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Intensification of Methanol Steam Reforming Process using Cu-modified Ni-based supported catalysts

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1. Introduction

Hydrogen is conventionally manufactured in large scale by the steam reforming of methane or naphthas. The perspective of using hydrogen as a fuel depends of finding alternatives to the existing production technologies and feedstock. Oxygenated compounds are an interesting alternative and are been investigated extensively [1]. The process of steam reforming of mixtures of oxygenated hydrocarbons does not contribute to a net increase in atmospheric CO_2, as oxygenated obtained from renewable resources are considered to be CO_2 neutral. In previous works has been demonstrate that Steam Reforming of oxygenated compounds is a complex reactions network where in a previous step, decomposition reaction take place followed by the reforming of decomposition products. Its known that DME (or methanol) receives particular attention due to its properties similar to those of liquefied petroleum gas (LPG)and it can be used as a clean high-efficiency compression ignition fuel with reduced NOx, SOx, and particulate matter formation. In other way, it has been demonstrate that DME-SR to produce H_2 occurs through two main reactions in series, DME-Hydrolysis and MeOH-Steam Reforming. Therefore, bifunctional catalysts are necessary, with and acid funcion active in DME-HYD and a redox for reforming step [2-4]. On the other hand, methanol is also regarded as an important feedstock for hydrogen production due to its high energy density and superior transportability, especially for small-scaled and portable fuel cell applications. In comparison with CH_4-SR, the reaction temperature of methanol steam reforming is much lower (150–300ºC) and the gas off contains typically 60%-70% H_2 and less than 5% CO.

Noble metal catalysts such as Rh, Ru, Pt and Pd, are widely used in the steam reforming of single-component oxygenated hydrocarbon feedstock because of their high activity and hydrogen selectivity, although noble-metal based catalysts can be deactivated with time on stream when carbon monoxide is formed. Ni-based catalysts have been demonstrated to be efficient in reforming processes of oxygenates with high and stable activity and hydrogen selectivity resulting in only minimal coke formation over surface.

In this contribution the Steam Reforming of DME and/or MeOH for H_2 production has been studied using a Ni-based supported catalysts modified with copper and a pseudo optimized formulation was considered to incorporate in a microreformer designed to be feed with methanol (or DME), as an intensification of process to direct hydrogen supply on board.

2. Experimental

Bimetallic Ni-based supported alumina catalysts were synthesized with Ni (20%wt.) modified with Cu (0.5-3%wt.) by wetness impregnation method in multiple stages with intermediate calcination (Ni/@450°Cx4h. Cu/@500°Cx4h) using Al_2O_3 Puralox TH as support (Sasol, A_{BET}=144$m^2.g^{-1}$, V_p=0.97$cm^3.g^{-1}$) and characterized by DRX, HRTEM, XPS and TPR-H_2.

In order to analyze the reaction mechanism, *in situ* reactivity tests were performed using MeOH and MeOH +H_2O pulses and analysing the spectral response as function of temperature in the range between 50 and 550°C.

Activity isothermal experiments were carried out in order to find the optimized Ni/Cu ratio and the tests were performed in a fixed bed flow reactor (di=9 mm) equipped with a co-axial thermocouple placed at the center of catalytic bed to monitor the rector temperature; analysing gas-stream by GC (Agilent 7820A) working at 3,000 h-1 and feeding mixtures according to the H_2O/MeOH ratio close to the stoichiometry value. Process was also study in a decoupled way, testing MeOH-SR reaction as second step in DME-SR.

Micro-reactors offer a high heat transfer rate and short diffusion time and ensured with minimal size of reactor. So, a μ-reformer has been developed for the on board H_2-supply using a Cu-modified Ni-based catalyst to operate at ultra-short contact times. A plate-type micro-reformer was designed and constructed as a five parallel microchannels reactor of 0.5x0.5x30 mm (Figure 1). The channels were coated by incorporation, after aconditioning of internal channel surface, of a stabilized solution of the corresponding Cu and Ni ratio and activated in air at 500°C. MeOH conversions and hydrogen yield were evaluated using parallel flow pattern and operating at 150.000 h^{-1}.

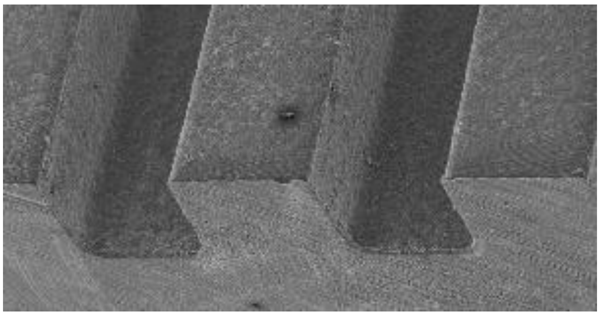

Figure 1. SEM image of μ-reactor channels

3. Results and Discussion

The 3CuNi/Al2O3 catalyst has shown a better performance in terms of activity, selectivity and stability. The presence of partially reduced mixed species Cu-Ni (Cu^{+1} and Ni^{+2}, XPS), favors the second stage of the DME reforming process, which corresponds to the methanol reforming stage (MeOH-SR). It has been proved that CuO and Cu-Ni-Ox species coexist over surface catalysts (TPR-profiles); related to the formation of mixed species Ni-Cu-Ox partially enriched in Cu (HRTEM-EDX), whose population further depends on the Cu/Ni atomic ratio.

In the MeOH-SR, was registered two regions: the corresponding to direct MeOH decomposition($\mathrm{CH_3OH} \leftrightarrow 2\mathrm{H_2} + \mathrm{CO}$) at low temperature achieving a H_2/CO molar ratio close to stoichiometric value (≈2); and a second associated to the MeOH-SR ($\mathrm{CH_3OH} + \mathrm{H_2O} \leftrightarrow \mathrm{CO_2} + \mathrm{H_2}$) at temperature over 300ºC. For 3CuNi-catalyst (Figure 2), a H_2 selectivity over 65% is reached from 250ºC, with a maximum close to 70% at 500ºC. An almost complete methanol conversion was registered from 350ºC. Copper incorporation enhanced the interaction with Ni that provides a stable H_2-yield profile and favores methanol reforming conditions, achieving a H_2/CO_2 ratio close to stoichiometric value at low temperature (@300ºC).

The comparison between decomposition experiments (in absence of steam) and the steam reforming runs suggests a competition in the adsorption between DME/MeOH and steam over surface catalyst (FTIR-expriments). MeOH is not detected when steam is co-adsorbed, suggesting a fast methanol conversion into H_2 rich stream. In DME-SR, signals related to methanol adsorbed over surface was not registered in FTIR runs suggesting the occurrence of MeOH-SR immediately after being produced DME-hydrolysis, as was checked in ss-flow reactor experiment,achieving similar results to those obtained in MeOH-SR experiments.

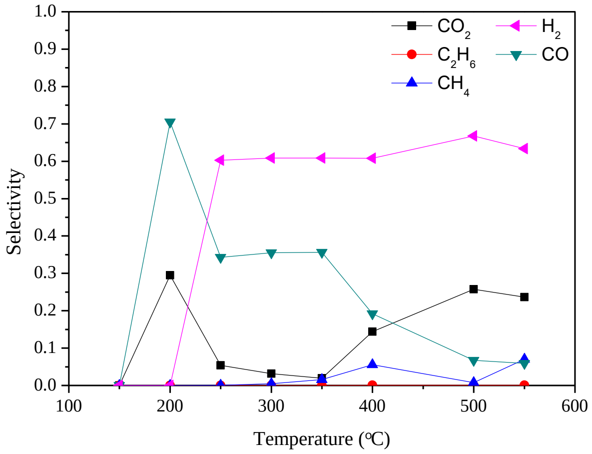

Figure 2. Products distribution for MeOH-Steam Reforming for 3CuNi catalyst as function of reaction temperature

Regarding micro-reformer results, using a Cu/Ni coating with same atomic ratio as for the 3CuNi/Al_2O_3 catalyst, when MeOH is feed at H_2O/MeOH=3 ratio working at 400ºC and a space velocity close to 150000 h^{-1} and during five hours of reaction, an almost complete conversion of methanol was registered. H_2 and CO_2 in a ratio close to the stoichiometric were recorded and negligible concentrations (<2%) of CH_4 and C_2H_6 were detected in dry base. A high DME and MeOH reforming efficiency in a finite space with a useful volume of 0.03 cm^3 produce a hydrogen-rich gas by a device occupying a minimal volume and this stream is susceptible to being co-injected in diesel thermal engines.

4. Conclusions

The effectiveness of the CuNi bimetallyc system in the production of hydrogen-enriched streams by methanol reforming has been proven. Thus, the incorporation of Cu modifies the structure of the catalytic system stabilizing the Ni species through the formation of mixed species Cu-Ni-Ox scattered partially enriched in Cu that improve the results in terms of conversion and selectivity. This optimized Cu-Ni formulation has been used in a micro-reformer fed by methanol obtaining a H_2/CO_2 fuel stream with a volumetric ratio close to the thermodynamic one from 350°C.

Acknowledgements

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