EXECUTIVE SUMMARY OF THE THESIS

Study of Reverse Water Gas Shift (RWGS) over Cu-Fe/CeO2 catalysts

LAUREA MAGISTRALE IN CHEMICAL ENGINEERING

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1. Introduction

It has been extensively reported that the dramatic increase of the carbon dioxide (CO_2) content into the atmosphere is causing severe environmental and economical damages. In order to face this problem, alongside the reduction of emissions, capturing CO_2 and using it as raw material for chemical processes is an interesting solution. Among the different possibilities, the captured carbon dioxide could be adopted as feedstock for Reverse Water Gas Shift (RWGS) reaction to produce CO, which is a key bulk chemical usually obtained from methane. This solution is appealing because it can take advantage of the wide know-how about heterogeneous catalysis while at the same time exploiting the already existing industrial infrastructure for CO utilization [1].

The RWGS reaction consists of the endothermic hydrogenation of CO_2 to CO, producing water as a byproduct (Eq.1). At the same time, the exothermic Sabatier reaction, also known as CO_2 methanation (Eq.2) competes with RWGS for the consumption of carbon dioxide.

$$CO_2 + H_2 \leftrightarrow CO + H_2O \qquad (1)$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \qquad (2)$$
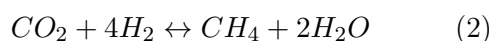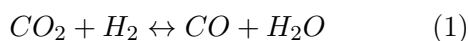
A good catalyst for RWGS reaction should have two different functionalities. It must be able to adsorb CO_2 allowing for the cleavage of one of the two $C{=}O$ bonds, and it should also have some available sites for the dissociative adsorption of H_2. Moreover it is crucial to correctly balance these two functionalities in order to ensure CO as the main final product.

In order to make this process feasible it is necessary to have the best possible performing catalyst. This work assessed the novel combination of Cu and Fe on the active support CeO_2 as catalyst for RWGS reaction. Moreover the effect of K as a promoter has been evaluated [2]. CeO_2 is a reducible support that participates directly to the reaction thanks to its oxygen vacancies. Cu is reported to be very active on reducible supports. Fe has been introduced to prevent Cu sintering. K was selected as possible promoter to improve CO_2 adsorption and potentially catalyze coke gasification whether it was formed on the surface.

2. Experimental

2.1. Catalyst preparation

The porous support CeO_2 was prepared through hydrothermal method. A 8M solution of $NaOH$ (Sigma-Aldrich) in millipore water was added to

10g of $Ce(NO_3)_3 \cdot 6H_2O$ (Sigma-Aldrich) under stirring until a total volume of 70ml was reached. After 30 minutes under stirring the mixture was treated into a stainless steel autoclave at 100°C for 24h. The product was filtered and washed with water and ethanol. The solids were dried at 100°C for 2 hours and then calcined at 750°C for 2 hours. Cu and Fe active phases were deposited on the surface by successive incipient wetness impregnation with intermediate drying. The adopted precursors were $Cu(NO_3)_2 \cdot 3H_2O$ (Sigma-Aldrich) and $Fe(NO_3)_3 \cdot 9H_2O$ (VWR chemicals) respectively. The final product was dried and later calcined at 750°C for 2 hours. Two portions of the catalyst were impregnated with two differently concentrated solutions of KNO_3 (Alfa Aesar). The K-loaded catalysts were dried and calcined at the usual temperatures. The synthesized samples presented a nominal composition of:

- $Cu - Fe/CeO_2$ (10-0.6/CeO_2)
- $Cu - Fe - K/CeO_2$ (10-0.6-0.52/CeO_2)
- $Cu - Fe - K/CeO_2$ (10-0.6-1.9/CeO_2) [1]

2.2. Catalyst characterization

BET characterization: surface area and pore volume were evaluated using a "Micrometrics ASAP 2020 surface and porosity analizer".

XRD characterization: X-ray diffraction patterns were obtained with a "PANalytical X'Pert PRO Powder X-ray Diffractometer" (scanning a range from 5° to 90°, scan interval of 0.008°).

ICP-MS analysis: elemental chemical analysis was performed using inductively coupled plasma mass spectrometry (analysis performed by external partner, ALS Scandinavia Luleå, Sweden).

H$_2$-TPR studies: H_2 temperature programmed reduction of catalyst was performed at atmospheric pressure in a "Micrometrics Autochem 2510". The catalysts placed in a U-shaped tube reactor were flushed with inert gas and heated in 5% H_2/Ar stream from 100°C to 900°C at 5°C/min.

2.3. Catalytic activity test

The catalytic performance of the synthesized materials was tested in a purpose-built experimental setup. The feed gases were sent to a

packed bed quartz tubular reactor placed inside an oven after passing through a mixer. The outlet stream was analyzed with a Rosemount NGA 2000 infrared CO-CO_2 analyzer, while H_2, byproducts and N_2 (added as inert gas in order to close the mass balances) were detected by a Thermo Scientific C2V-200 Micro GC (micro gas cromatograph). A three way valve, placed before a water condenser, allowed to select whether to analyse the inlet or outlet stream. The packed bed, kept in position by two quartz wool layers, was placed between two thermocouples, used to ensure isothermy along the bed.

Before RWGS reaction the catalysts were reduced in situ at 650°C for 2 hours in a stream with composition 81.25% N_2 and 18.75% H_2 in order to activate the surface species. The catalytic tests were performed at atmospheric pressure with a feed flowrate of 1600 Nml/min with 60 [mol%] of N_2. Each run loaded 0.5g of catalyst, with a density of 1.873g/ml and an average particle size of 70 µm. With the adopted operating conditions, the mass hourly space velocity (mhsv, defined as $\dot{Q}_{tot}/m_{cat}$) was 192 l/g/h and the gas hourly space velocity (ghsv, defined as $\dot{Q}/V_{cat}$) was 359543 h^{-1}, providing an average contact time between gases and catalytic bed of 0.01s (STP conditions).

The catalytic performances were evaluated in terms of CO_2 conversion and CO selectivity. After running blank tests with SiC in order to have reference data for the thermal reaction. The three samples were tested at temperature ranging from 300°C to 700°C. Furthermore, the effect of inlet composition was assessed by feeding H_2/CO_2 molar ratios of 1, 2 and 3 to the K-free catalyst. These experiments ran approximately for 3 hours, until a stable condition was observed, subsequently, in order to evaluate the long-term performances, deactivation tests were performed on Cu-Fe/CeO_2 and Cu-Fe-0.5K/CeO_2 leaving them at 600°C for 90-100 hours on stream with H_2/CO_2 inlet ratio of 2. Under these conditions good activity should be ensured and Cu sintering is usually observable.

3. Results and discussion

3.1. Characterization

BET characterization: the synthesized samples showed a type IV isotherm, typical of meso-

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[1] Numbers refer to weight percentage. The three samples will be addressed as Cu-Fe/CeO_2, Cu-Fe-0.5K/CeO_2, Cu-Fe-1.9K/CeO_2 respectively.

porous structures, with the formation of hysteresis loop ascribed to the capillary condensation of the adsorbed N_2. The CeO_2 support presented the highest surface area and adsorbed volume, followed by Cu-Fe/CeO_2, Cu-Fe-$0.5K/CeO_2$, Cu-Fe-$1.9K/CeO_2$. This was expected since from the first to the last sample more metals were impregnated reducing the available surface area and partially occupying the pore volume. Surface area decreased significantly from 39.6 to 5.5 m^2/g, while pore volume faced a reduction from 0.29 o 0.059 m^3/g.

XRD characterization: the XRD patterns of the three catalysts and free support reported nine peaks associated to Cerianite (CeO2)[2]. These peaks do not appear weaker or broader in the metal-containing catalysts, hence it can be deduced that the impregnated species do not affect the support crystallinity.

Some characteristic peaks associated to copper oxide CuO[3] appear in the patterns belonging to copper containing catalysts, but their intensity is lower compared to the ones associated to CeO_2 because copper loading is low (10%). Neither Fe nor K crystalline phases could be identified, partly because their peaks partially overlap with the peaks for CeO_2 and CuO, and partly because their content is low and their crystals could be very dispersed with dimensions below the threshold for crystal detection (typical for XRD = 2 nm).

No peak associated to alloying compounds of Cu and Fe has been detected, suggesting that these two species remain independent on the catalytic surface.

ICP-MS analysis: the elemental analysis of the synthesized catalysts reported amounts of Cu and Fe similar to the desired amounts: 11% instead of 10% for Cu and 0.42-0.48% against the desired 0.6% for Fe. On the other hand, significant difference between the aimed and actual loading of K was observed: 0.2% instead of 0.5% and 0.65% instead 1.9% . This difference could be due to the saturation of pore volume. Indeed, even though the available pore volume (0.099 cm^3/g) was theoretically sufficient to deposit the desired amount of K, during the impregnation procedure the particles with lower pore vol-
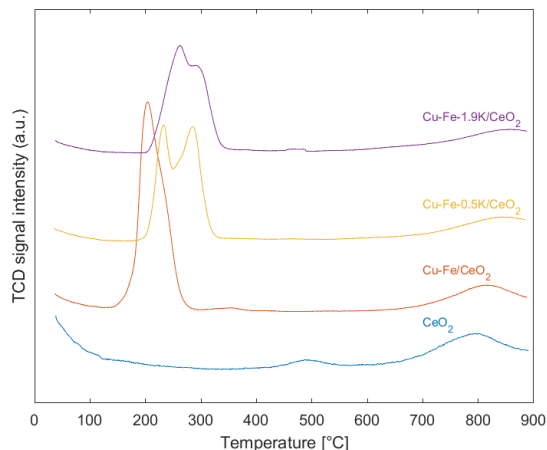

Figure 1: H_2-TPR curves for CeO_2, Cu-Fe/CeO_2, Cu-Fe-$0.5K/CeO_2$, Cu-Fe-$1.9K/CeO_2$.

ume started to agglomerate prematurely. Indeed CeO_2 support did not present uniform characteristics because it was obtained mixing different synthesis batches. Hence the uniform distribution of K was hindered. However, the effect of the increasing K loading on Cu-Fe/CeO_2 samples can still be assessed, because two catalysts with different amounts of promoter were available. Moreover they presented an atomic ratio between K and Cu within the range reported by literature for effective promotion of RWGS reaction.

H$_2$-TPR studies: as it can be observed in Figure 1, CeO_2 presents two reduction peaks at 489° and at 795°C respectively. The deposition of metals induces the loss of the low temperature peak, due to the higher reducibility of transition metal oxides, indeed a strong reduction peak associated to highly dispersed CuO is detected at 200°C-250°C. On the other hand, the second peak of CeO_2 is shifted towards higher temperatures by the introduction of Cu and Fe. This could be due to an interaction between metal oxides and ceria that makes the support less available for reduction, or to the covering of CeO_2 by reduced metallic phases. In agreement with the XRD result, which did not show any defect in ceria lattice after the addition of metal oxides, no peak associated to Cu-Ce alloy is identified. Cu-Fe/CeO_2 presents a weak peak at 352°C, which can be attributed to the reduction of Fe_2O_3 to FeO. The weakness of this peak is due to the small amount of iron loaded, which could also explain its absence in the pro-

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[2]28.546°, 33.080°, 47.482°, 56.341°, 59.088°, 69.413°, 76.699°, 79.074°, 88.427°

[3]35.544°, 38.709°, 48.7°, 61.46°, 66.144°, 68.008° (PDF-2 Release 2015 RDB database)

moted samples. K-containing catalysts present a reduction peak between 280°C and 295°C, associated to the reduction of potassium phases. The small stepwise bump in Cu-Fe-$1.9K/CeO_2$ profile around 500°C is due to an instrumentation problem, hence it shouldn't be ascribed to any surface species.

Considering the amount of hydrogen consumed during TPR analysis (calculated by integration of the area under the peaks), it can be stated that the introduction of metals strongly increases the catalyst reducibility below 700°C with respect to the free support. On the other hand, the amount of hydrogen consumed at higher temperatures is larger for CeO_2, partly because of its higher surface area and partly because of its reduced availability when covered by reduced metal oxides.

To further assess the catalytic properties, H_2-TPR was performed on spent samples with a time on stream larger than 90 hours at 600°C. All samples reported the drop of the peak associated to CuO, and the disappearance of the peaks associated to potassium oxides. It is worth mentioning that RWGS reaction is carried out over Cu and Fe through a cyclic redox mechanism [2], where the active phase consists of partially reduced metals. Thus, the significantly lower reducibility of spent samples demonstrates the capability of such catalysts to maintain their surface under a reduced state for the considered time interval, not undergoing deactivation by progressive oxidation.

3.2. Catalytic activity

Figure 2 reports CO_2 conversion for the synthesized catalysts, together with equilibrium conditions and thermal results[4]. Improvement from thermal performances becomes considerable at 400°C, while substantially higher conversion is observed from 500°C, getting closer to equilibrium value with increasing temperature. This indicates that lower temperatures are not sufficient to activate the catalytic reaction paths. After 400°C, Cu-Fe/CeO_2 displays the best conversion, while the increasing amount of K leads to worse performances. This is probably due to the coverage of the main active species by

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Figure 2: Conversion vs temperature for equilibrium conditions, inert catalyst, Cu-Fe/CeO_2, Cu-Fe-$0.5K/CeO_2$, Cu-Fe-$1.9K/CeO_2$.

potassium, which is not active for RWGS catalysis. Moreover, as reported in Section 3.1, the addition of K strongly reduces the surface area. On the other hand, K-containing samples, despite the low conversion, present better performances at 400°C, hence their application might be interesting for low temperature applications. Selectivity was evaluated in the first place from the CO outlet stream, while the ratio between H_2 and CO_2 consumption was used as check indicator. At low temperature CO selectivity resulted quite high, but the consumption ratio of H_2 and CO_2 was around 3.5, suggesting a prevalent production of CH_4. On the other hand, above 500°C, high CO selectivity was in agreement with a consumption ratio H_2/CO_2=1. At the same time CH_4 was never detected. The discrepancy between results is due to the inaccuracies of the experimental setup and instrumentation. Indeed, at low temperatures small fluctuations of inlet flows are reflected into heavy variations of CO production, being its amount very limited compared to the total flow. On the other hand, these inlet fluctuations, slightly affect the larger flows of CO_2, H_2 and CO when produced in considerable amount (i.e. at high temperature). For this reason, the consumption ratio H_2/CO_2 is a more reliable reliable parameter to assess selectivity. In conclusion it can be stated that the synthesized catalysts reported selectivity above 70% at 500°C and above 80% at 600-700°C, while at lower temperatures they achieved lower selectivity.

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[4]Missing data for thermal run at 500°C, but it is reasonable to expect CO_2 conversions in the range of 1% between 0.55%(400°C) and 1.26%(600°C).
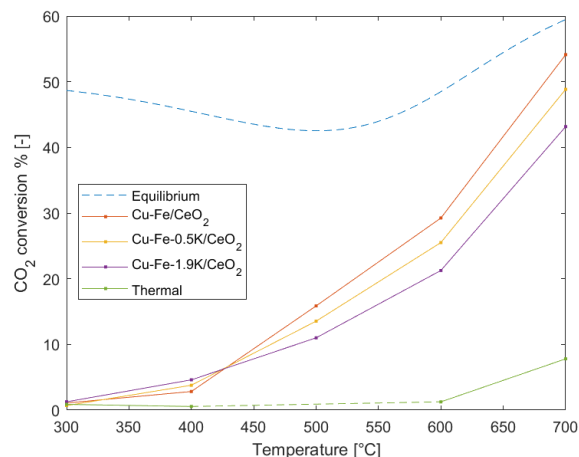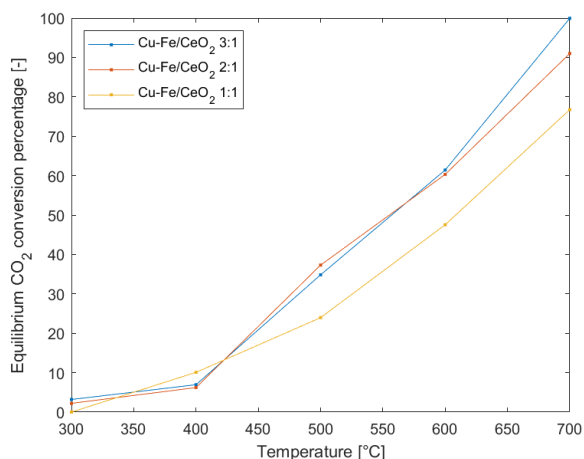
Figure 3: Percentage of equilibrium conversion vs temperature for Cu-Fe/CeO_2 with inlet H_2/CO_2=1,2,3.

3.3. Effect of inlet H_2/CO_2

The effect of inlet molar ratio H_2/CO_2 on conversion is reported in Figure 3. The higher is the amount of H_2 in the feed, the closer the catalysts get to equilibrium conversion. Once again it is evident that a minimum temperature of 500°C is required in order to activate the catalytic paths. Adopting higher amount of H_2 it is possible to reach 30-40% of equilibrium conversion at 500°C despite the high ghsv (ca. 360000h^{-1}). No big difference is observed comparing the results for ratios 2:1 and 3:1 at 500 and 600°C, indicating that, in this temperature range, adopting the lower ratio 2:1 might be more effective from the feasibility point of view. As a matter of fact, H_2 production, either produces more CO_2 than what RWGS is able to convert if H_2 is obtained from fossil sources, or it accounts for the main expenditure if H_2 is produced in a green way [3]. A similar discussion can be made about the operating temperature: from one side higher temperature provides better performances, on the other hand it involves more CO_2 emissions and higher costs (with different relevance depending on the heating source) [2]. For this reason intermediate operating temperatures (500-600°C) might be the best choice from a feasibility point of view.

Excellent results are obtained at 700°C where conversion reaches 77% of equilibrium with a ratio 1:1, 91% with a ratio 2:1, up to 100% with a ratio 3:1. Given the previously mentioned inaccuracies about selectivity evaluation at low tem-

perature, the comparison between selectivity results obtained from CO with the ones obtained from the consumption ratio between reactants (see Section 3.2) was performed. Low temperature is found to be again ineffective for catalyst activation. But from 500°C good CO selectivity is obtained, without significant dependence on the inlet H_2/CO_2 ratio.

3.4. Long term stability test

Running the catalytic tests for 2-3 hours was sufficient to develop the catalytic activity and to bring the involved surface species to steady state regime, which means, according to the studied chemical system, a steady state redox reaction cycle [2]. But on the long term, catalytic performances can deteriorate. The studied catalytic system could be affected by two deactivation mechanisms: sintering and coking. The former is typically experienced by Cu, while the second is often observed on iron-based catalysts. An other deactivation process that could affect the studied catalysts, is the progressive oxidation of surface species [4]. As a matter of fact, the surface metals are activated thanks to the initial reduction. The reaction with CO_2 oxidizes the surface and an efficient catalyst should be able to be reduced again by H_2 to its original state. Nevertheless, oxidation rate can be higher than reduction rate, leading to deactivation. Fe was added in order to prevent Cu sintering, and to enhance the reaction rate, because Fe is more easily oxidized with respect to Cu and it is more easily reduced by H_2. The drawback of Fe adoption is the possible formation of carbonaceous material on the surface. For this purpose potassium ability of coke gasification was evaluated.

Figure 4 reports conversion of Cu-Fe/CeO_2 and Cu-Fe-$0.5K/CeO_2$ for a time span of 100 and 69 hours respectively[5]. The first catalyst shows higher conversion along the whole time range. Both samples display an opposite step discontinuity just before 20 hours of operation. The reason for these sudden variations is the adjustment of operating temperature. After 18 hours of time on stream, Cu-Fe/CeO_2 was actually running 5 degrees below the setpoint value, while Cu-Fe-$0.5K/CeO_2$ was running 10-12°C

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[5]The two samples were tested for a similar period of time, but experimental failure invalidated results of Cu-Fe-$0.5K/CeO_2$ after 69 hours
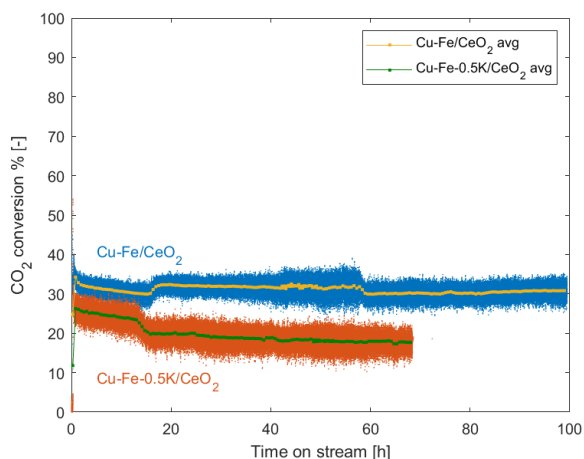
Figure 4: Instantaneous and averaged CO_2 conversion vs time for Cu-Fe/CeO_2, Cu-Fe-$0.5K/CeO_2$.

above the setpoint value. Hence, temperatures were corrected to reach the setpoint of 600°C. It is interesting to note that the non promoted sample provided higher conversion at the beginning even though it was running at lower temperature by almost 20°C. These results indicate that potassium, possibly, blocks the main sites involved into RWGS reaction. The conversion variation after 60 hours on stream in Cu-Fe/CeO_2 conversion profile, is ascribed to a minor flow variation in the feed gases.

Cu-Fe/CeO_2, after a first settlement (0-20h), presents an almost steady state average conversion of 30.5% (the yellow line is almost horizontal). On the other hand, Cu-Fe-$0.5K/CeO_2$ shows a decreasing conversion, observable by looking at the slightly negative slope of the green line between 20-69 hours. Even though data after this time are not available, it is reasonable to expect a flat profile in the best case scenario, or a progression of the deactivation trend. The unchanged conversion of Cu-Fe/CeO_2 in time indicates that Fe is effective in preventing Cu sintering and enhancing surface reducibility. On the other hand, it is possible to assess that K alters the Cu-Fe interaction, hindering their beneficial combination. From the results of TPR on spent samples (see Section 3.1) it can be stated that K is not detrimental for the redox catalytic cycle, on the other hand it could weaken the stabilization effect of iron upon Cu sintering, possibly because of some electronic interaction between the surface species. At the same time, not observing an improvement in deactivation

prevention with the adoption of K, might be conducive to not consider coking as a relevant phenomenon on this type of catalyst, at least within these operating conditions. Selectivity resulted quite steady state in time, remaining around 82% for Cu-Fe/CeO_2 and around 80% for the other catalyst.

4.   Conclusions

The three synthesized catalysts required a minimum temperature of 500°C to provide high conversion and selectivity. The best performing catalyst was Cu-Fe/CeO_2, while K deposition obstructed the active sites. Cu-Fe/CeO_2 was more efficient with inlet H_2/CO_2=2 at 500 and 600°C, while conversion equilibrium was reached at 700°C, with an inlet ratio 3:1 and high ghsv. The novel combination of Cu and Fe on CeO_2 effectively catalyzed RWGS reaction without deactivation for 100h, whereas the addition of K on reducible support hindered the beneficial Cu-Fe interaction, leading to deactivation, probably due to sintering. The gasifying action of K was not observed, suggesting the absence of coking phenomenon.

References

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