Synthèse assistée par microondes de catalyseurs hétérogènes pour la combustion catalytique de mélange CH_4-H_2

Microwaves-assisted synthesis of heterogeneous catalysts for catalytic combustion of CH_4-H_2 mixture

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Keyword(s): CH_4-H_2 catalytic combustion /supported metals catalysts/Microwave irradiation/ environmental TEM

Scientific context : Natural gas-hydrogen mixtures constitute a gaseous fuel presenting considerable economic and environmental challenges. Flame combustion is usually used in a conventional burner for mixtures containing less than 10% of H_2 while for higher concentration this technology is no longer suitable and catalytic combustion appears the only possible solution. The use of catalytic combustion prevents the formation of NOx, which occurs during flame combustion, and requires lower energy consumption. Numerous studies in the literature show that catalysts based on noble metals are the most active in methane catalytic combustion.
A new generation of catalysts consisting of noble metals inserted into oxide matrixes in the form of metal ions, are described to be more active than conventional catalysts which are based on noble metals particles dispersed on the supports.
The literature describes the combustion efficiency of CH_4 and /or H_2 of M^{2+} ions (M=Pt, Pd, Rh,..), trapped inside reducible or non-reducible metal oxides matrixes, serving as host structure. Dispersed metal ions and oxygen vacancies in the support structure are identified as active sites. Compared to conventional catalysts, an optimal dispersion of the noble metal is achieved and very low metal contents are required to develop a very high catalytic activity and the anchoring of the metal ions in the oxide matrix gives them high resistance to sintering.
Development of new routes for the synthesis of solids is an integral aspect of materials chemistry. Some of the important reasons for this are the continuing need for fast and energy-efficient techniques, necessity to avoid competing reactions in processes. In recent times, several reports have appeared where conventional preparative techniques have been substituted by microwave methods. Dielectric heating is considered as a good alternative for carrying out many chemical or physical processes such as catalysts synthesis and catalytic heterogeneous reactions. This method is a very rapidly developing area of research. Besides, compared to conventional heating, the temperatures are appreciably lowered and the time of irradiation is extremely short which allows an economy of energy.
The research project focuses on the catalytic combustion of CH_4-H_2 mixtures. The addition of hydrogen during reaction reduces the greenhouse effect of methane and can also modify the surface state of the catalyst, which may play an important role in the activity and/or selectivity to CO_2.
Hydrogen-assisted combustion of methane has been studied with Pt-based catalysts and recently with Pd-based catalysts (noble metal particles dispersed on supports). Studies on the influence of hydrogen on the catalytic combustion of methane on monometallic catalysts such as Pd/Al_2O_3 and Pt/Al_2O_3 have shown that their behavior is different in the presence of hydrogen.

This study will first focus on monometallic catalysts (made up of noble metals inserted into oxide matrices in the form of metal ions), it will be extended to bimetallic catalysts, which are generally more active and stable than monometallic catalysts.
The addition of a second metal often improves activity and prevents deactivation of the catalyst. This improvement could be due both to a strong interaction between the active species and to a better stability of the bimetallic system at high temperature.

Description of the research project:

The research project contains two wings:
1/ Microwaves-assisted synthesis of catalysts
The program of research is centered on the synthesis of supported metals based catalysts, with the aim of their use in methane-hydrogen catalytic combustion. The objective is to develop stable catalysts and the settling of an original method for the preparation of active and selective catalysts having low propensity to sintering.
Dielectric heating (absence of temperature gradient, high speed of heating) will allow the preparation of catalysts of which textural or structural characteristics can be modulated. In particular, the use of microwaves will allow favoring the nucleation particles stage with regard to the growth stage, so improving the physicochemical properties of the solid obtained compared to conventional methods for which the control of these two processes is particularly difficult.
A comparative study with catalysts obtained by conventional methods will be made.

2/ Catalysis under microwaves
The catalytic properties (solids prepared under microwaves irradiation and by conventional methods) will be studied and connected with the physicochemical properties.
Additional catalytic activities measurements in drastic conditions will be performed in order to estimate the resistance of catalysts to sintering (in the presence of steam). This step will be particularly studied by environmental TEM so that the dynamic behavior of the catalysts under reaction conditions can be devised leading to a better understanding of the mechanisms of deactivation that will allow optimizing the catalyst formulation so as to reduce catalyst sintering or even to prevent it and so to maintain the catalytic activity. The nature and the stability of eventual poisons species will be analyzed both by microscopy and spectroscopy.
It is known that catalytic supports can play an important role in the process of sintering or poisoning. Several supports will be chosen according to their physicochemical properties and the catalysts will be studied.
Catalytic tests will be performed under microwaves irradiation and the results will be compared with those obtained in the presence of conventional heating.

Profile of the candidate: Master degree M2 or Engineer having good knowledge in heterogeneous catalysis and physical chemistry.

References :

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