for a test run in an industrial multitubular reactor; the lifetime of sample C was practically doubled with respect to sample B.

Suggested operating conditions

The reported data indicate that the water content in feed has a double effect; (i) it affects the catalyst activity; and (ii) it causes a slow hydrolysis of the main component of the catalyst, the silicon phosphates, with a destruction of the catalyst itself; this phenomenon is enhanced for higher water contents.

The best operating conditions are dictated by the type of application. In the case of the oligomerization reactor, it would be best to operate with a relatively low water content in the feed; in fact in this case the catalyst end-of-life is due to the hydrolysis phenomenon, while the propene conversion usually remains high all life long. However, the propene or propene/propane feedstocks are very often water-saturated (with water contents higher than 500 ppm), and therefore in this case the utilization of a catalyst particularly resistant against hydrolysis phenomena is strongly recommended. Alternatively, it could be convenient to take into consideration some drying pretreatment of the feedstock.

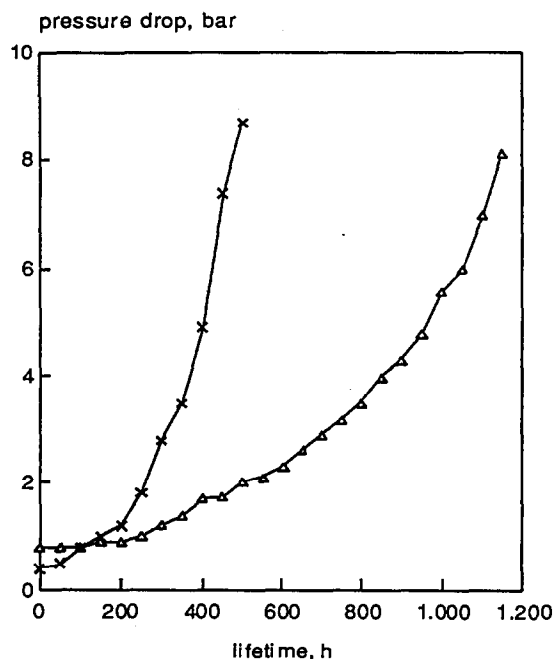


Fig. 12. Industrial test-run for two different grades of catalysts in the reaction of propene oligomerization. Samples B (x), C (Δ).

In the case of chamber reactors (for both benzene alkylation and propene oligomerization), where the catalyst lifetime is conditioned by the propene conversion, the water content can be of lower importance, even if high contents have to be in any case avoided. The optimal amount of water to be fed can therefore be obtained by interpolation in the given figures. In the case of cumene synthesis, the operation with 100–150 ppm of water gives rise to an equilibrated amount around 16 wt.-% of “free P_2O_5 ” in the catalyst (see Figs. 3 and 6). Fig. 6 shows that the corresponding activity is high and, most important, the selectivity to alkylaromatics is highest.

In the case of propene oligomerization, it is convenient to operate with approximately 250–300 ppm of water, corresponding to approximately the 12–13 wt.-% of “free P_2O_5 ” in equilibrated catalyst (Fig. 3). Under these conditions, the catalyst activity is relatively high (see Fig. 5).

The given conditions are those which allow to obtain the best catalytic performance as well as longer lifetime and easier catalyst unloading (because the catalyst pellet is left essentially unaltered in its morphology). Of course it has to be kept in mind that this parameter, as well as the other reaction conditions, are strictly a function of the physico-chemical features of the catalyst itself,

and can therefore vary on account of the significant differences found in the solid phosphoric acid catalysts marketed by the different companies.

CONCLUSIONS

The tests performed do not allow to reach a definite conclusion about the real active species in the alkylation and oligomerization reactions. As demonstrated in the previous sections, the nature of the active phase strictly depends on the utilized reaction conditions; as it is virtually impossible to determine the acids distribution on the catalyst under reaction conditions, only indirect correlations between activity and physico-chemical features of the catalyst are possible. Nevertheless, the reported data indicate that rather fixed water contents in the feed are necessary to maintain a defined phosphoric acids distribution, that gives rise to the best catalytic performance.

The improvement in the catalyst resistance towards hydrolysis remarkably lowered the phosphoric acid leaching, prolonging the catalyst overall lifetime. The catalyst destruction has been lessened, but remains, however, irreversible; the spent catalyst can not be regenerated, and must be disposed of. This remains indeed the most stringent drawback of the solid phosphoric acid catalyst.

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