

Hydrogen production from oxidative reforming of methanol over catalysts prepared by novel combustion synthesis methods

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Introduction

Novel combustion synthesis¹ methods are used to prepare catalysts for oxidative reforming of methanol (ORM). It follows the previous work² in our group to obtain an optimized ratio of CuO/ZnO/ZrO₂ along with Pd to enhance the activity and selectivity for hydrogen production from methanol partial oxidation.

Materials and Methods

Mixtures of metal nitrates Me^c (NO₃)_c · yH₂O (where Me = Cu, ZrO, Zn, or Pd) and glycine (as fuel) were used to synthesize catalysts in three modes of combustion synthesis techniques: volume combustion synthesis (VCS), impregnated layer combustion synthesis (ILCS), and a novel combination of the ILCS and VCS, so-called, second wave impregnation (SWI) approach. 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 ILCS method, a homogeneous solution of metal nitrates and fuel is impregnated in a cellulose paper which is dried at room temperature. This dried paper is ignited at one end to start the combustion reaction, which moves in a self sustained manner as a combustion front, leaving behind the final product of the required composition. In the SWI method, catalyst without Pd is prepared using ILCS and then the required amount of Pd is loaded on this catalyst using the VCS mode.

Results and Discussion

Table 1 gives a brief summary of the catalysts composition, preparation method and BET area. Catalyst 731-CuZnZr-0Pd-ICS implies that CuO/ZnO/ZrO₂ are present in a molar ratio of 7/3/1, Pd amount is given in wt% of the total oxides present and impregnated layer combustion synthesis(ICS) method is used to prepare the catalyst. Fig 1 illustrates the activity and selectivity graphs for ORM reaction. It is apparent that SWI-3Pd is the most active catalyst at low temperatures, giving more than 50% conversion at ~50°C. This high activity at lower temperature is related to the better dispersion of Pd on the surface as it was loaded in the second wave, which is also confirmed by CO pulse experiments. The VCS/ZrO₂-3Pd catalyst, having a BET area ~6 times that of SWI-3Pd, is relatively more active and selective for hydrogen production than other two catalysts at higher temperature values.

The various combustion synthesis modes of catalyst preparation were carefully studied by monitoring temperature distribution and combustion front movement using FLIR SC6000 IR camera. We observed the presence of two different combustion waves. The first wave at low temperature (~300°C) was followed by a second wave at higher temperature (~600°C) before

resulting into the final products. In order to study the phase transformations, samples were obtained from quenched areas in these two fronts, and were analyzed using XRD, SEM and EDS techniques. The temperature profile across the combustion front shows a sharp temperature gradient toward the product side, indicating a fast cooling of the products which prevents them from sintering and helps in making fine particles. SEM images obtained indicate particles as small as 10 nm. Final products are also being characterized by ICP-MS, XPS and EDS techniques.

Table 1. Summary of catalyst properties

Catalysts	Symbol	Prep. method	Fuel/Oxidizer ratio	BET area (m ² /g)
731-CuZnZr-0Pd-ICS	ILCS-0Pd	ILCS	0.5	9.2
731-CuZnZr-3Pd-SWI	SWI-3Pd	SWI	0.5	15.1
731-CuZnZr-3Pd-VCS On ZrO ₂ support	VCS/ZrO ₂ -3Pd	VCS	0.5	88.2

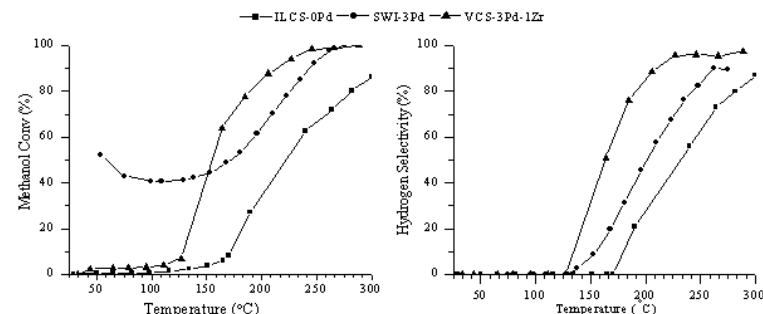


Figure 1: Activity and selectivity for H₂ production

Significance

Combustion synthesis is a well known technique for material synthesis. The present study uses a variation of conventional combustion synthesis to control the explosive nature of the process. Highly active reaction media is diluted by impregnating it in a thin cellulose paper. Access to a larger area makes the product cool faster by improving the heat transfer effects. All these features of ILCS help in lowering down the combustion temperature in comparison to the conventional CS. Further study is underway to explore this method for various compositions and supports, as a novel catalyst synthesis method for the ORM reaction.

References

1. Dinka, P. and Mukasyan, A.S. *J. Phys Chem B*. **109**, 21627-21633(2005).
2. Schuyten, S.J. and Wolf, E.E. *Catal. Lett.* **106**, 7-14(2006).

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