



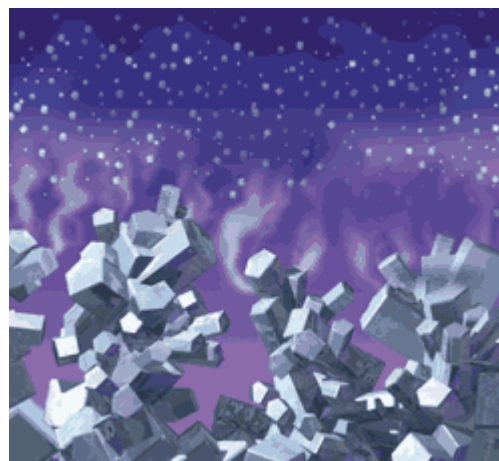
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Gaseous acid catalysis: An intriguing new process



Our furfural expert is back and offers you what he calls “a story against all odds”.

Acid catalysis, a common reaction mechanism in organic chemistry, implies the involvement of oxonium, or hydronium, ions, H_3O^+ (see box, “[H₃O[±] nomenclature](#)”). “Acid catalysis” is inherently understood to be a process that occurs in aqueous solution. Nobody seems to have thought of using a gas as an acid catalyst, and with good reason. As shown in Figure 1, gases are not ionized until very high temperatures are reached ([1–3](#)).

As can be seen, there is no significant thermal ionization below 2500 °C for water and below 5000 °C for HCl. Ionization by cosmic rays and ambient radioactivity is also negligible, together amounting to no more than 10 ion pairs/(s cm³) with a life span of 70 s ([4](#)). Thus, gases at all but extremely high temperatures may be considered completely nonionized, as demonstrated by their being perfect electrical insulators.

Obviously, a nonionized gas cannot be an “acid catalyst”; therefore, it has been the universal belief that acid-catalyzed processes must be carried out in the liquid phase. However, recent studies of

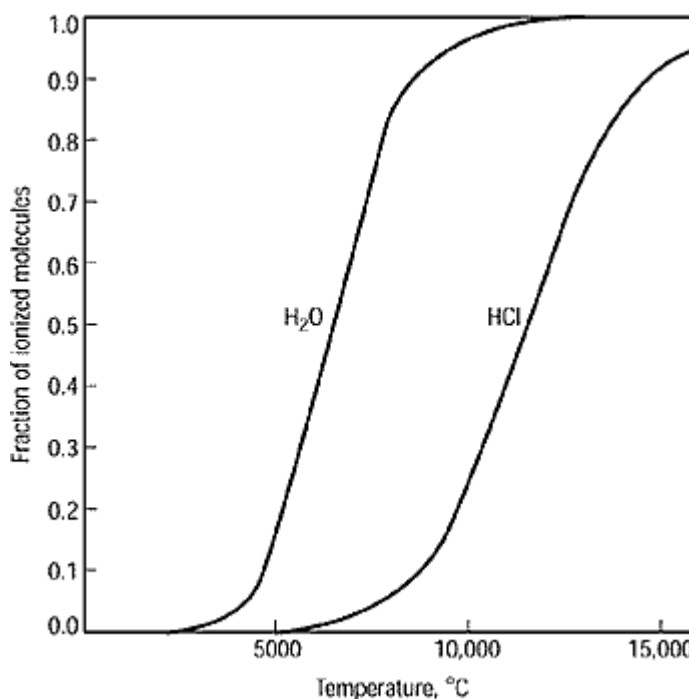


Figure 1. The thermal ionization of water and HCl vapor at atmospheric pressure. The curves are based on Saha’s equation for thermal ionization ([1](#)) as applied to

stratospheric chemistry and the depletion of the ozone layer have shown that HCl vapor, usually stable, becomes ionized in the presence of ice crystals that are abundant in the stratosphere. HCl and water vapor molecules are strongly adsorbed on the surface of the ice crystals. In the state of adsorption, each HCl molecule reacts preferentially with four water molecules to form an ionized cluster, $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3\text{Cl}^-$, in which the three water molecules form the equatorial plane of a trigonal bipyramid, with Cl^- and H_3O^+ ions at the apexes (5). The chlorine atom carries a charge of $-0.80 e$ and the oxonium ion a charge of $+0.85 e$, so that the electrical activity of the cluster is almost equal to that of free Cl^- and H_3O^+ ions. The role of the solid surface is to permit HCl molecules to come into contact with four water molecules, which is not possible via collisions in a gas phase devoid of adsorbing surfaces.

Against this background, I theorized that what takes place on ice crystals might also take place on other solids studded with polar hydroxyl groups. Sugars fall into this category, so that gaseous HCl and water molecules should adsorb on the surfaces of solid sugars, and on these surfaces they should react with each other to form $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3\text{Cl}^-$ clusters. Having an oxonium ion on one apex, these clusters should act very much like oxonium ions in an aqueous acid catalyst, so that when the sugar is pentosan or pentose, the clusters should be capable of triggering the hydrolysis and dehydration reactions leading to furfural (6, 7).

To create the appropriate conditions for such a process in a reactor, it is only necessary to

- place comminuted raw material in the reactor,
- introduce a stream of superheated steam at atmospheric pressure, and
- disperse a small quantity of hydrochloric acid into this stream with a vaporizer.

The superheated steam in the second step dries the material by raising its temperature far above the dew point of water or hydrochloric acid. Adding the acid forms a mixture of gaseous water and HCl molecules passing through a dry charge, to provide a situation in which I expected the gas in combination with the solid raw material to catalyze the conversion of pentosan to furfural.

Against all odds

Much to the surprise of skeptics, when this process was tried at $155\text{ }^\circ\text{C}$, the exiting gas stream was heavily loaded with furfural, low boiling compounds, and carboxylic acids (8), thus demonstrating that, against all odds, gaseous acid catalysis is an intriguing new option.

Just as surprisingly, the generated furfural ends up in the gas phase, even when the process is carried out below its boiling point ($161.7\text{ }^\circ\text{C}$). This indicates that when pentose is dehydrated by gaseous acid catalysis, the water molecules participating in the process render the furfural more volatile than it would be in an abundance of furfural molecules. In gaseous acid catalysis, seven water molecules participate per furfural molecule generated: three liberated in the dehydration of pentose and an additional four incorporated in the ionized cluster. So, the molar water concentration on the catalyzing surface is $7/8 = 0.875$. This is very close to the furfural–water azeotrope, which lies at a molar water concentration of 0.9083 (65 wt%).

Although in the case of gaseous acid catalysis it would be inappropriate to speak of the

formation of an azeotrope, conceptually applicable only to a liquid phase, the fact remains that the attractive force between a furfural molecule and surrounding water molecules is smaller than the force between furfural molecules. Consequently, inasmuch as every furfural molecule generated in gaseous acid catalysis behaves as if it were “floating” on seven water molecules, this situation makes the furfural molecule roughly as volatile as in a liquid azeotropic mixture.

Another important feature of the new process is that the absence of a liquid phase greatly increases the furfural yield. In conventional furfural processing (6), the furfural generated dissolves in the liquid phase, where, under the catalyzing influence of oxonium ions, it undergoes loss reactions with itself and with intermediates of the pentose-to-furfural conversion. In addition, with sulfuric acid as the customary catalyst, there are losses by sulfonation. Consequently, the yield in conventional furfural plants is only on the order of 50%. By contrast, in gaseous acid catalysis, with no liquid phase in which to dissolve, the generated furfural is instantly vaporized and loss reactions are avoided.

Advantages of the new process

In conventional furfural processing, high pressures are needed to keep the aqueous catalyst in the liquid state; the customary catalyst, H_2SO_4 , is nonvolatile, so that it is lost in the residue where it presents a disposal problem.

As compared with this conventional processing, the new gaseous catalysis process has the following advantages:

- The process can be carried out at atmospheric pressure, at any given temperature.
- Because the H_2O – HCl catalyst is used far above its dew point, there is no corrosion, and the reactor can be made of mild steel.
- The acid portion of the catalyst can be completely recovered and recycled, so that there is no acid consumption and no acid disposal problem. Known technology is available for the acid recovery.
- The residue is dry and free of acid, and is thus eminently suited for a simple combustion without any problems. By partial combustion in air, it is also possible to use the residue for the manufacture of “producer gas” consisting mostly of carbon monoxide, hydrogen, and nitrogen.
- The yield is nearly 100% because there is no liquid phase in which loss reactions can take place. Yields of up to 95.8% have been measured.

An example

A typical gaseous acid catalysis process is illustrated in Figure 2. Reactor 1 is charged

H_3O^+ nomenclature

In the course of editing this article, the staff of *Chemical Innovation* was surprised to learn that the name “hydronium ion” is not the preferred one for H_3O^+ . This is the case in spite of our finding that almost every general chemistry text, encyclopedia, and dictionary, old and new, that we could find uses “hydronium ion”.

But the author has pointed out that “oxonium” is recommended by the International Union of Pure and Applied Chemistry (*Nomenclature of Inorganic Chemistry*; Leigh, J. G., Ed.; Blackwell Scientific Publications: Oxford, U.K., 1990; p 104). Accordingly, we have used “oxonium” throughout this article.

The author also stresses that oxonium ions should never be called “hydrogen ions” or “protons”.

—Eds.

with comminuted raw material of high pentosan content, such as sunflower stems, corncobs, or bagasse. Steam at atmospheric pressure is passed through a superheater 2 fueled by combustion gas, and this stream is then passed through the charge to heat it to a temperature far above the maximum atmospheric dew point of hydrochloric acid.

When the desired temperature is reached, a small quantity of hydrochloric acid is continuously dispersed into the superheated steam by means of a vaporizer 3 to give the gas stream an HCl content of ~1.5 wt%. The gas stream leaving the reactor is liquefied in a condenser 4, and the condensate is collected in a buffer tank 5 before it enters a separation plant 6 that isolates furfural, low boiling compounds, and carboxylic acids and recovers HCl as its azeotrope with water. This hydrochloric acid is used to feed the vaporizer 3, so that the catalyst is contained in a closed circuit. The “pervaporation” of the charge is continued until no more furfural is produced. Then, the residue is discharged under nitrogen, to prevent self-ignition, and a new batch is started.

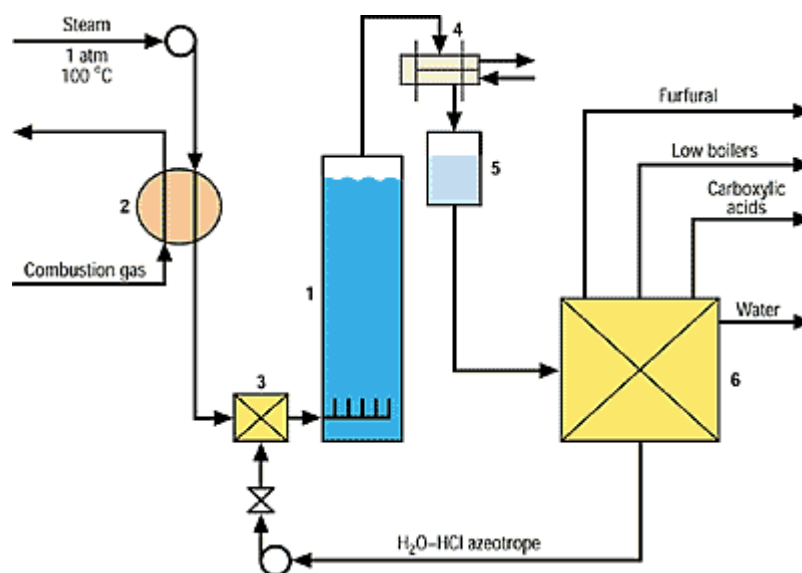


Figure 2. Gaseous acid catalysis process. 1, reactor; 2, superheater; 3, vaporizer; 4, condenser; 5, buffer tank; 6, separation plant.

The phase diagram of the HCl–H₂O system at atmospheric pressure is shown in Figure 3. It features a maximum azeotrope at 20.2 wt% of HCl, with a boiling point of 108.6 °C. Thus, the new process must be carried out above this temperature.

A fleeting catalyst

The discovery of gaseous acid catalysis demonstrates the existence of a complex process in which the surface of a solid reagent sets the stage for the formation of a strange ionized species from nonionized gases, with the result that the ionized species catalyzes the conversion of the reagent on which it was formed. The ionized species acts as a “fleeting catalyst” that exists for only as long as the reagent exists. Its charge distribution produces the same catalytic effects as oxonium ions in aqueous solution, although a liquid phase never materializes.

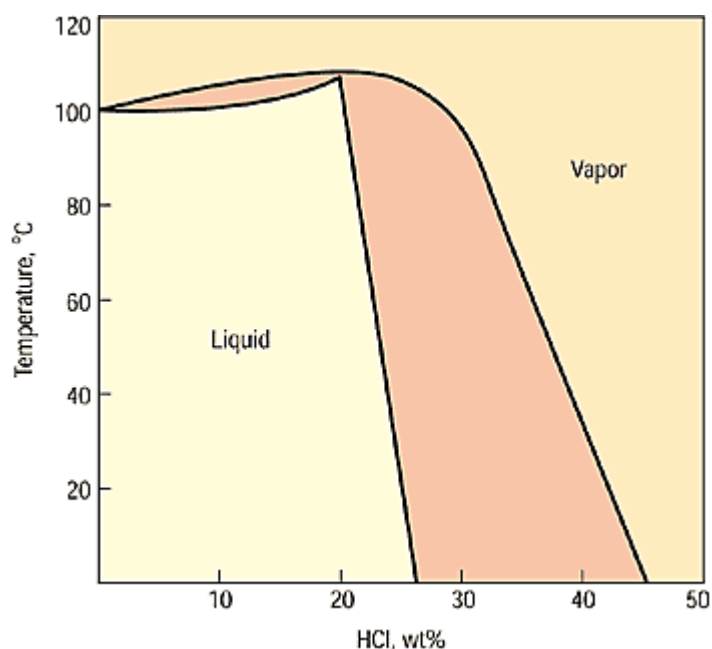


Figure 3. Phase diagram of the HCl–H₂O system at atmospheric pressure, illustrating the azeotrope at 20.2 wt% HCl.

It is conceivable that gaseous acid catalysis on ice crystals has played a major role in reactions that produced precursor compounds of life on earth. In the early terrestrial atmosphere, formaldehyde was produced in quantity by solar ultraviolet photolysis of water vapor and carbon dioxide. On catalytic surfaces, by aldol condensation from the gas phase, formaldehyde is known to form sugars (9).

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For more information

For information on commercial applications of gaseous acid catalysis, contact

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