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[54] PROPYLENE OXIDATION IN THE PRESENCE OF GOLD METAL

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[52] **U.S. Cl.**.....**260/604 R,** 260/597 R, 260/533 R

[51] **Int. Cl.**.....**C07c 45/04**

[58] **Field of Search**.....260/604 R; 252/468

[56] **References Cited**

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[57] **ABSTRACT**

Propylene is oxidized with oxygen to primarily acrolein by oxidation in the contact presence of gold metal.

8 Claims, No Drawings

PROPYLENE OXIDATION IN THE PRESENCE OF GOLD METAL

This invention relates to a process for oxidizing propylene to obtain a useful mixture of organic compounds comprising acrolein, with much smaller amounts of acetone, acetaldehyde and acetic acid.

In addition to the useful organic oxidized compounds, by-products, such as carbon dioxide and water, are also formed. It was believed from the literature (W. R. Patterson and C. Kemball, *Journal of Catalysis*, Volume 2, page 465, (1963)) that the oxidation of propylene would yield only water and carbon dioxide. Quite unexpectedly, it has been found that the main product of the oxidation reaction is acrolein so long as the oxidation reaction is carried out in the presence of gold metal.

In accordance with the invention, therefore, propylene is oxidized to a product comprising acrolein by reacting propylene under oxidation conditions with a gas containing free molecular oxygen in the contact presence of gold metal.

In order to obtain good selectivity to the desired oxygenated compound, it is important that the propylene together with a gas containing free molecular oxygen be contacted with the gold metal, either support or unsupported, at a temperature within the range of about 150°C. to 450°C. and preferably within the range of about 200°C. to about 350°C.

Since the reaction is exothermic, means must be provided to control the temperature of the reaction within the limits defined above. Below the lower temperature limits defined above the reaction rate becomes too low to be economically feasible, whereas at temperatures above the upper limit the yield of desired oxygenated compounds decreases with the concurrent production of excessive amounts of water and carbon dioxide. The temperature can be controlled by any suitable means, and one method of at least partially controlling the temperature is to dilute the gold metal by distending it on a suitable support material such as silica, magnesia, alumina, thoria or mixtures thereof. The gold metal can, of course, be used unsupported and when this is done the metal can be in any suitable form, such as sponge form. When the gold is distended on a support, the surface area of the support is not critical and can suitably be between 0.1 and 600 square meters per gram. In addition to the above named supports, materials such as carbon, kieselguhr, pumice, the natural clays, mullite and alundum are also suitable. When the gold metal is supported, suitable amounts of gold metal are from 0.2 to 30 weight percent of the total catalyst, with preferred amounts from 1 to 10 weight percent and the more preferred amounts from 1 to 5 weight percent of the total catalyst.

Any suitable method can be used to prepare the catalyst although it is preferred to utilize a supported catalyst and further preferred to deposit the gold catalyst onto the support by the method of incipient wetness from organic solution of a gold salt such as $HAuCl_4 \cdot 3HC2O$ and particularly from an acetone solution of a gold salt. The gold can also be deposited from an ether solution or, of course, from an aqueous solution.

Another method of controlling the temperature is to dilute the propylene-oxygen mixture with an inert gas

such as nitrogen, helium or a hydrocarbon such as propane. For example, the propane-propylene stream from a refinery cracking unit may suitably be used as a charge stock for the process of this invention. Yet another method of controlling the reaction temperature is to pass the admixture of propylene and oxygen over the gold metal catalyst at very high space velocities. Suitable gaseous space velocities are within the range of about 1 to about 2000 volumes of propylene measured at standard temperature and pressure per volume of catalyst per hour, and the preferred space velocities are from about 5 to about 200.

A total operating pressure of about one atmosphere is the desired operating pressure. Higher or lower pressures can be used; for example, a total pressure of about 0.5 to 15 atmospheres or more can suitably be employed.

The ratio of the partial pressure of oxygen to the partial pressure of propylene can suitably be between 0.2 and 50, and is preferably between one and five. The partial pressure of propylene should be at least 0.05 psia and is preferably from 0.1 to 1.0 psia when the total pressure is atmospheric (14 psia). Correspondingly higher partial pressures of propylene would be employed at correspondingly higher total operating pressures.

The propylene is oxidized in the presence of a gas containing free molecular oxygen. Pure oxygen can be used, but this creates problems of temperature control as noted above. It is preferred that the free molecular oxygen be diluted with an inert gas such as nitrogen, propane or helium. The volume percent of free molecular oxygen in the gas containing it can suitably be from 1 to 100 and is preferably from 1 to 20 percent. When propylene is mixed with this gas containing free molecular oxygen, the partial pressure of oxygen is usually from 0.5 to 10 psia and is preferably from 1 to 4 psia. If the partial pressure of oxygen is below about 0.5 psia or above about 4 psia, the selectivity to the desired oxygenated products decreases, whereas from about one to four psia selectivity to the desired oxygenated compounds remains substantially constant.

The invention will be further described with reference to the following experimental work.

In all of the examples to follow, the following procedure was employed. A single pass flow system was used wherein a feed mixture of propylene, oxygen and helium was passed through a bed (approximately two parts by volume of catalyst) of the catalyst at a given temperature from 262°C. to 332°C. The flow rate was from 2,000 to 6,000 volumes of total feed per hour. The contact time was between 1 and 3 seconds and the space velocity based on the total feed was between 1,200 and 3,000 volumes per volume of catalyst per hour. The reaction products were cooled to −80°C. by indirect cooling to condense the reaction product which was mostly acrolein with minor amounts of other oxygenated organic products, such as acetone, acetaldehyde and acetic acid. These amounted to less than 10 percent of the acrolein formed. Water and CO_2 were formed as by-products.

EXAMPLE 1

In the run for this example, the feed mixture was passed through a bed of unsupported gold sponge

catalyst of 99.99 percent pure gold. The flow rate was about 2,500 volumes of total feed per hour, the oxygen pressure was about 65 mm with the propylene pressure as specified in the Table. Results of this run are summarized in the Table below.

EXAMPLE 2

In the run for this example, the feed mixture was passed through a bed of a non-porous silica supported gold catalyst containing 5 weight percent gold. The silica support was a commercial Cab-O-Sil material obtained from the Cabot Company. The catalyst was prepared by the method of incipient wetness by contacting the Cab-O-Sil with an aqueous solution of $HAuCl_4 \cdot 3H_2O$, drying the material and reducing with hydrogen at 300°C. to convert the salt to metallic gold. The results of this run are summarized in the Table below.

Referring to the Table below, Examples 1 and 2 show the use of gold either supported or unsupported resulted in a selectivity to acrolein of 25 to 33 percent. The selectivity to acetone, acetic acid and acetaldehyde was less than 2 percent.

TABLE.—THE OXIDATION OF PROPYLENE OVER GOLD CATALYSTS

Example No.	Solvent in preparation	Sample weight (grams)	Propylene pressure (mm.)	Reaction temperature (° C.)	Propylene conversion (percent)	Selectivity to acrolein (percent)
1	None	6.80	22	265	5	25
2	Water	1.18	19	262	4.5	33
3	Acetone	0.67	22	332	4	47
4	do	0.67	8.5	332	1	62
5	Ether	0.51	22	330	3	25

EXAMPLE 3

Example 2 was repeated except the gold catalyst was prepared from an acetone solution and the reaction temperature was increased to 332°C. The results of this run are summarized in the Table above.

A comparison of Examples 2 and 3 shows that the conversion of propylene was slightly lower, despite the higher reaction temperature, with a surprisingly increased selectivity to acrolein from 33 to 47 percent. Apparently, preparing the gold catalyst by precipitation of the gold salt from an acetone solution in some manner improves the selectivity of the catalyst for the production of acrolein.

EXAMPLE 4

Example 3 was repeated with reduced propylene pressure, an oxygen pressure of 25 mm and a flow rate of about 5,000 volumes of total feed per hour. The propylene conversion was only one percent. The results of Example 4 are summarized in the Table above.

A comparison of Examples 3 and 4 shows that as the propylene conversion is reduced, the selectivity to acrolein is further increased to a high of 62 percent.

EXAMPLE 5

Example 3 was repeated except the gold was deposited from an ether solution rather than acetone. The results of this run are summarized in the Table above.

A comparison of Examples 2, 3 and 5 shows that preparation of the catalyst by precipitation of the gold salt from ether or water results in lower selectivities to acrolein than the precipitation of the gold salt from acetone.

Resort may be had to such variations and modifications as fall within the spirit of the invention and the scope of the appended claims.

We claim:

1. A process for producing a product comprising acrolein, which process comprises reacting propylene at a temperature from 150°C. to 450°C. with a gas containing free molecular oxygen in the presence of a catalyst consisting of gold metal.

2. A process according to claim 1 wherein the reaction occurs at a partial pressure of oxygen above about 0.05 pounds per square inch absolute and a propylene space velocity from about 1 to about 2,000.

3. The process of claim 2 wherein the temperature in the reaction zone is maintained in the range of about 200° to about 350°C.

4. A process according to claim 2 wherein the partial pressure of oxygen is within the range of about 1 to about 4 pounds per square inch absolute.

5. A process for producing a product comprising acrolein, which process comprises reacting propylene at a temperature from 150°C. to 450°C. with a gas containing free molecular oxygen in the presence of a catalyst consisting of gold metal and a support selected from the group consisting of silica, magnesia, alumina, thoria and mixtures thereof.

6. A process according to claim 5 wherein the reaction occurs at a temperature from 200°C. to 350°C. and the amount of gold is between 1 and 10 weight percent of the total catalyst.

7. A process according to claim 5 wherein the gold is deposited from an organic solvent solution.

8. A process according to claim 7 wherein the organic solvent is acetone.

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