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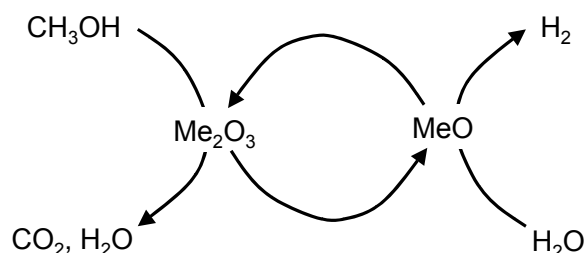
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A Redox Cycle Approach for the Production of H₂ by Two-step Methanol Reforming

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1 Introduction

During recent years, many processes for the production of hydrogen from renewable sources have been proposed, comprising thermal, catalytic, electrolytic and photolytic processes [1]. Catalytic steam-reforming (coupled with the WGS reaction), currently the most used process for the production of hydrogen from natural gas, is also an option that can be used for the transformation of renewables, e.g., bioalcohols, into hydrogen. However, SR+WGS has the drawback that due to thermodynamic reasons CO impurities cannot be avoided, and further downstream technologies (e.g., CO/H₂ separation with membranes or CO-PrOx reaction) have to be used in order to obtain high purity hydrogen streams, to be used, e.g., as the feed for fuel-cell devices. Due to this reason, and also because of the fascinating challenge of obtaining an inherent separation of hydrogen from the C-containing products, during last years various alternative approaches have been proposed, in which the SR reaction is decoupled into two spatially and temporarily separated steps [2]. In the chemical-loop approach, during the first step a reductant (usually methane) is first contacted with a metal oxide, which oxidizes the former into carbon oxides and water. The reduced metal oxide is then reoxidized with water, to produce hydrogen and restore the original oxidation state and the O²⁻ content of the metal oxide (Scheme 1).



Scheme 1: Chemical-loop approach for methanol SR.

An example is the process recently developed by ENI, in which Fe₂O₃ is used as the electrons/O²⁻ carrier for the production of hydrogen from natural gas [3]. Worth of note, similar redox-decoupled approaches have also been proposed for the catalytic selective oxidation of organic substrates with molecular oxygen, that use metal oxides-based catalysts (Mars-van Krevelen redox mechanism) [4].

Materials employed for the cycle SR are similar to those used for thermochemical water splitting [5]. Amongst the most interesting systems described in the literature, ferrite-type spinel mixed oxides of general composition Me^{II}_xFe^{II}_{1-x}Fe^{III}₂O₄ (where Me = Co, Ni, Zn) offer

the possibility to modulate their redox properties by means of changing the divalent metal type and content.

In the present work, we report about a study on the feasibility of a two-step cycle approach for the catalytic production of hydrogen from methanol and water, using the spinel-type oxide CoFe_2O_4 as the electrons carrier.

2 Experimental

The spinel oxide CoFe_2O_4 was prepared by co-precipitation, via drop wise addition of an aqueous solution containing Fe(III) and Co(II) nitrates (total nitrates concentration 1.5M) into a NaOH 2M solution, at 50 °C, while maintaining the pH at 12. The precipitate was then separated under vacuum filtration, washed with abundant water, dried at 120 °C for 4 h and finally calcined at either 450 or 750 °C, for 8 h. The ferrite formation occurred already after digestion of the precipitate at 40 °C. The materials (both after thermal treatment and after reduction with methanol) were characterized by means of XRD. Calcined catalysts were also characterized by means of surface area measurement (BET) and Thermal-Programmed-Reduction analysis.

Reactivity experiments were carried out at atmospheric pressure, using a glass-made tubular flow reactor, loaded with 0.4 g catalyst. The reduction step was carried out using an inlet feed containing 15.6 vol% methanol in N_2 carrier; residence time was equal to 0.21-0.26 s, and reactor temperature was varied between 300 and 450 °C. The oxidation step was carried out using an inlet stream containing 29.3 vol% water in N_2 carrier; residence time was 0.20 s. The reactor outlet flow was kept at 200 °C and fed to an automatic sampling device for GC (microGC Agilent 3000A) analysis of unconverted methanol and of reaction products. Due to the presence of condensable products like water or methanol, the overall outlet volumetric flow (V_{out}), could not be directly estimated. Therefore, conversion and product yields were calculated using an iterative procedure on concentrations analytically determined, using an indirect estimation of V_{out} . Hydrogen was taken as the basis for calculation, because it was the only element for which an inlet-outlet atomic balance has to be 100 %. In fact, during methanol oxidation, the instantaneous C balance was less than 100 % because of coke accumulation on the ferrite, and O balance was higher than 100 % during the initial period, because of the O deriving from the reduction of the ferrite mixed oxide. On the other hand, the H balance was used to estimate the carbon deposition and the contribution to products formation deriving from ferrite bulk oxygen. For the reoxidation step, the change of flow was neglected, because the main reaction (reoxidation of the reduced oxide with water) did not imply a variation of the number of moles with respect to the fed ones.

3 Results and Discussion

3.1 Characterization of materials

During these specify experiments aimed at the characterization of reduced samples, residence time of 1s (higher than that used for reactivity tests) was used. Table 1 compiles the main characteristics of two samples calcined at 450 (CF-450) and 750 °C (CF-750). In both cases, XRD patterns evidenced the formation of the inverse spinel structure, but CF-450 was less crystalline than CF-750. X-ray diffraction patterns and Raman spectroscopy

confirmed the different morphology of the two samples. TPR measurements evidenced the presence of more reactive surface sites in CF-450 sample; a model was proposed in which smaller crystallites expose predominately (111) facets, preferentially terminated in tetrahedral Fe^{3+} surface sites, while sintering favours (110) and (100) facets and Co/Fe surface compositions is closer to the bulk inverse spinel phase [6]. The crystallinity of the samples greatly affected the rate of solid reduction and hence the reactivity behaviour.

X-ray diffraction pattern of samples were recorded after different times of exposure to the methanol stream (Figure 1).

Table 1: Main characteristics of samples prepared, both calcined and after reduction with methanol.

Sample	Treatment	Crystallite size, nm	Surface area, m^2/g
CF-450	After calcination	13	55
CF-450	After reduction with methanol (30 min) and reoxidation with steam	32	14
CF-750	After calcination	32	10
CF-750	After reduction with methanol (30 min) and reoxidation with steam	33	10

Contacting the CF-450 sample with methanol at $T > 300^\circ\text{C}$ led to the progressive reduction of the spinel, with development of a metallic Co-Fe phase. At high temperature, the formation of metal carbide was also observed. With the more crystalline CF-750 sample, instead, no bulk reduction of the spinel was observed at 300 and 360°C within 2 h reaction time. With both samples, the reoxidation of the reduced spinel with water led to the formation of CoFe_2O_4 ; however, some residual CoFe alloy hinted for an incomplete bulk oxidation of the material by steam. Moreover, the reoxidized CF-450 showed a remarkable increase of crystallinity with respect to the fresh sample, morphological and structural parameters finally being similar to those of fresh CF-750 (Table 1); sintering of the less crystalline material was due to the strongly exothermal oxidation process.

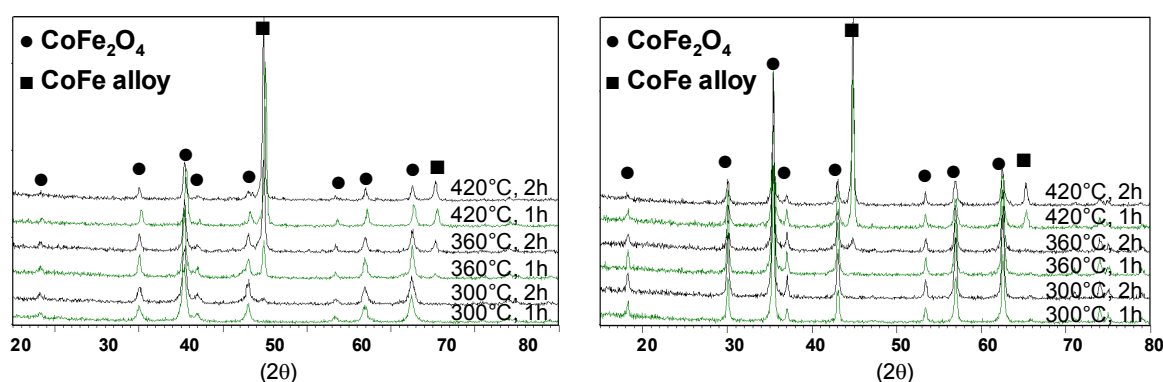


Figure 1: XRD patterns of CF-450 (left) and CF-750 recorded after different times of exposure to the diluted methanol stream, at various temperatures. (Residence time = 1s).

3.2 Reactivity tests

An example of the results obtained with sample CF-450 during the first step of the cycle, at 420 °C, is shown in Figure 2. The figure reports the instantaneous methanol conversion, and yields to CO, CO₂, CH₄, H₂O, H₂ and coke. The unsteady-state behaviour was due to the progressive reduction of the spinel oxide. The conversion of methanol was total during the entire experiment time. The ferrite catalysed the combustion of methanol to CO₂ and H₂O, but also the decomposition of methanol into CO and H₂; in fact, the yield to H₂ was relatively high even with the fully oxidized catalyst. Moreover, the yield to H₂ was much greater than that to CO, suggesting that additional reactions producing hydrogen were coke formation and methanol reforming, the latter using the in-situ produced H₂O. A contribution deriving from WGS can be excluded, due to high concentration of CO₂ from combustion. A reaction also contributing to CO₂ formation, a compound that was produced even with the strongly reduced material, was the Boudard reaction (disproportion of CO to CO₂ and coke). Methane formed by hydrogenation of CO, but possibly also by decomposition of methylformate, the latter being formed by the Tishchenko dimerization of formaldehyde.

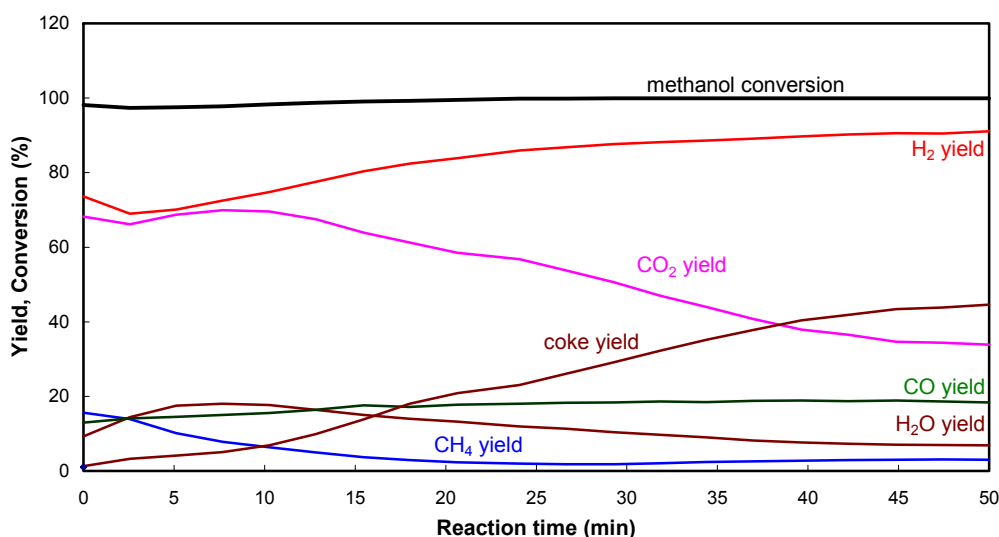


Figure 2: Instantaneous yields to products in methanol oxidation over CF-450 spinel in function of the reaction time (T=420 °C).

When the first step was carried out at low temperature, e.g., at 360 °C or 300 °C, the relative amount of the various products changed, and also the variation of yield observed during time for each product, was considerably modified with respect to the case of the reduction done at 420 °C. A critical point of this step was the accumulation of coke, which however formed with a lower rate when temperatures less than 400 °C were used (but with the drawback of an incomplete conversion of methanol).

Figure 3 shows the effect of reaction time during the reoxidation of the pre-reduced spinel with water, carried out at 420 °C after the reduction at 300 °C.

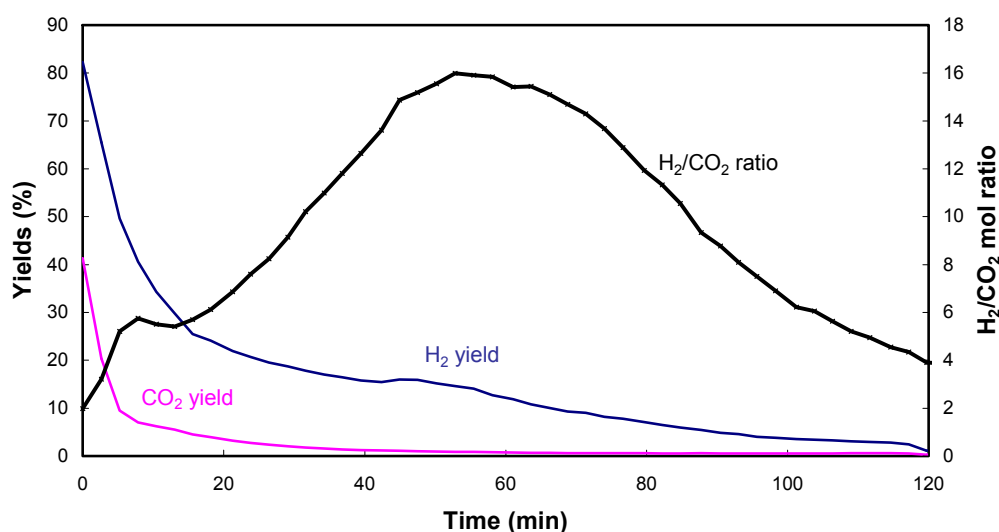


Figure 3: Instantaneous yields to products during reoxidation of the pre-reduced CF-450 spinel with water, at 420 °C, in function of the reaction time.

Carbon dioxide formed by coke gasification; the H_2/CO_2 molar ratio was low at the beginning of the reoxidation step, then increased reaching a maximum value after approximately one hour. The maximum did correspond to the zone at which the gasification of coke had been completed, and hence the production of CO_2 was minimal.

The reduction step was repeated three times after the corresponding reoxidation step; results obtained were very similar to those obtained during the first cycle. This indicates the feasibility of the chemical-loop approach with the $CoFe_2O_4$ spinel.

4 Conclusions

The chemistry of the two-step reforming (chemical-loop) reforming of methanol has been investigated using $CoFe_2O_4$ as the electrons/oxygen carrier. The main chemical-physical features of the ferrite were greatly affected by the temperature used for the thermal treatment of the mixed oxide. Reduction-reoxidation cycles were repeated, confirming the complete reversibility of the redox process. The major drawback was the accumulation of coke during the reduction step; however, the amount of coke was a function of the main reduction parameters, i.e., temperature and reaction time.

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