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Solid phosphoric acid oligomerisation: Manipulating diesel selectivity by controlling catalyst hydration

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Abstract

Solid phosphoric acid (SPA) catalyst is traditionally used in crude oil refineries to produce unhydrogenated motor-gasoline by propene and butene oligomerisation. SPA is also used in High-Temperature Fischer–Tropsch refineries (HTFT) to produce synthetic fuels albeit with a different emphasis. The petrol/diesel ratio of an HTFT refinery is very different from crude refining and it is often necessary to shift this ratio depending on market requirements. The influence of hydration was investigated as a means of improving diesel selectivity. This was achieved by studying SPA over a hydration range of $99–110\%$ H_3PO_4, a temperature range of $140–230$ °C and using $C_3–C_6$ model and synthetic FT-derived olefinic feedstocks. A direct correlation was found between the selectivity towards diesel range products and the distribution of the phosphoric acid species viz. H_3PO_4, $H_4P_2O_7$ and $H_5P_3O_{10}$. For various olefinic feedstocks, diesel selectivity increased with decreasing catalyst hydration with a maximum around 108% H_3PO_4 for propene oligomerisation. Commercial tests confirmed the increase in diesel selectivity with lowered catalyst hydration.

1. Introduction

Phosphoric acid catalysis for light olefin oligomerisation and alkylation has been around since the early 1930s in various forms: liquid phase acid [1], phosphoric acid supported on quartz [2] and solid phosphoric acid [3]. The latter is produced by mixing (85%) phosphoric acid with Kieselguhr (silica) and then extruding and calcining at high temperature. The resulting catalyst can be described as a "glassy layer" of different phosphoric acid species on a mixture of silica and silicon phosphates that acts as an active support. The term "supported liquid-phase" catalyst has also been used to describe solid phosphoric acid [4].

Arguably the most important characteristic of the solid phosphoric acid catalyst is that of hydration (water content), which is the equilibrium value between the water in the feed and the phosphoric acid at the operating conditions. It dete-

rmines the nature and structure of both the active phase and the support. If the catalyst is over-hydrated, swelling of the catalyst is observed associated with a rapid increase in pressure drop. When it is under-hydrated, the catalyst loses activity, becomes brittle and disintegrates. Traditionally hydration is expressed in terms of phosphoric acid (H_3PO_4) content which only refers to the active/liquid phase. When 85% H_3PO_4 is dried/calcined, the H_3PO_4 is not only concentrated but it also forms linear polymers of higher acids (pyro- and tripoly-phosphoric acid) while releasing water. A quantitative description of the acid distribution was given by Jameson [5]. A catalyst thus described as having a hydration level (or acid "strength") of 100% H_3PO_4 does not imply that it is 100% pure H_3PO_4, it merely refers to a state of dryness where the active phase consists of some water and approximately 14% and 86% pyro- and ortho-phosphoric acid, respectively. Brown and Whitt [6] measured the equilibrium data from which the hydration of the phosphoric acid can be estimated using the process temperature and water content of the feed at equilibrium. Cavani et al. [7] also demonstrated that a partition equilibrium is established between the P_2O_5/H_2O mixture adsorbed on the catalyst

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surface and the reactant phase, modifying the distribution of the phosphoric acid species viz. H_3PO_4, $H_4P_2O_7$ and $H_5P_3O_{10}$, on the catalyst.

While attempts to describe the hydration of the catalyst have been limited to the "free" phosphoric acid, the hydration of the support could also be used. The support, consisting of different silicon phosphates, will also respond to variations in the feed water content albeit at a slower rate. Depending on the hydrolysis rates of the different phosphates, the relative ratio of the silicon phosphates can give an indication of catalyst hydration. Commercial experience has shown that the ratio of ortho-/pyro-silicon phosphates is a good indicator of spent catalyst hydration. A quantitative description (similar to that of Jameson) of the relative concentration of the silicon phosphates with regard to water content is, however, not found in literature.

Apart from "polygasoline" production in crude oil refining, SPA has also found application in the production of nonene, dodecene and cumene. It has also been employed in the synthetic fuels environment, more specifically in High-Temperature Fischer–Tropsch (HTFT) refining, for propene and butene oligomerisation. Due to the nature of a Fischer–Tropsch refinery, the relative ratio of gasoline to middle distillates is quite different from that of a crude oil refinery. Here, the ability to change this ratio has been a topic of study. This would enable the refinery to respond to changes in the market demand.

It would seem from the literature that the selectivity of the *solid* phosphoric acid catalyst has typically been studied for cumene production but has been playing second fiddle to conversion and catalyst life when it comes to polygasoline production [7]. Remarkably, for a catalyst that is well known to have the capability to produce C_4 trimers and C_3 tetramers, the literature reports no systematic investigation of the effect of hydration on diesel selectivity. The only reference to "heavy polymer" selectivity or carbon number distribution is by Bethea and Karchmer [8] which related it to the strength (or hydration level) of the *liquid* phosphoric acid. It is even more remarkable since it is well known that processes using solid phosphoric acid require careful control of the water content of the feed and thus of the catalyst hydration [1,4,9].

Zhirong et al. [10] managed, through high performance liquid chromatography (HPLC) analysis of the free phosphoric acid, to determine the ortho and pyro content of the free phosphoric acid. From this, he showed a correlation between the acid distribution and therefore hydration/acid strength, and selectivity to nonene and dodecene.

It is therefore reasonable to assume that the selectivity to higher polymers, i.e. diesel range products, can be manipulated by careful control of the catalyst hydration through controlling the water content of the feed and the process temperature. This hypothesis was tested in the laboratory with model feeds and commercial feedstocks. It is our intention to show that hydration can indeed be used as a process control parameter to manipulate diesel selectivity. The concept was also tested on a commercial scale. Results of the laboratory tests and, where possible, commercial results are reported.

2. Experimental

2.1. Catalyst preparation and characterisation

Several solid phosphoric acid catalysts, which were prepared as described in the patent literature [11], were obtained from Süd-Chemie and other catalyst suppliers. Selected Süd-Chemie samples were analysed with a Siemens X-ray diffractometer using Cu Kα radiation. The relative ratio of the ortho- to pyro-silicon phosphates was measured using the peak areas at 2θ values of $25°$ and $24°$, respectively. The "free acid" content of the catalysts was determined by titration with 0.1 M NaOH of the leached acid after submerging a finely ground catalyst sample in water at room temperature. The average pore diameter, pore area and total intrusion volume of the catalysts were determined using a Micromeritics (Mercury, 3 bulb, 0.412 stem, solid) penetrometer.

2.2. Effect of hydration on diesel selectivity

The bench-scale reactor system used for this evaluation consisted of a fixed-bed, stainless steel reactor (internal diameter of 35 mm), containing 100 g of a commercial solid phosphoric acid catalyst ground to a particle size of 1.2–2 mm. The reactor was heated with three external heating elements (clamped around the reactor tube) and catalyst bed temperatures (axial gradients) were measured with wire thermocouples inside a thermowell. An industrial mixture of propane/propene (Sasol Synfuels Refinery, Secunda, South Africa) was purified in a high-pressure column on pilot plant scale (Sasol Technology R&D, Sasolburg, South Africa). The purified mixture consisted of 58% propene, 41% propane, <1% ethane

Table 1
Fresh catalyst characterisation

| Catalyst	C84/5L	C84/5S	C84/3	CA131
Place of manufacture	Süd-Chemie Louisville	Süd-Chemie Sasolburg	Süd-Chemie Sasolburg	Süd-Chemie Louisville
Mass loaded (g)	32	32	32	32
Free acids (wt.%)	24.8	23.5	22.4	25.0
Ortho-/Pyro-silicon phosphate (XRD counts)	465:35	499:1	284:216	499:1
Average pore diameter (Å)	397	357	279	452
Total pore area (m^2/g)	21	31	36	39
Total intrusion volume (ml/g)	0.21	0.28	0.25	0.44
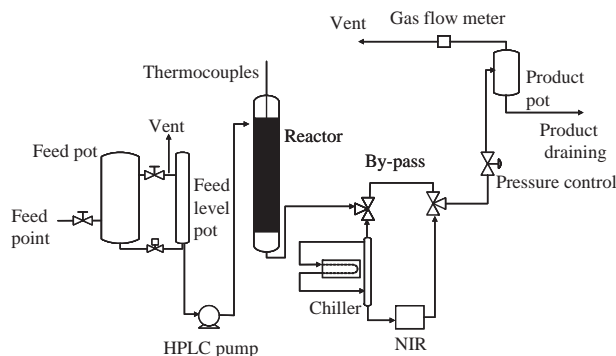
Fig. 1. Simplified flow diagram of laboratory reactor system.

and some C_4 impurities (<0.1%) (by mass). This was fed from a gas cylinder (30 bar), through a temperature-controlled saturator, to the reactor, using a positive displacement pump.

The saturator consisted of a temperature controlled water reservoir through which the dry feed was passed. A sparger was employed to improve water solubility. Using a back-pressure regulator, the reactor was run at 38 bar (typical commercial pressure). The water content of the feed was varied by controlling the temperature of the saturator. The water content was measured periodically using a Mettler Toledo Karl Fischer titrator. These analyses were verified with estimates of the feed water content (assuming complete saturation) using the composition and solubilities of water in hydrocarbons. The solubility of water in the feed was calculated using the following equations [12]:

Propane: $\ln(X_w) = 7.84827 - 4709.76/T$

$\quad$ (T in K; X_w molar fraction of water)

Propene: $\ln(X_w) = 6.61939 - 3968.98/T$

From the water content in the feed, the water partial pressure was calculated via Henry's law. This was related to the hydration of the catalyst using the equations of Brown and Whitt [6].

Experiments were carried out at liquid hourly space velocities (LHSV) of 3 and 14 h^{-1} and average bed temperatures between 180 and 200 °C. The oligomer product was analyzed with the ASTM D86 method in order to determine the distillation properties which were related to the diesel selectivity.

2.3. Effect of catalyst on the hydration vs. diesel selectivity relationship

This experiment entailed the parallel screening of four different solid phosphoric acid catalysts (Süd-Chemie C84/5L; C84/5S; C84/3 and CA131 – characterisation in Table 1) to find the catalyst with the highest diesel selectivity. Four identical reactors (internal diameter of 35 mm) of similar configuration as used above, were loaded with 30 g of catalyst. A simplified flow diagram of the reactor system is shown in Fig. 1. Catalyst morphology was unaltered, with particles loaded as received from the supplier. The "dry" propene/propane mixture (70 ppm H_2O) described earlier, was again used as feed. Only temperature and LHSV were varied while the pressure was kept constant (38 bar). An NIRSystems online near infrared spectrometer on the product line (at 3 °C) of one of the four reactors was used to determine when stable conditions were achieved. Using the feed composition and process temperature, the hydration level of the catalyst was estimated in the same manner as for the first experiment. Only the results showing the effect of catalyst hydration on diesel selectivity and propene conversion are reported.

2.4. Effect of feed on the hydration vs. diesel selectivity relationship

Several laboratory qualitative tests were also performed, using similar equipment as described above albeit with larger catalyst capacities. Two commercial solid phosphoric acid catalysts, including one from Süd-Chemie, were used in this test (Table 2). No saturator was employed and the feed water content was constant. Various olefinic feedstocks of commercial (Sasol Synfuels Refinery, Secunda, South Africa) and pilot plant (Sasol Technology R&D, Sasolburg, South Africa) origin were used (Table 2). Commercial recycle operation was simulated by pre-mixing feed with typical product.

2.5. Commercial tests

A test run was performed on a commercial oligomerisation unit referred to as the Catpoly unit at Sasol in Sasolburg, South Africa. The purpose of the test was to confirm the increase in the

Table 2
Effect of process temperature (hydration) on diesel selectivity for varying feed compositions

Catalyst	Feed composition	Temperature (°C)	Diesel selectivity (%)	Olefin conversion (%)
Commercial SPA	C_3-C_4 and recycled gasoline[a]	167	53	51
Commercial SPA	C_3-C_4 and recycled gasoline	180	58	60
Commercial SPA	C_3-C_4 and recycled gasoline	197	76	64
Süd-Chemie C84/3	C_3-C_4 and recycled gasoline	167	40	71
Süd-Chemie C84/3	C_3-C_4 and recycled gasoline	180	56	72
Süd-Chemie C84/3	C_3-C_4 and recycled gasoline	197	66	82
Commercial SPA	C_3 mixture[b], C_5-C_6 olefins[c] and recycled gasoline[d]	180	50	79
Commercial SPA	C_3 mixture, C_5-C_6 olefins and recycled gasoline	230	70	84

[a] Composition of the recycled gasoline and the C_3-C_4 feedstock was typical of a HTFT refinery [13]. Recycle ratio=2.5:1.
[b] 50% propane/50% propene (by mass).
[c] 1% C_4's/7% pentanes/45% pentenes/3% hexanes/35% hexenes/9% C_7's and heavier.
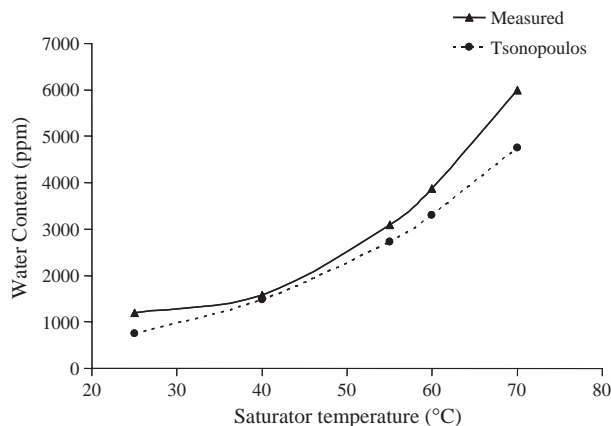[d] Mixing ratio (by mass) of C_3 mixture/C_5-C_6 olefins/recycled gasoline=9:1:10.

Fig. 2. Water content in feed – measured and estimated.

Fig. 3. Effect of hydration on diesel selectivity at different space velocities.

diesel selectivity with increase in process temperature and consequently lowered catalyst hydration, as indicated by laboratory experiments. The unit (designed by UOP) has been in operation since the early 1960s with a catalyst similar to the UOP solid phosphoric acid catalyst as described in the patent [11]. The feedstock was a mixture of light olefins with a composition typical of a High-Temperature Fischer–Tropsch process [13]. Assuming constant water content of the feed, hydration of the catalyst was thus adjusted by varying process temperatures.

In an attempt to increase the diesel production, the observations from the foregoing test run were applied to the Catpoly units in Secunda, South Africa. Here the catalyst hydration was maintained by a controlled addition of water to the feedstock. In one of the reactor systems, the water addition was stopped, and in the other reduced together with an increase in reactor temperature. After several weeks of operation, the increase in diesel selectivity was confirmed and the reaction temperature was kept at the new level. The hydration of the spent catalyst was determined and compared with similar samples from previous production periods. The methods used for the catalyst characterisation were the same as for the laboratory evaluations.

3. Results and discussion

3.1. Effect of hydration on diesel selectivity

Fig. 2 shows the measured versus estimated [12] water content of the propene/propane feed at different saturator temperatures. The results of the catalyst hydration vs. diesel selectivity experiment are presented in Fig. 3. In the range from 100% to 105% H_3PO_4, the diesel selectivity increases with an increase in acid strength (decreasing hydration level) and higher diesel selectivity is favoured at the lower space velocities for comparable hydration levels. Directionally, it follows the same trend as presented by Bethea and Karchmer [8] for supported liquid phosphoric acid and Zhirong et al. [10] for solid phosphoric acid, both dealing with propene oligomerisation.

The results obtained here indicate that it could be beneficial for commercial diesel production to run at an acid strength of
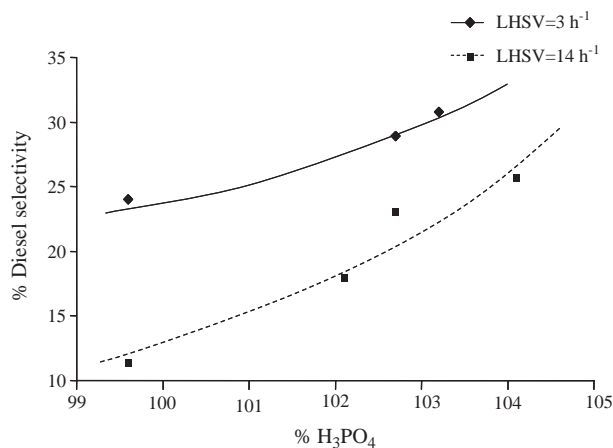
105% H_3PO_4 or even higher. This would be contrary to commercial experience, where catalyst strength is seldom controlled above 104% H_3PO_4, as catalyst life is reduced due to coke formation and embrittlement. A typical acid strength of 102% H_3PO_4, which is aimed at maximum petrol yield, is more commonly employed.

3.2. Effect of catalyst on the hydration–diesel selectivity

Diesel selectivity (Fig. 4) increased with increasing acid strength/decreasing hydration with a maximum around a hydration level of 108% H_3PO_4. This corresponds with the work by Zhirong et al. [10] where the tetramer selectivity for propene oligomerisation peaked at roughly 108% H_3PO_4 content. According to Jameson [5], this is where the highest concentration of pyro-phosphoric acid is found. If one further considers that the phosphoric acid species have different acid strengths (i.e. pKa values) and that pyro-phosphoric acid is a stronger acid than the ortho-phosphoric acid, it could explain the shape of the selectivity/conversion curves (Figs. 4 and 5). Although the pKa value of the tri-phosphoric acid indicates that it is an even stronger acid than the pyro-phosphoric acid, it
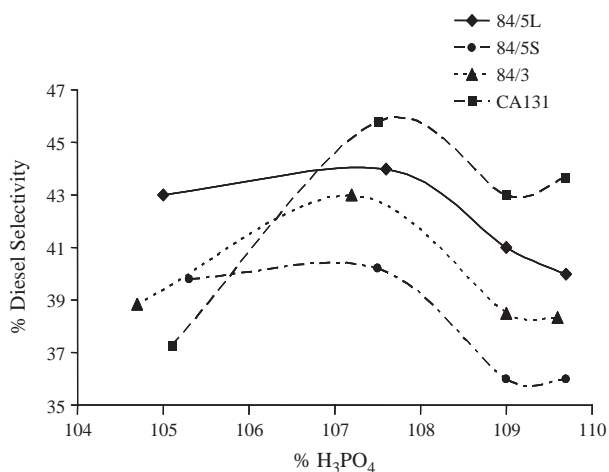

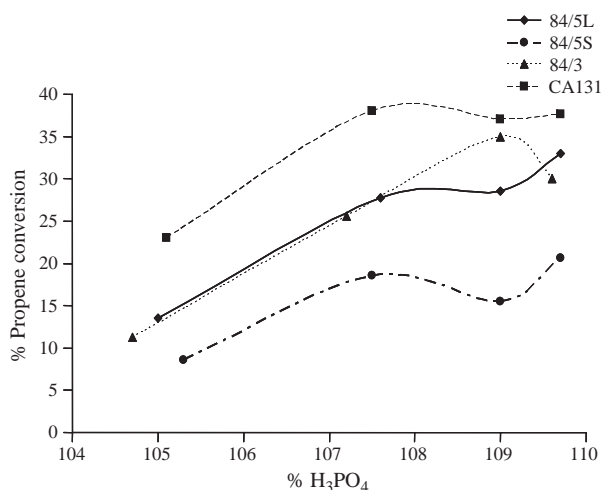Fig. 4. Effect of hydration on diesel selectivity – various catalysts.

Fig. 5. Effect of hydration on propene conversion – various catalysts.

does not seem to impact the selectivity/conversion curves– probably due to its very low concentration.

At higher acid strengths, diesel selectivity decreases significantly but seems to either stabilize or even increase thereafter. No similar inflection (occurring roughly at 10g% H_3PO_4) was previously observed since the hydration ranges studied were typically between 98% and 108% H_3PO_4 [8,10].

Except for the C84/3 catalyst, propene conversion (Fig. 5) increased with acid strength, displayed an inflection at 109% H_3PO_4, and increased thereafter. This is in line with the observation by Cavani et al. [7] in which they related the first conversion maximum in their data to the pyro-phosphoric acid, stating that it determines the activity of the catalyst. The catalysts not displaying the inflection had a very different initial ortho-/pyro-silicon phosphate ratio (Table 1) indicating a much "dryer" catalyst.

The results obtained here confirm that hydration is a primary driving force for diesel selectivity. Despite the differences in the catalysts, the selectivity peaked at the same hydration level, while this was not true for conversion. The diesel selectivity and propene conversion vs. hydration trends are influenced by the composition and morphology of the catalyst.

3.3. Effect of feed on the hydration–diesel selectivity relationship

Since the aim was to implement this concept commercially, it was necessary to confirm that the observed increase in diesel selectivity would also be valid for feedstocks other than propene. Gevert et al. [14] studied the oligomerisation of isobutene on solid phosphoric acid. It would seem from their

work that the relation between hydration (acid strength) and diesel selectivity for butene oligomerisation could be different to that for propene oligomerisation. They showed some differences in selectivity but did not relate it to hydration, but rather to catalyst pore size distribution.

Experiments were subsequently performed to confirm that increasing temperatures (without increasing the water content of the feed) would result in an increase in diesel selectivity for a variety of commercial Fischer–Tropsch feedstocks (Table 2). These experiments showed qualitatively that for various feedstocks, increasing temperatures without increasing the water content of the feed resulted in an increase in diesel selectivity and thus followed the expected trend. Despite similarities in the commercial catalyst used, they differed with regards to diesel selectivity at similar hydration levels.

It is known from the work by Krawietz et al. [9] and others, that the support does not contribute to the catalysis and that the phosphoric acid is the active phase, which is similar for all SPA catalysts at equilibrium. However, the support plays a role in determining the accessibility to the active phase. This cannot be ignored and manifests itself in differences in product selectivity between catalysts manufactured from different Kieselguhrs, and by different preparation procedures.

3.4. Commercial experience

The first commercial test yielded expected results with a clear increase in diesel selectivity observed with an increase in the acid strength. This resulted in the second test run at the larger facility being performed. Knowing that the maximum diesel yield would be limited by the maximum practical acid strength without undue reduction in catalyst life, a cautious approach was followed. After several months of "normal operation" following a fresh catalyst loading, catalyst samples were taken at various positions throughout the catalyst beds in two identical reactor systems designated as Catpoly East and Catpoly West. Since catalyst hydration could not be estimated from feed compositions (not all the streams are saturated or accessible for sampling during normal operation), the analysis of the catalysts was the only alternative (Table 3). Results show that when the average ortho/pyro counts of the two reactor systems were compared, the catalyst of Catpoly East was over hydrated. Catpoly West was in the "normal" regime which could translate to a hydration level of 102–104% H_3PO_4.

It was decided that the water addition be stopped at the Catpoly West plant with no temperature adjustment. The water addition at Catpoly East was reduced by half and the average

Table 3
Catalyst analysis confirming hydration reduction associated with diesel selectivity increase

Catpoly production unit	Ortho/Pyro fresh catalyst	Ortho/Pyro before adjustments	Water addition	Temperature adjustment	Ortho/Pyro after adjustments	Diesel selectivity increase
West	460:40	440:60	Stopped	No adjustment	425:75	Nominal
East	445:55	495:5	Reduced	±10 °C increase	440:60	Significant

inlet temperature of the process was increased by roughly 10 °C. After a few months of continuous operation, the catalyst was again analyzed. Results (Table 3) indicated a small change in the hydration of the Catpoly West catalyst towards the under hydrated regime (roughly 103–105% H_3PO_4). A nominal increase in diesel yield was observed during this period.

The catalyst from Catpoly East showed a decrease from over hydrated to normal hydration with a significant increase in diesel yield being observed. Similar conversions and catalyst lifetimes were observed despite differences in hydration.

4. General discussion

Given a certain feedstock and solid phosphoric acid catalyst, it will be possible to optimize the diesel production by increasing the diesel selectivity through manipulation of the catalyst hydration. This could be achieved by finding the temperature conditions where conversion is still high, but then adjusting the hydration with water addition such that optimum selectivity is achieved. As catalyst conversion drops and process temperatures are adjusted upwards, water addition should be increased to keep the catalyst at the optimum hydration level. The fact that Zhirong et al. [10] finds a maximum for C_{12} selectivity implies that there is a limit to the amount of diesel that can be produced and therefore a limit to the benefit of using hydration to increase diesel selectivity. It may be necessary to sacrifice conversion and catalyst lifetime to gain diesel selectivity. This would make sense only if local economic drivers favour such operation.

5. Conclusion

It was confirmed that there is a direct correlation between the selectivity towards diesel range products, and the distribution of the phosphoric acid species. In the range from 100% to 105% H_3PO_4, the diesel selectivity increases with an increase in acid strength (decreasing the hydration level) and higher diesel selectivities are favoured at lower space velocities for comparable hydration levels, due to an increase in conversion. The correlation between propene conversion and the distribution of the phosphoric acid species was again observed. Catalyst morphology influences conversion, but does not seem to influence selectivity. Commercial tests proved that it is possible to optimize the diesel production by increasing the diesel selectivity through manipulation of the catalyst hydration.

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