

IMPREGNATED LAYER COMBUSTION SYNTHESIS METHOD FOR CATALYSTS PREPARATION FOR HYDROGEN PRODUCTION FROM OXIDATIVE REFORMING OF METHANOL

Anand Kumar, A. S. Mukasyan, E. E. Wolf*
Chemical and Biomolecular Engineering
University of Notre Dame, IN-46556

Summary

A novel method for catalysts preparation using combustion synthesis techniques has been used to prepare Cu/Zn/Zr and Pd based catalysts for oxidative reforming of methanol. IR-Images, TGA/DTA, SEM and XRD analysis have been used to describe the systematic evolution of the catalyst particles from the initial reactants mixture. These particles have been characterized by their activity/selectivity for methanol oxidation/hydrogen production, BET area, and dispersion of Pd on the surface. Results obtained show that they are extremely active and selective at low temperature range.

Keywords

Impregnated Layer Combustion Synthesis, Hydrogen Production, Methanol Partial Oxidation.

Introduction

Combustion synthesis¹, being an economical way of material synthesis, has been used increasingly these days for variety of applications. However the conventional combustion synthesis is difficult to control due to its explosive nature. A novel method known as Impregnated layer combustion synthesis (ILCS) is described as a way of preparing catalysts in a controlled manner. In this method a reactive solution containing the catalysts' precursor and a fuel, such as glycine, is impregnated into a thin cellulose paper. After drying, the cellulose is ignited at one end resulting in a combustion front that moves in a self-sustained mode leaving behind the desired oxides with high surface area. A high speed IR Camera (FLIR SC6000) as well as by conventional visible range SONY Camcorder, are used to follow the temperature-time evolution during combustion. The catalysts produced by this method have been tested for their activity and selectivity for hydrogen production from oxidative reforming of methanol.

Three different modes of combustion synthesis were used to prepare catalysts with optimized Cu/Zn/Zr ratio²: volume combustion synthesis (VCS), impregnated layer combustion synthesis (ILCS), and a novel combination of the ILCS and VCS, referred as second wave impregnation (SWI). In the VCS method, a homogeneous solution was prepared by dissolving reactants in water. This solution was uniformly heated till it reaches the ignition temperature to start the combustion. In the SWI method,

catalysts without Pd are prepared using ILCS and then the required amount of Pd is loaded on this catalyst using VCS mode. The activity and selectivity of the catalysts produced by three methods of combustion synthesis have been measured for hydrogen production from oxidative reforming of methanol.

Results and Discussion

Fig. 1 shows the temperature distribution across a moving combustion front. The presence of two combustion zones at different temperatures can be distinguished. The first dark zone, at lower temperature, is followed by a bright region at higher temperature. SEM images show that there is not much difference in the microstructure of the pure cellulose paper and impregnated cellulose paper except the latter gets slightly swollen. The cellulose microstructure even after first combustion front does not change much and the fibers remain unburned, but some small particles could be seen dispersed at higher magnification. The product obtained after second combustion front gives crystalline materials with hollow tube like structure, which have dimensions similar to that of the cellulose fibers. Detailed analysis using TGA/DTA and XRD show that only the second combustion front is responsible for the crystalline products with high surface area. A theoretical model is being developed to describe the process of combustion wave self propagation and the effect of

* ewolf@nd.edu

different experimental parameters on the combustion characteristics and materials' catalytic properties.

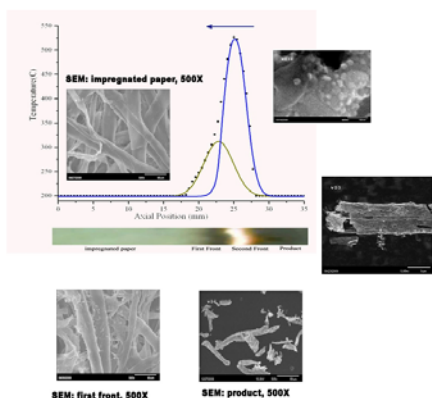


Fig 1: Evolution of Catalyst in ILCS process

Table 1 gives a brief summary of the catalyst composition, preparation method and crystallite size. Catalyst composition $7\text{Cu}/3\text{Zn}/1\text{Zr}/0\text{Pd}$ implies that $\text{CuO}/\text{ZnO}/\text{ZrO}_2$ are present in a molar ratio of 7/3/1 and the Pd amount is given in wt% of the total oxides present. Fig 2 illustrates the activity and selectivity results for the ORM reaction. It is apparent that SWI-3Pd is the most active catalyst at low temperatures, giving ~40% conversion at ~70°C. This high activity at lower temperature could be associated with the good dispersion of Pd on the surface as it was loaded in the second wave method. ZrO_2 supported catalyst (not shown in Fig 2) having a BET area ~6 times that of SWI-3Pd, is relatively more active and selective for hydrogen production than other catalysts at higher temperature values. Further work is going on in our group to understand to role of each element in the ORM reaction.

Table 1. Summary of catalyst properties

Catalyst	Composition	Prep. method	Crystallite Size(nm)
ILCS-0Pd	7Cu/3Zn/1Zr/ 0Pd	ILCS	-
ILCS-3Pd	7Cu/3Zn/1Zr/ 3Pd	ILCS	22
SWI-3Pd	7Cu/3Zn/1Zr/ 3Pd	SWI	25

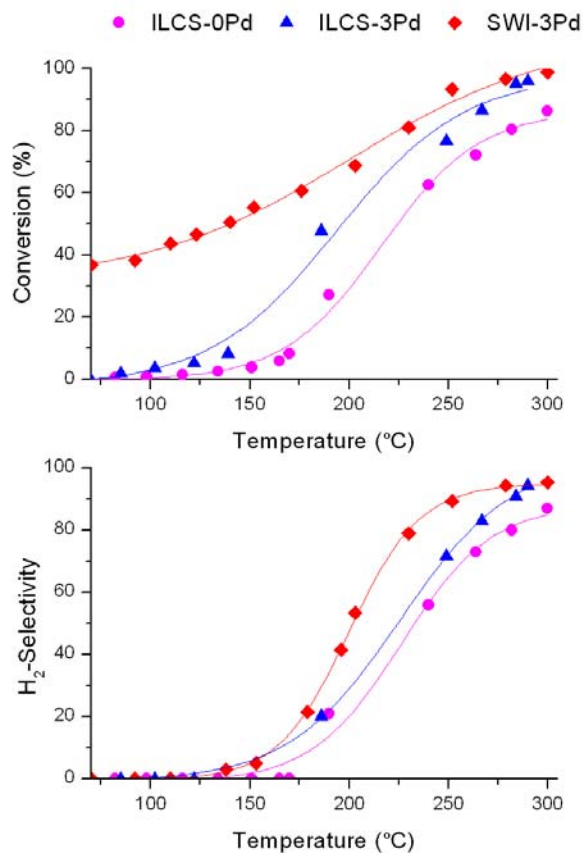


Fig 2: Activity and hydrogen selectivity for ORM and the effect of Pd loading

References

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