NEW NOBLE METAL-FREE CATALYST FOR THE PRODUCTION OF PROPYLENE OXIDE

PATENTED TECHNOLOGY

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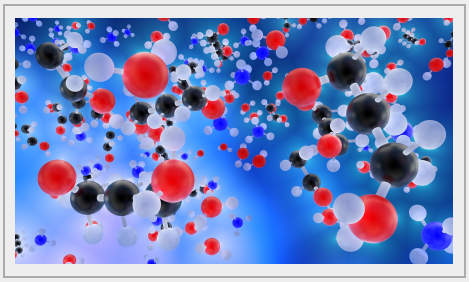
ABSTRACT

The **Institute of Materials** of the **University of Alicante** has developed a new and cost-effective catalyst without noble metals to obtain propylene oxide from the selective oxidation of propylene.

The catalytic system is characterized by not making use of dangerous or highly contaminating agents, and by not producing high quantities of reaction by-products. In addition, it shows a high selectivity towards propylene epoxide in the selective oxidation of propylene.

Companies interested in acquiring this technology for commercial exploitation are sought.



INTRODUCTION

Propylene oxide (PO) is a compound that presents a high reactivity and chemical specificity towards the formation of polymers. These properties make this compound useful as a prepolymer for the synthesis of polyurethanes, polyether, polyols and other polymers. It is estimated that more than 13 million tonnes of this chemical will be produced by 2020.

Nowadays, the industrial scale synthesis of PO is carried out using propylene as raw material, based on non-catalysed reactions in liquid phase using dangerous and highly polluting agents such as chlorine and hydrogen peroxide. In addition, these processes produce large quantities of by-products in the reaction. These by-products reduce the efficiency of the process and significantly increase the cost of the target product.
For these reasons, in recent years, the scientific community is focusing on the development of catalysts as a more sustainable alternative, which produce the minimum amount of reaction by-products, both in liquid and gas phases. In particular, there is a growing interest in performing the selective oxidation of propylene to generate PO in the gas phase, because the reagents used to carry out this reaction are less toxic and hazardous.

In the latter case, there are several works in the literature with new heterogeneous catalysts that present good catalytic properties (propylene conversion and selectivity towards the PO) for the reaction of selective oxidation of propylene to PO in gas phase. Among these, the catalysts based on gold nanoparticles deposited on titanosilicates (Au/Ti-SiO_2) stand out. These systems have been developed by the scientific community until reaching a 90 % selectivity towards propylene oxide at relatively moderate temperatures (140-200ºC) and using H_2/O_2 mixtures as reaction gases. Maintaining the selectivity around 90 % is an indispensable requirement because these catalysts have conversions below 10 %. However, these catalysts have several drawbacks. One of the main drawbacks is the use of noble metals such as gold, due to their high cost.

In this sense, the use of catalysts based on nanoparticles of Ag, significantly cheaper than those of Au has been studied obtaining good selectivity (> 90%) towards the formation of PO, but with very low conversions (< 1.5%). However, in general, the works found in the literature show that the nanoparticles of Ag deposited on different supports present significantly worse results with respect to the catalytic systems based on Au.

To overcome these drawbacks, scientific efforts are focusing on developing catalysts that do not contain noble metals and only use O_2 as an oxidizing agent. It should be noted that none of the studies described in the literature have reahed selectivities as high as the catalysts based on gold nanoparticles (Au/Ti-SiO_2).

There is therefore a need to provide improved catalysts that allow the oxidation of propylene to propylene oxide that do not generate large amounts of by-products during use and are able to give a high performance without the need to include noble metals

TECHNICAL DESCRIPTION

The **Institute of Materials** of the University of Alicante has developed a noble metal-free catalytic system for its use in the selective oxidation reaction from propylene to propylene oxide (PO), mainly using gas-phase H_2/O_2 mixtures. This system presents catalytic properties (in terms of propylene conversion, selectivity to PO and H_2 efficiency), superior to catalysts based on noble metals such as gold.

This catalyst is composed of nickel nanoparticles dispersed on an inorganic silica-based support. The inorganic support, in powder form, is selected from silicate and titanosilicate.

The preparation of this catalytic system involves the following steps:

a) impregnation of the inorganic support with a nickel precursor (nickel nitrate) dissolved in water,

b) addition to the solution obtained in step (a) an alkaline substance to reach a pH of 9-11,

c) washing and filtering the suspension obtained in step (b) until reaching a neutral pH,

d) drying the product obtained in step (c).

While the inorganic support obtained in stage (a) is obtained through the following stages:

i. addition of the silica based precursor to a previous solution of urea and surfactant with acetic acid,

ii. heating the product obtained in stage i to a temperature between 30 - 45 ºC for 15-25 h,

iii. removal of urea,

iv. calcination of the product obtained at iii between 500-600ºC for 5-7 hours.

This catalytic system has been used in selective oxidation reactions to obtain propylene oxide from propylene in gas phase, obtaining conversions higher than 7% with a selectivity towards the desired product above 90% using small amounts of Nickel and with high hydrogen efficiencies for the generation of propylene oxide.

ADVANTAGES AND INNOVATIVE ASPECTS

The catalytic system described above has the following advantages:

- Free of noble metals, reducing the cost of the catalyst and therefore the overall cost of producing propylene oxide from propylene.

- Conversions and selectivities similar to those obtained with noble metals (specifically, gold) are obtained.

- It does not use dangerous or highly contaminating agents.

- No large quantities of by-products are produced in the reaction.

INNOVATIVE ASPECTS

The main innovative aspect of the catalytic system is that it is based on Nickel, presenting itself as a sustainable alternative for the industrial production of PO at low cost and without the use of noble metals.

CURRENT STATE OF DEVELOPMENT

The technology is developed on a laboratory scale. Samples in quantities of around 5-10 g can be prepared simply and reproducibly. Given the extremely simple nature of the experimental procedure (comprising a sol-gel process and an impregnation), it could be synthesized at pilot pre-plant scale and even up to pilot plant scale (1 kg of product) in a relatively simple way.

MARKET APPLICATIONS

This invention falls within the general field of chemical engineering and, in particular, concerns a noble metal-free catalyst comprising an inorganic carrier and nickel nanoparticles. This catalyst is useful for the selective oxidation reaction of propylene in the gas phase.

COLLABORATION SOUGHT

Companies interested in acquiring this technology for commercial exploitation through technology transfer agreements are sought.

Company profile searched:

Catalyst manufacturing companies interested in obtaining cost-effective catalysts based on non-noble metals (Ni) with a high selectivity towards propylene epoxide in the selective oxidation of propylene.

INTELLECTUAL PROPERTY RIGHTS

This technology is protected by **patent application**.

- Title of the patent: "Catalysts based on Ni on inorganic supports and their use in the selective oxidation of propylene in gas phase".
- Application number: P201930310.
- Date of application: 5 April 2019.

MARKET APPLICATION (2)

Materials and Nanotechnology
Chemical Technology