

PREPARATION OF HYDROPHOBIC Pt-CATALYSTS FOR DECONTAMINATION OF NUCLEAR EFFLUENTS

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ABSTRACT

Based on the long experience of the authors, in the preparation, testing and evaluation of the performances of hydrophobic catalysts, and based on the reviewed references, this paper presents up-to-date R&D activities on the preparation methods and applications of the hydrophobic catalysts, in deuterium and tritium separation. The objectives of the paper are: (1) to provide a database for selection of the most appropriate catalyst and catalytic packing for above mentioned processes, (2) to evaluate the potentiality of hydrophobic Pt-catalysts in the deuterium and tritium separation (3) to assess and to find a new procedure for preparation a new improved hydrophobic catalyst. The merits of the hydrophobic catalysts are shown in comparison to hydrophilic catalysts.

As results of the review some general conclusions about the applications of hydrophobic catalysts in environmental field are as follow: (1) the hydrophobic Pt-catalysts packed in the trickle bed reactors showed a high catalytic activity and long stability; (2) the utilization of the hydrophobic Pt-catalysts for tritium removal from liquid and gaseous effluent in nuclear field was entirely confirmed on industrial scale; (3) the extension of the utilization of the hydrophobic Pt-catalysts in other new processes, which take place in presence of liquid water or high humidity are subjected to testing.

Key words: hydrophobic catalyst, tritium removal

1. Introduction

The hydrophobic catalysts were initially conceived for the deuterium enrichment and tritium separation by hydrogen-liquid water isotopic exchange in nuclear field. For this process, the conventional hydrophilic catalysts become inefficient due to loss of their activity upon the direct contact with liquid water or by capillary condensation of water vapor. Therefore, it was necessary to prepare a catalyst, which repels the liquid water but allows the transport of the gaseous reactants and reaction products to and from catalytic active centers. In principle, the mode of preparation of hydrophobic catalysts is similar to that of conventional hydrophilic catalysts. The main differences between them consist of support nature, wet-proofing method and active metal deposition method [2-6]. The main research was focused on the improvement of the catalyst's activity and stability, on their geometry as well as on the decrease of their cost price. High performances have been proved in hydrogen isotopes separation process and recently, by the new applications in environmental field the interest for this type of catalysts became of large topical interest.

This paper, reviews a wide range of preparative methods and applications of hydrophobic catalysts for the removal of tritium from liquid and gaseous effluents. Also is presented a proposal for a new improved hydrophobic Pt-catalyst for hydrogen isotopes separation.

2. PROGRESS CONCERNING THE ENGINEERING APPLICATIONS OF THE HYDROPHOBIC PT- CATALYSTS IN ENVIRONMENTAL FIELD

2.1 Tritium Removal from Aqueous Effluents

During spent nuclear fuel reprocessing and generally during nuclear activities involving tritium, significant quantities of intermediate and low-level liquid waste are generated. The detritiation of aqueous waste stream by hydrogen-water isotopic exchange were intensively researched and developed.

A demonstration pilot based on cryogenic distillation coupled with catalytic exchange on platinum on carbon and TEFLON (Pt/C/PTFE) hydrophobic catalyst in liquid phase is under testing in Romania [5] having as main goal the detritiation of heavy water from CANDU nuclear power plant from Cernavoda. The key point in all these processes for removal of tritium from aqueous effluents is the activity and stability of hydrophobic catalyst, which promote the isotopic exchange, in two steps:



To promote reaction (1), over 100 catalysts with hydrophobic properties have been prepared and tested [1-5]. The main types of tested and selected catalysts for hydrogen isotope separation process are summarized in Table 1. The high performances of hydrophobic Pt-catalysts and their long stability to promote reaction (1) was demonstrated on plant scale, in the process of the tritium recovery from heavy water used as moderator in CANDU reactors.

The experiments carried-out by some authors [6] showed that by diluting the currently hydrophobic catalyst with hydrophilic materials, the liquid hold-up increased, the water distribution was improved and the performances of the mass transfer between water vapors and liquid water increased considerably.

The main mixed catalytic packing types selected after long experiments in some countries for tritium removal by isotopic exchange on hydrophobic catalysts are presented in the Table 1 [1-5]. Usually the selected packings are operated at atmospheric pressure and at the temperatures below 80° C in columns of less 10 m height. Finally, it was also proved that an arrangement of the packing in ordered bed was more efficient than that in random bed.

2.2 Cleanup of the Airborne Tritium at Nuclear Facilities

Oxidation of tritium on catalyst surface followed by adsorption of tritiated water vapor in a molecular sieve drier was a widely accepted method for the recovery of airborne tritium to ensure that environmental releases from tritium handling facilities are minimized. The tritiated hydrogen-oxygen recombination (to cleanup of airborne tritium at tritium handling facilities) with platinum/silica and platinum /carbon hydrophobic catalyst showed a decontamination factors of 10^3 to 10^6 and a stability of the catalyst up to 120 days.

3. Discussions

Properties of hydrophobic catalysts like lifetime, catalytic activity, mechanical stability and susceptibility to poisoning and leaching are higher than of hydrophilic catalysts. Their applicability to tritium removal from wastewater effluents from nuclear activities was proved on industrial scale and the extension of their application for similar process which take place in presence of liquid water or humid air was proved in many laboratory experiments.

Table 1. The main types of hydrophobic catalysts and mixed packing tested and selected for tritium removal by H_2 - H_2O isotopic exchange

COUNTRY	Tested catalyst types and metal content (wt%)	Selected catalyst type and its stability	The type of selected mixed packing
CANADA	0.5%- Pt / Al ₂ O ₃ [6] 0.4%- Pt / PTFE 0.1-0.4%- (Pt / C)/PTFE (emulsion) Pt / zeolite Pt / SiO ₂	0.1% - (Pt/C)/PTFE After 170 days running the catalyst lost 13 % off initial activity	1) A matrix of platinized hydrophobic carbon and PTFE deposited on corrugated screening and wound with alternate layers of hydrophilic cotton cloth 2) Random packing consisting of 50% 0.37% Pt/C PTFE catalyst and 50% hydrophilic packing
INDIA	1% - (Pt /C)/PTFE [4] 1% - (Pt/Al ₂ O ₃)/PTFE [4] 1% - (Pt/zeolite)/PTFE[4]	1% - Pt/C/ PTFE Minimum some weeks	
JAPAN	1.5% - Pt/PTFE [3] 0.1-2% - Pt/SDBC [1, 3] 1.2-1.4% - Pt/SDBC-film type Pt /FC-PTFE Pt/Al ₂ O ₃ [1]	0.5% - Pt/SDBC (Kogel catalyst) 13 years in separated bed reactor process without any regeneration	1) Separated beds of 0.5%Pt/SDBC catalyst and Mac Mahon hydrophilic packing in which the liquid water is not in contact with the catalyst. 2) 1.5%Pt/PTFE rings (7 x 3 x 0.8 mm) and mists water (particle size 5 m) in con-current with H ₂ gas
GERMANY	0.4% - Pt/C/PTFE [2]	0.4% - Pt/C/PTFE	-
ROMANIA	0.1-1% - Pt/C/PTFE [5] 0.1-2% - Pt/SDB 0.1-2% - Pt/SDB/PS 0.5% - Pt/SDB/PTFE	0.45% - Pt/C/PTFE One year half in LPCE process, without any regeneration	Alternated beds of 0.45% Pt/C/PTFE and thermo-chemical activated metal hydrophilic packing
BELGIUM	Pt; Pd; Ni; Pt-Ni; Pt-Pd; deposited on carbon or TEFLON (over 30 different types)	1% - Pt/C/ PTFE 5000 hours	67% etched Dixon packing and 33% Pt/C /PTFE catalyst
RUSSIA	0.8% - Pt/Polysorb Pd/Al ₂ O ₃	0.8% - Pt/Polysorb	Alternated beds of granulated platinum / Polysorb catalyst and hydrophilic metallic packing (Levin's packing)
U.S.A	0.1% - Pt/C/PTFE (Canadian catalyst)	0.1% - Pt/C/PTFE	Ordered packing consisting of Pt/C/PTFE dispersed on corrugated stainless steel screen mesh with a cotton fabric overlaid on the screen and wound in a cylindrical shape

From the analysis of reported data it is beyond any doubt, that platinum under 1 wt% remains the best active metal and the Teflon the most effective wet-proofing agent. In all applications, the hydrophobic Pt-catalysts showed a high activity, long stability, as well as an easy and repeatable way for their regeneration. The high efficiency in tritium removal from liquid and gaseous at low temperature on hydrophobic catalyst can be explained only by their hydrophobic property. By using of hydrophobic support, liquid water and the water vapor (as reaction product or from atmosphere) would not be adsorbed on the surface, thus the active sites would not be blocked, and catalyst activity can be maintained long time even at lower temperature. When a catalyst becomes hydrophobic, the reactants (hydrogen, hydrocarbon, oxygen etc.) may be more readily adsorbed on the surface of the catalyst where it can react.

Recording all available data concerning preparative methods and test results of the hydrophobic catalysts we consider that hydrophobic Pt-catalyst can be improved. Our proposal for a new improved hydrophobic Pt-catalyst is a method based on the introduction in the catalyst composition of some special metallic oxides, which could have also a hydrophobic properties and a role of binding agents.[7]

The demonstrated role of the metallic oxides is also to facilitate chemical reactions which involves oxygen molecule (catalytic recombination H_2-O_2 , oxidation of CO and organic compounds, etc). [8-11]

The new improved Pt-hydrophobic catalyst is underway to be prepared. A classic laboratory installation for isotopic exchange process was made and the new catalyst will be tested. Also the new catalyst will be tested in the catalytic recombination H_2-O_2 process and in the oxidation of some volatile organic compounds.

4. Summary

Compared with conventional hydrophilic catalysts, the pollutants removal from liquid and gaseous effluent by means of hydrophobic catalyst offers a higher efficiency; lower operation temperature and pressure and energy requirements as well as lower costs.

According to available references data, the most catalytic active metal is platinum deposited on hydrophobic support or made wet-proofed by using Teflon. In the most applications, to improve its performances it is recommended the utilization of hydrophobic catalysts as ordered mixed catalytic packing in a trickle bed reactor. Due to their unique property, the hydrophobic Pt-catalyst may thus provide a cost effective environmentally attractive option to manage the complete removal of pollutants from liquid and gaseous effluents.

We propose a new preparative method for an improved hydrophobic Pt-catalyst used for hydrogen isotopes separation.

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