
Mitigation of CO₂ emissions in FCC: USY zeolite regeneration in the presence of Vanadium-Lithium-Alumina catalyst

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Abstract

The transformation of biomass into liquid fuels using the standard oil refinery structure is strategically important in a transition period to a more sustainable energetic matrix. One of the alternatives is the co-process of bio-oil in the FCC process, which is associated with a regeneration under a wealthy atmosphere in CO₂. CO₂ emissions are reduced and it produces CO for sequential uses.

In this work the catalyst Li-V/Al₂O₃ was studied as reverse-Boudouard reaction promoter, in the regeneration of the spent USHY. The coke was resulted of catalytic cracking of 10% DX, derived from sugarcane bagasse, in n-hexane. At atmosphere of 10% CO₂/He, it was obtained a good performance for oxidation up to a ratio of 0.10 Li-V/Al₂O₃ to 1 USHY parts, and it was demonstrated, by comparison with the hydrocarbon coke, that the additive was effective regardless of the supporting coke.

Finally, in order to account for a more industrial purpose of Li-V/Al₂O₃, it was also studied the possibility to reduce simultaneously SO_x and CO₂ emissions. It was proved that the CO₂ conversion had decreased slightly in the SO₂ presence but SO₂ capture, DeSO_x mechanism, was unaffected when introducing CO₂ in the gas stream.

Keywords: Carbon dioxide, FCC regenerator, Bio-coke, Reverse-Boudouard Reaction Additive,

1. Introduction

Greenhouse gas mitigation is a timely topic, due to the large amount of energy, mainly provided by fossil fuels burning required for all Human being activities. Global warming is a very complex topic and the uncertainty about the reason of it being anthropogenic or not was extensively debated in the literature. Indeed, the obsolescence of a large amount of capital goods and the increasing demand for energy in the world is certainly related to the higher amount of greenhouse gas emission. As a consequence, sustainability can only be achieved by improving simultaneously the amount of bio-resources in the energetic matrix and mitigating emissions, e.g. like nature does in its several cyclic processes.

Over the years, the Fluid Catalytic Cracking process (FCC) was responsible for about 15-30% of the total carbon dioxide emissions within the refinery. The integration of biofuels with petroleum refineries is essential in transition between fossil fuels

and renewables. One proposed alternative was the co-processing of a bio-oil (upgrading lignocellulosic biomass) together with the loads of conventional FCC process to produce a greener fuel. Still, with the aim of controlling CO₂ emissions, studies for using this oxidant gas as a reactant in the regeneration step have been developed.

The strategy of performing spent catalyst regeneration in rich CO₂ atmosphere under Fluid Catalytic Cracking process (FCC) conditions, simultaneously combines CO₂ capture with CO production for sequential uses, i.e. hydrogen, methanol, dimethyl ether and hydrocarbons production. Moreover, coke formation is a consequence of hydrocarbon cracking reactions on FCC catalyst. The amount of coke spent on the catalyst is related to the processed feed, i.e. lower quality feeds or bio-feed result in greater coke formation on the spent catalyst.

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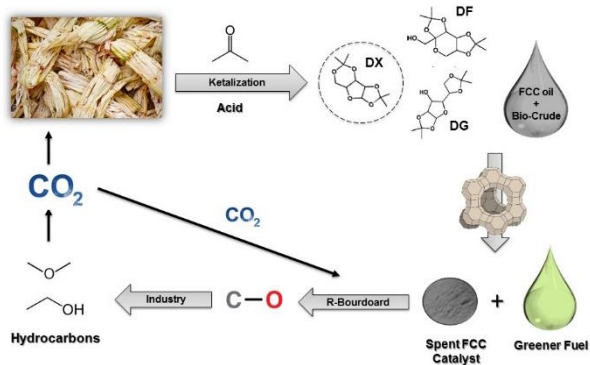


Figure 1.1 Integrating the production of liquid fuels to the rescue of CO₂ for regeneration of the spent FCC catalyst.

Second-Generation biofuel

Lignocellulosic biomass is made up of hard and fibrous structures mainly polysaccharides linked by covalent bonds and hydrogen bonds. The main components are cellulose (40-60%) and hemicellulose (20-40%), interspersed with lignin (macromolecule composed of aromatic alcohols). Recently it was published a lignocellulosic biomass conversion process combining acid hydrolysis and the ketalization producing a bio-crude (with diacetals as major compounds) which is more thermally stable and soluble in hydrocarbons, non-polar compounds. It facilitates the co-processing of this charge with those conventionally used in FCC process. One of diacetals obtained by this route is 1,2:3,5-di-O-isopropylidene- α -D-xylofuranose (DX), aromatic five-carbon compound, whose melting point is 46 °C and the boiling is equal to 272 °C, which was used along with model compound work.

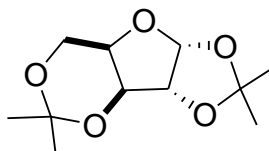


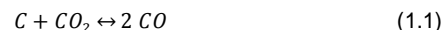
Figure 1.2 Structure model compound DX, 1,2:3,5-di-O-isopropylidene- α -D-xylofuranose.

Reverse-Boudouard reaction in FCC conditions

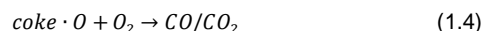
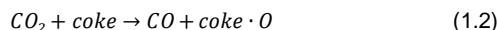
CO₂ and coke reaction are currently present in gasification processes where, for example, alkaline metals are added to coke in order to promote RB reaction. In dry catalytic reforming, hydrogen, supplied by hydrocarbons (formed on metal particles), reacts with CO₂ which also acts as a strategy for catalyst regeneration.

As CO₂ and coke reaction (Reverse-Boudouard reaction, RB) changes from a slightly to largely endothermic reaction, the goal was to overcome the O₂ reactivity as oxidant, with several orders

of magnitude higher than that of CO₂. Thus the coke burnt by oxygen can supply the energy required for CO₂ and coke reaction maintaining the FCC process heat balance.



Partial reactions between the deposited coke and CO₂ are:



Previous work demonstrated that the spent catalysts can be regenerated in CO₂/O₂ atmosphere in the presence of a spent alumina modified by both group I, II elements and vanadium under realistic FCC conditions. Still, the addition of group I and II elements and vanadium to the typical FCC catalyst is not possible since its act as poisonous. Therefore, for a proper industrial application this catalyst was tested as an additive to the actual FCC catalyst.

SOx Removal in FCC

Fluid catalytic cracking is one of the main processes responsible for sulfur emission in the refinery. Herein the effect of vanadium loading over an alumina modified with potassium was previously studied for sulfur mitigation. Vanadium is a key variable and even at very low amount all reaction steps involved in such process were improved. DeSO_x tests showed that vanadium acts on the two main process steps: sulfur oxidation (SO₂) to SO₃ and reduction of hydrogen sulfide (H₂S) and water (H₂O).

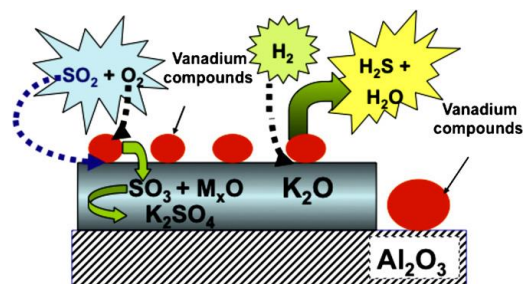


Figure 1.3 Application of alumina modified by both group I, II elements and vanadium by SO_x removal under realistic FCC conditions.

The main goal was then to study the vanadium-lithium-alumina as a multiadditive for FCC regeneration step, while reduce the CO₂ and SO_x emissions.

2. Experimental Section

2.1 Catalyst preparation

2.1.1 Reverse-Boudouard reaction precursors

The alumina (Al_2O_3) used as support for all the catalyst used in this work was obtained by calcination of bohemite (diffraction pattern *JCPDS 74-1985*) for 20h at 800 °C under air atmosphere. Lithium was impregnated on the alumina support through the incipient wetness technique using LiCl (*VETEC*, 95wt%). The amount of salt used in the impregnation was determined to obtain 5wt% Li. After impregnation the sample was dried over 12 h at 120 °C. The $\text{Li}/\text{Al}_2\text{O}_3$ catalyst was obtained by calcination of the dried impregnated alumina at 800 °C for 10 h under air atmosphere.

Vanadium was added to $\text{Li}/\text{Al}_2\text{O}_3$ in order to obtain the $\text{Li-V}/\text{Al}_2\text{O}_3$ catalysts. Vanadium was impregnated on the referred supports by using an aqueous solution of vanadyl acetylacetonate, VAA, (*Aldrich*, 95wt%), 25 mL of solution per gram of catalyst. The samples were placed in contact with the VAA solution and heated at boiling temperature until all water had dried. The remaining solids were dried at 120 °C over 12 h and thermal treated at 600 °C for 3h under air atmosphere. The catalyst preparation was performed to obtain a loading of 1wt% of vanadium.

2.1.2 USHY – catalytic cracking active phase

Na-USHY ($\text{SAR}=13$, $\text{S}_{\text{BET}}=605 \text{ m}^2\cdot\text{g}^{-1}$, $\text{V}_{\text{micropore}}=0.24 \text{ cm}^3\cdot\text{g}^{-1}$) zeolite was gently supplied by *PETROBRAS*. The acid form of the zeolite was obtained by performing ion exchange using a $(\text{NH}_4)_2\text{SO}_3$ 1M solution (200 mL per 10 g of zeolite) at 70 °C for 1 h. The ion exchange procedure was performed 4 times to completely eliminate any trace of sodium. Afterward, the sample was dried over night at 120 °C and calcined at 500 °C for 4 h under air atmosphere.

2.2 Catalyst characterization

Textural characterization was carried out in a Micromeritics ASAP 2010. Initially, the catalysts were pretreated at 200 °C under vacuum during 2 h, then the isotherms of adsorption of nitrogen at 77 K were performed and specific surface area was determined through the BET method.

X-ray powder diffraction (XRD) patterns were obtained using a *Rigaku X-ray* diffractometer with nickel-filtered $\text{CuK}\alpha_1$ radiation source ($\lambda=0.15406 \text{ nm}$) and graphite monochromator. The XRD profiles were collected in the 2θ angle region between 5 and 80 θ , at a step width of 0.05 θ , counting 1 s between each step.

2.3 Catalytic Cracking Reaction

The samples were heated at 500 °C ($10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$) under nitrogen flow ($100 \text{ mL}\cdot\text{min}^{-1}$). Once 500 °C attained, $0.2 \text{ mL}\cdot\text{min}^{-1}$ of a mixture of 10% DX in n-hexane was feed at the entrance of the reactor during 15min, in addition to the $100 \text{ mL}\cdot\text{min}^{-1}$ nitrogen flow. 500 mg of catalyst were used each time.

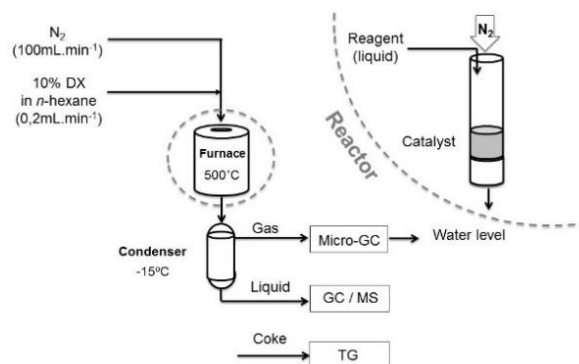


Figure 2.1 Layout of the fixed bed catalytic cracking unit.

The product gases (H_2 , CH_4 , CO , CO_2 and hydrocarbons $+C_4$) were collected at the top of the reactor and analyzed on-line using an *Agilent Technologies MicroGC 490*. The amount of gas produced during the reaction was estimated by the difference of water displaced during reacting the pure nitrogen flow. The composition of formed gas was estimated using the average of 5 injections effected during the reaction time. The liquid fraction was obtained by condensing (-15°C), using a condenser placed immediately after the reactor outlet, whereby the liquid mass is calculated by weight difference of the condenser assembly plus collecting container before and after the reaction. For qualitative analysis of the type of products that make up the liquid used is a liquid chromatograph (*Agilent Technologies 7890A*) coupled with a mass spectrum detector (*Agilent Technologies 5975C*), at which DX joined unreacted. The spent catalysts coke loading was determined through thermogravimetric analysis in a *Netzsch TG-IRIS* equipment. The samples were dried under a N_2 flow at 250°C for 30 min (heating rate of $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$). Afterwards, the sample was heated to 700°C under airflow at heating rate of $10 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$. The coke loading corresponded to the samples weight loss under airflow.

2.4 Samples Coking

Two different types of coke were used in this study. The first resulted from vacuum gasoil feed and the second from the catalytic cracking of 1,2:3,5-di-O-isopropylidene- α -D-xylofuranose (10%wt) in n-hexane (*VETEC*, 99wt%). In order to differentiate the samples, gasoil and DX indexes were added to the catalysts name respectively for coking with vacuum gasoil (VGO) and DX in n-hexane.

2.4.1 Reverse-Boudouard reaction precursors

Vacuum gasoil coke

Prior to coking the samples were impregnated with a vacuum gasoil / n-hexane mixture with a weight proportion of 1 gasoil for 2 of catalyst. The n-hexane amount was the minimum required to dissolve all vacuum gasoil. The samples were added to the gasoil/n-hexane mixture and stirred at room temperature until complete n-hexane evaporation, after which the sample was heated at 120 °C overnight. The sample was then heated at 530 °C for 15 min under nitrogen flow (60 mL.min⁻¹).

1,2:3,5-di-O-isopropylidene- α -D-xylofuranose (DX)

Previous to coking the samples were heated at 500 °C (10 °C.min⁻¹) under nitrogen flow (100 mL.min⁻¹). Once 500 °C attained, 0.2 mL.min⁻¹ of a mixture of 10%DX in n-hexane was feed at the entrance of the reactor during 15 min, in addition to the 100 mL.min⁻¹ nitrogen flow. 500 mg of catalyst were used each time. The coked sample were the cooled until room temperature under nitrogen flow.

2.2.2 USHY

Two different types of coke were deposited on USHY for this study. The first resulted from the catalytic cracking of 10wt% DX in n-hexane (previously described procedure) and the second from the fructose labeled in all carbons (¹³C₆-fructose, *Omicron Biochemicals Inc.*, 99wt%).

¹³C₆-Fructose coke

Fructose labeled in all carbons was used to produce ¹³C-coke over USHY zeolite. The USHY zeolite and the labeled fructose were mixed together in a weight proportion of 2:1. Afterwards the mixture was heated at 500 °C for 15min under a nitrogen flow of 100 mL.min⁻¹.

2.5 Coke Oxidation: RB Reaction

The spent catalysts were submitted to two experimental procedures as described below. In all cases the formed gases were monitored by on line *Mass Spectrometer MKS* (model PPT430).

In the first experimental procedure the mass spectra were collected continuously during the sample heating from 25 °C to 1000 °C at a heating rate of 10 °C.min⁻¹ under a 10% CO₂ in Helium flow of 60 mL.min⁻¹.

In the second experimental procedure the spent catalysts were heated from 25 °C to the reaction temperatures (680, 720, 760, 800°C) at a heating rate of 10 °C.min⁻¹ under a He flow of

60 mL.min⁻¹ and kept under these conditions until the mass spectra profiles stabilized. Once stabilized the He flow was switched to a 30 mL.min⁻¹ flow of one of the following atmospheres: ¹³CO₂ (1.9%) in He; ¹³CO₂(1.9%)/ O₂(0.8%) in He and ¹³CO₂(1.9%)/ O₂ (0.8%)/ SO₂(0.2%) in He.

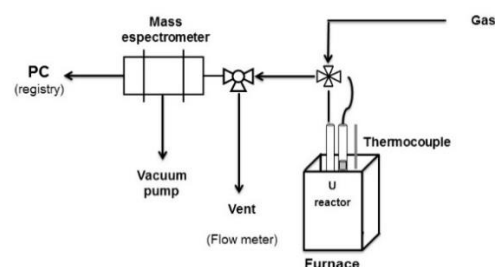


Figure 2.2 Simplified representation of laboratory oxidation unit coupled to the mass spectrometer.

2.6 SOx Removal Test

The tests used a thermogravimetric from *Netzsch* system (*STA-449F1 Jupitermodel*) equipped with a thermobalance high precision that mediates mass variations versus time (TG) coupled with a mass detector in-line to identify the gaseous species (MS). Samples 10mg were used with and without coke in the presence of O₂(1.4%)/ SO₂(0.35%) in He and O₂ (1.4%)/ SO₂(0.35)/ CO₂ (1.3%) in He (separated). The main steps of the process were simulated: pretreated, SO₂ capture and MxSO₄ oxidation (725 °C, 45 min), and also SO₄ reduction to H₂S (575 °C, 45 min).

3. Results and Discussion

3.1 Catalyst Characterization

3.1.1 Hexane Adsorption

It was observed that the samples prepared from alumina adsorbed between 0.6 and 0.9wt% to n-hexane, of 160 to 40 °C. Zeolites exhibiting a range of 5 to 8%, in the respective temperature range. As the amount of adsorbed hexane vary with the nature of the material, the corresponding textural properties showed significant differences.

Table 3.1 Results of hexane adsorption test in Na-USY and USHY zeolites.

| | $\mu\text{mol n-hexane in ESW}_{\text{minimo}}$ | $T_{\text{min}} \text{ (K)}$ | $V_{\text{micropores}} \text{ (cm}^3 \cdot \text{g}^{-1}\text{)}$ |
|-------------------------------------|---|------------------------------|---|
| Al ₂ O ₃ | 60 | 431 | 0.012 |
| Li-V/Al ₂ O ₃ | 75 | 433 | 0.013 |
| Na-USHY | 1424 | 400 | 0.22 |
| USHY | 1407 | 389 | 0.21 |

From Table 3.1 it was found that all the alumina based samples show very small volume of micropores: twenty times smaller than the USHY zeolite and ten times less than the ZSM-5. This was expected because such materials typically follow a mesoporosity profile. It was also proved that almost exclusive presence of micropores in zeolite USHY as compared with the pore volume provided by PETROBRAS, $0.22 \text{ cm}^3 \cdot \text{g}^{-1}$.

3.1.1 Nitrogen Adsorption

The evaluation of the textural properties was made through nitrogen adsorption for evaluating the textural characteristics using the BET and BJH methods. The results are shown below.

Table 3.2 Results nitrogen adsorption test in pure and modified alumina catalysts (Al_2O_3 and $\text{Li-V/Al}_2\text{O}_3$).

| | S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$) | V_{P} ($\text{cm}^3 \cdot \text{g}^{-1}$) | d_{P} (\AA) |
|------------------------------|--|---|------------------------------------|
| Al_2O_3 | 127 | 0.43 | 118 |
| $\text{Li/Al}_2\text{O}_3$ | 48 | 0.23 | 174 |
| $\text{Li-V/Al}_2\text{O}_3$ | 54 | 0.24 | 153 |

As can be seen from Table 3.2, $\text{Li-V/Al}_2\text{O}_3$ had the lower average pore distribution comparatively with base support. This can be explained by the presence of other crystalline phases, which come from the precursor salt, causing the blockage of the pores. Consequently, there was a reduction of the pore volume and pore diameter, the walls being partially occupied. $\text{Li-V/Al}_2\text{O}_3$ dimensions were compatible with mesoporosity.

3.1.2 X-ray diffraction

The structural analysis of the catalyst by XRD showed that there wasn't any phase change after the metal impregnation and subsequent calcining additive $\text{Li-V/Al}_2\text{O}_3$. Furthermore, there was a loss of crystallinity of both materials after the catalytic cracking tests caused by coke deposition on the catalyst. When comparing the angle corresponding to each peak of $\text{Li-V/Al}_2\text{O}_3^{\text{DX}}$ with $\text{Li-V/Al}_2\text{O}_3$ and USHY^{DX} with USHY, it is observed that the phase remains unchanged but the intensity decreases 2% and 1%, respectively, due to the presence of coke on the surface.

3.2 Fixed Bed Catalytic Cracking Tests

Applying a model test, currently studied for the catalytic cracking 10% DX in n-hexane (representative of the common FCC hydrocarbon feedstock) under USHY and $\text{Li-V/Al}_2\text{O}_3$, was intended to simulate the reaction stage in a fixed bed. The mass yield in Table 3.3 showed that the mass fraction of solids obtained in a test using $\text{Li-V/Al}_2\text{O}_3$ is three times lower than the USHY, which indicated a higher coke deposition in the active phase, later evidenced by thermal analysis tests.

Table 3.3 Mass yield of catalytic cracking tests 10%DX in n-hexane performed under $\text{Li-V/Al}_2\text{O}_3$ and USHY.

| | $\text{Li-V/Al}_2\text{O}_3$ (g), 15 min | USHY (g), 15 min |
|--------------|---|---------------------|
| Catalyst | 0.502 | 0.500 |
| DX injected | 1.81 | 1.83 |
| Gas phase | 0.159 | 0.179 |
| Liquid phase | 1.59 | 1.27 |
| Solid phase | 0.029 | 0.089 |

The analysis of the major formed gaseous compounds showed that when it was used USHY, the compounds with 3 carbon atoms and methane were preferably formed while in the presence of $\text{Li-V/Al}_2\text{O}_3$ the amounts of carbon dioxide and hydrogen produced substantially increased forty three and six times molar, respectively, when compared to the USHY. Liquid chromatography separated the major components of this phase (acetone, benzene, toluene, xylene, aromatic with 8 and 10 carbons, DX and hexadecane, standard compound).

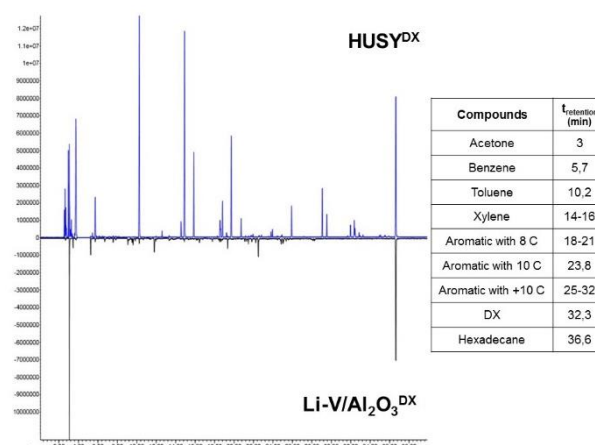


Figure 3.1 Identification of liquid compounds obtained in the catalytic cracking test in a fixed bed with 10% DX in n-hexane feedstock.

In Figure 3.1 proceeded to the direct comparison of the type of goods and intensity obtained under each of the catalysts. The results indicate that cracking 10%DX in n-hexane $\text{Li-V/Al}_2\text{O}_3$ promotes a rise only to a minor proportion of aromatic compounds that could be included in liquid fuel, since only the acetone peaks (from the reverse reaction to shape DX) and hexadecane (internal standard in which the diluted sample) have considerable intensity. The others were mostly oxygenates. In the case of zeolite USHY, appears that the compounds produced were of interest to the petrochemical industry (BTX- benzene, toluene and xylene) and aromatic of 8-10 carbons which may be included in the gasoline.

It was important to note that the peak intensity is not directly proportional to the amount of each formed compound.

3.3 Cracking Coke Characterization

The characterization of the solid phase obtained from the catalytic cracking test of 10%DX in n-hexane feedstock is presented in a separate section. A good knowledge of the products deposited on the catalyst (Li-V/Al₂O₃ and USHY) it was important for a proper interpretation of the results of the coke oxidation tests.

3.3.1 Thermogravimetric analysis

Thermogravimetric analysis were made to quantify the coke supported on Li-V/Al₂O₃ and USHY in result of catalytic cracking of 10%DX in hexane. It was analysed VGO coke supported on Li-V/Al₂O₃ and fructose coke on USHY (for a mechanistic study). The masses lost up to 250 °C concern mainly the water adsorbed in the samples, while above this temperature, in an inert atmosphere, corresponding to organic fractions (coke compounds). The final mass respect to inorganic part of the process, majorly supports. As might be expected, TG showed that different power loads and supports lead to different amounts of coke deposited on the catalyst surface. To the resulting samples of catalytic cracking 10% DX in n-hexane gave 5.8% and 18.1%, respectively Li-V/Al₂O₃ and USHY, while Li-V/Al₂O₃ with VGO coke supported 500 °C was 4.0%. For tests with labelled coke used a USHY with fructose at ¹³C labelled coke, 14.7%. The microporosity associated with the zeolites leads to an increased blocking of the pores consequently higher percentage of coke, then a more effective deactivation of the catalyst.

3.3.2 Functional groups of bio-coke

The studies to characterize the coke from the catalytic cracking DX mixture in n-hexane, were carried out by heating in an inert atmosphere (helium) allowing to distinguish the functional groups. The type of functionality present on the coke was analysed for CO and CO₂ profiles observed under a helium flow and are presented in Figure 3.2.

The results of the CO₂ profile for modified alumina, Li-V/Al₂O₃ showed the presence of carboxylic acid, lactones and quinones (oxidized compounds). Another important feature is that the type of catalyst slightly affected the functionality of the coke. The activation of CO₂ on glassy carbon surfaces was more difficult to occur when there was oxygen species present on the surface, identified in the test with helium. Above 700 °C there is still a large number of oxygenated compounds so, the maximum temperature of CO formation must be above this value.

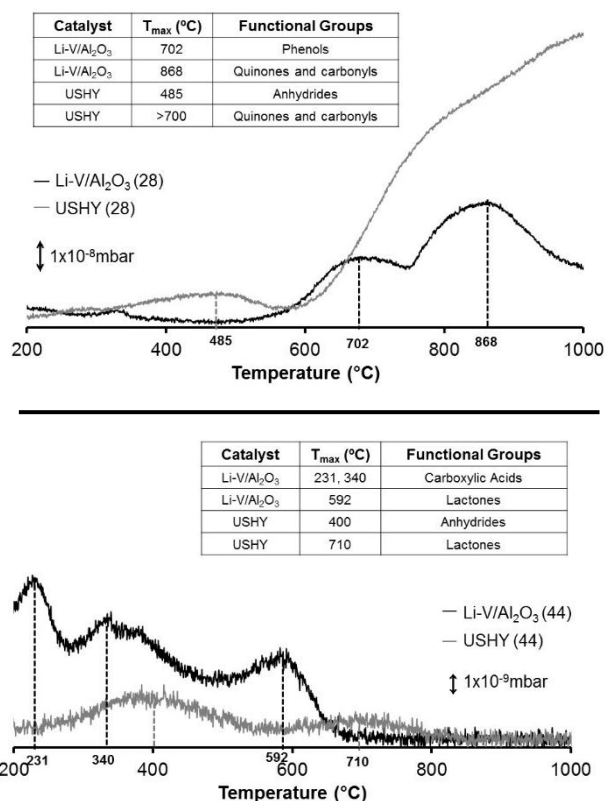


Figure 3.2 CO (28) and CO (44) formation profiles in a pure He atmosphere with a heating ramp of 10 °C.min⁻¹. T_{max} represents a maximum temperature which occurred the CO and CO₂ formation.

3.4 Temperature programmed CO₂ oxidation

The addition of vanadium or lithium to the actual FCC catalyst is out of question, since both can work as poisons to the catalyst. Still, their usage as an additive to the FCC catalyst can be applied, i.e. able to be used in a small amount compared to that of FCC catalyst. In order to be used as additive a simple question must be answered: Is Li-V/Al₂O₃ (when added in small amounts) able to promote the reverse-Boudouard reaction on the coke deposited on the FCC catalyst.

3.4.1 Additive for Reverse-Boudouard Reaction

A spent Li-V/Al₂O₃ and USHY were compared to a mixture of spent USHY and Li-V/Al₂O₃ (spent and pristine) in several proportions. Figure 3.3 showed CO profiles obtained for the referred mixtures under CO₂ (10%) in He flow under increasing temperatures (10 °C.min⁻¹). This study was conducted in spent catalysts used in the cracking of a 10%DX in n-hexane. The coke nature did not significantly affected the RB reaction, as discussed previously.

As expected HUSY^{DX} sample was quite inefficient in promoting the reverse-Boudouard reaction with the maximum CO formation

not being achieved before the temperature reached 1000 °C. The samples composed of both USHY^{DX} and Li-V/Al₂O₃^{DX} resulted in intermediate profiles between USHY^{DX} and Li-V/Al₂O₃^{DX}. The mixture containing one to one part of USHY^{DX} and Li-V/Al₂O₃^{DX} resulted in a profile that achieved maximum CO formation at 887 °C, whereas when pristine Li-V/Al₂O₃ was used (in 1:1 proportion to spent USHY) the maximum in CO formation dislocated to 930 °C. Similarly, the Li-V/Al₂O₃^{DX}+USHY^{DX} mixture was able to promote the RB reaction starting at lower temperature, i.e. 590 °C compared to 650 °C of Li-V/Al₂O₃+USHY^{DX} and 700 °C of USHY^{DX}.

The results, clearly indicated that Li-V/Al₂O₃ is able to promote the RB reaction on the coke deposited on the USHY surface, however the RB reaction is improved when coke is present on the Li-V/Al₂O₃ surface. The importance of having coke deposited on (or near) the reactive ensemble for activate RB reaction is indeed expected and suggested that (taking in account the low vanadium availability on surface) that coke react with CO₂ from bottom to top. The slight improvement in RB reaction observed when no spent Li-V/Al₂O₃^{DX} catalyst was mixed up with spent USHY could be related to some proximity between the additive and spent USHY particle in fix bed test.

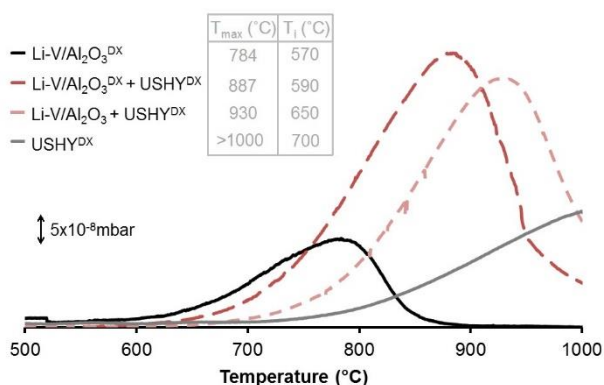


Figure 3.3 CO formation profile in an atmosphere of 10%CO₂/He with heating of 10 °C.min⁻¹ by reverse-Boudouard reaction with Li-V/Al₂O₃ and USHY coked. Li-V/Al₂O₃+USHY are representative of the mechanical mixture between Li-V/Al₂O₃ and USHY (1:1). T_{max} and T_i represent temperature for maximum CO formation and temperature at which CO begins to be formed.

3.4.2 Variation of coke nature

Another important feature is coke nature that is affected by the type of feed rather than the type of the catalyst. Li-V/Al₂O₃ capacity to promote the reverse-Boudouard reaction was tested for two different types of coke: vacuum gasoil coke and 1,2:3,5-di-O-isopropylidene-α-D-xylofuranose (DX) coke. DX resulted in a slight increase on T_i in the RB reaction compared to the former. However both Li-V/Al₂O₃^{DX} and Li-V/Al₂O₃^{VGO} catalysts spent showed similar T_{max}, i.e. respectively 784 °C and 778 °C.

The 1,2:3,5-di-O-isopropylidene-α-D-xylofuranose is an oxygenated molecule. As a partial conclusion of this section the results clearly demonstrate that Li-V/Al₂O₃ catalytic is effective in promoting the RB reaction regardless the coke nature. Therefore, the catalyst is playing an important role in promoting RB reaction overcoming the difficulty imposed by a more oxygenated coke

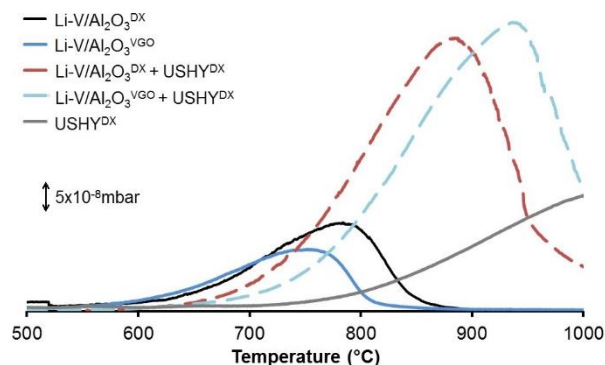


Figure 3.4 CO formation profile in an atmosphere of 10%CO₂/He with heating of 10 °C.min⁻¹ by reverse reaction Boudouard (RB). Mechanic mixture of Li-V/Al₂O₃ and USHY had vacuum gasoil coke and DX coke.

3.4.3 Study of proportion additive/zeolite

The proportion of this spent additive to the spent USHY was explored (from 1:1 to 0.05:1, respectively) as presented in **Figure 3.5**. In all proportions RB reaction started at lower temperature compare to that in spent USHY, particularly for 1:1 and 1:0.33 proportions the maximum temperatures obtained were lower than 1000 °C. As expected, when the proportion of additive decreased the effect on promoting the RB reaction becomes less evident and the CO formation profile became similar to that of spent USHY.

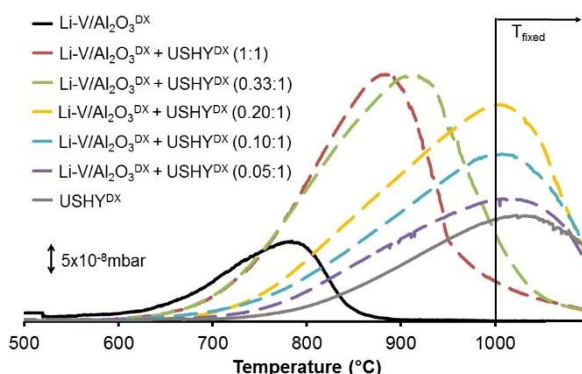


Figure 3.5 CO formation profile for the Reverse-Boudouard reaction under increasing temperature (10 °C.min⁻¹) and 10% CO₂/He atmosphere. y USHY : y Li-V/Al₂O₃ are representative of the mechanical mixture of x parts of USHY to y parts of Li-V/Al₂O₃ (in all cases the USHY are constant).

Still, even when the proportion of additive is twenty times lower than of USHY a slight effect on the promotion of RB reaction was observed. Despite this fact and considering that the typical reaction temperature for an FCC regenerator is around 720 °C, the results showed that Li-V/Al₂O₃ can only work as additive in proportions of USHY to promoter of 0.10 to 1.

3.4.3 Study of reaction mechanism

An experiment using labelled coke (¹³C) on spent USHY by means of labelled fructose (all carbons ¹³C) was mixed up with spent Li-V/Al₂O₃^{DX} catalyst.

It is important to highlight that ¹³CO was formed at lower temperature than that in spent USY^{DX}. The formation of ¹³CO (that can only be originated from spent USHY) is direct evidence that ¹²CO₂ reacts on Li-V/Al₂O₃^{DX}, producing ¹²CO and ¹²Coke-O then this oxygen undergoes mobility (on coke or on the catalyst) to the ¹³coke on spent USHY resulting in ¹³CO formation. On the base of this result it can be proposed that this additive can improve the regeneration of spent catalyst through oxygen migration, resulting in high CO selective compared to CO₂.

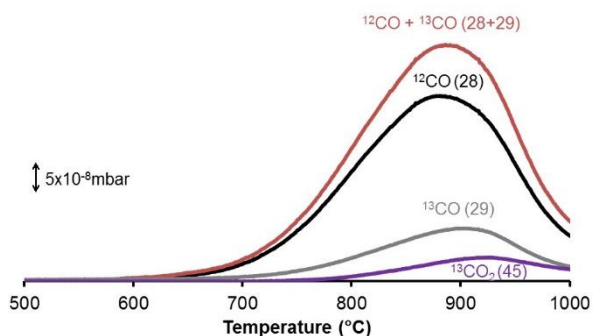
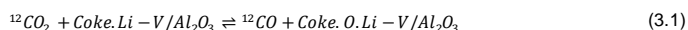


Figure 3.6 ¹²CO, ¹³CO, ¹³CO₂ formation profile for the RB reaction under increasing temperature (10°C.min⁻¹) and 10% ¹²CO₂/He atmosphere. A mechanical mixture of Li-V/Al₂O₃^{DX} and USHY^C (coke resulting from ¹³C labeled fructose) was used in the reaction.

The mechanism of RB reaction to mixture, Li-V/Al₂O₃^{DX} and USHY^C, was:



3.5 Reverse-Boudouard reaction at continuous-flow of ¹³CO₂

The promoter reverse-Boudouard reaction was studied under continuous flow of several mixtures (¹³CO₂(1.9%)/ He, ¹³CO₂(1.9%)/ O₂(0.8%)/ He and ¹³CO₂(1.9%)/ O₂(0.8%)/ SO₂(0.2%)/ He), different typical temperatures (680, 720, 760 and 800 °C) and ratios (1:1, 0.20:1 and 0.05:1), evaluating each parameter with remaining constant. It was possible to quantify the average conversion of CO₂ to CO to RB reaction subtracting the fragmentation of ¹³CO₂ (8%, recurring value in mass spectrometry equipment) for different situations.

3.5.1 Atmosphere modification

The figure showed the profile obtained for the first 5 min of reaction to a mixture of Li-V/Al₂O₃^{DX} and USHY^{DX} (1:1) at a temperature of 720 °C, changing the atmosphere to study the impact of the oxygen and sulfur dioxide presence on regeneration step.

Figure 3.7 demonstrates that for all studied atmospheres, the formation of ¹³CO reaches its maximum within a short operating time (TOS) and falls abruptly, remaining practically unchanged the remaining period. Comparing the relative amounts of ¹³CO between different atmospheres, it was cleared that oxygen slightly affected ¹³CO₂ average conversion and in return the opposite succeed in the sulfur dioxide presence (SO₂).

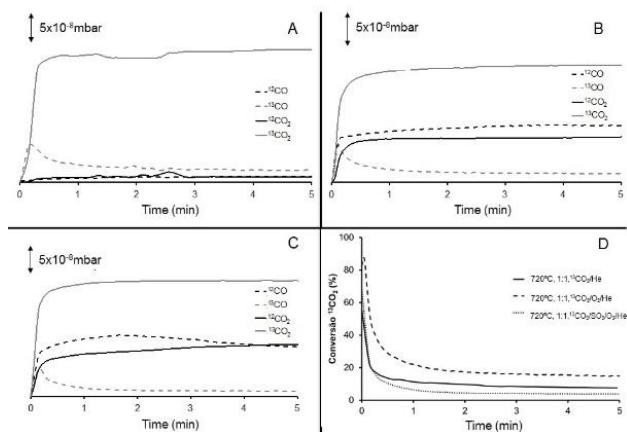


Figure 3.7 ¹²CO, ¹³CO, ¹²CO₂ and ¹³CO₂ profiles for the Reverse-Boudouard reaction of DX coke deposited on the Li-V/Al₂O₃:USHY with ¹³CO₂(1.9%)/ He (A), ¹³CO₂(1.9%)/ O₂(0.8%)/ He (B) e ¹³CO₂(1.9%)/ O₂(0.8%)/ SO₂(0.2%)/ He (C). (D) represent ¹³CO₂ conversion over catalysts as function of reaction time.

In the presence of ¹³CO₂(1.9%)/ O₂(0.8%)/ He, 7wt% of ¹³CO₂ was converted (3 percentage points below similar atmosphere without oxygen). It was in agreement with the literature because the oxygen activity while oxidizing agent is one hundred times

higher than CO₂, meaning that the O₂ presence was not affect RB reaction. Li-V/Al₂O₃ catalyst was even established that the reaction is essentially zero-order in relation to oxygen partial pressure.

Table 3.3 Average conversion CO/CO₂ ratio corresponding to testing isotopically labeled atmospheres, 720°C and constant additive:zeolite (1:1).

| Atmosphere | T (°C) | Average Conversion (%) | CO/CO ₂ |
|--|--------|------------------------|--------------------|
| ¹³ CO ₂ /He | 720 | 11.4 | 1.4 |
| ¹³ CO ₂ /O ₂ /He | 720 | 10.6 | 2.3 |
| ¹³ CO ₂ /O ₂ /SO ₂ /He | 720 | 9.8 | 1.4 |

Observing the ¹³CO₂(1.9%)/ O₂(0.8%)/ SO₂(0.2%)/ He obtained profile, it was found that the average conversion is even lower, 6wt% compared analysis with the first. However it is to safeguard that CO₂/SO₂, equal to 9.5, is much higher than the expected values for the regeneration process under study, approximately thirty, meaning that in this case the average conversion was less affected in the presence of SO₂, which is reinforced by the results in the table below. The sulfur dioxide, representative compounds of the SOx is processed from the crude oil refinery varying depending its source.

3.5.2 Temperature modification

At Catalytic performance with heating ramp in 10% CO₂/He, it was noted that CO varied with the temperature (680, 720, 760 and 800 °C).

Table 3.4 Average conversion CO/CO₂ ratio corresponding to testing isotopically labeled atmospheres, additive:zeolite constant (1:1) and variable temperature (680 - 800 °C).

| Atmosphere | T (°C) | Average Conversion (%) | CO/CO ₂ |
|--|--------|------------------------|--------------------|
| ¹³ CO ₂ /He | 680 | 7.1 | 1.1 |
| | 720 | 11.4 | 1.4 |
| | 760 | 20.3 | 1.8 |
| | 800 | 26.6 | 3.2 |
| ¹³ CO ₂ /O ₂ /He | 680 | 4.2 | 1.1 |
| | 720 | 10.6 | 2.3 |
| | 760 | 15.0* | 1.9* |
| | 800 | 28.4 | 4.2 |
| ¹³ CO ₂ /O ₂ /SO ₂ /He | 680 | 3.9 | 2.5 |
| | 720 | 9.8 | 1.4 |
| | 760 | 11.2 | 1.8 |
| | 800 | 26.1 | 1.1 |

* Probably there was air in system.

The labeled tests at fixed temperature (680, 720, 760 and 800 °C) showed increased ¹³CO₂ average conversion with temperature, at all of atmospheres analyzed. Less pronounced variations were observed between 760 and 800 °C.

3.5.3 Ratio modification

At 720 °C, for each of the atmospheres under study, the ¹³CO₂ conversion was decreased between 1:1 and 0.05 additive parts to 1 zeolite part.

Table 3.5 Average conversion CO/CO₂ ratio corresponding to testing isotopically labeled atmospheres, 720°C and variable additive:zeolite.

| Atmosphere | Ratio | Average Conversion (%) | CO/CO ₂ |
|--|--------|------------------------|--------------------|
| ¹³ CO ₂ /He | 1.1 | 11.4 | 1.4 |
| | 0.20:1 | 4.3 | 1.5 |
| | 0.05:1 | 2.0 | 1.7 |
| ¹³ CO ₂ /O ₂ /He | 1.1 | 10.6 | 2.3 |
| | 0.20:1 | 5.1 | 3.9 |
| | 0.05:1 | 4.6 | 4.2 |
| ¹³ CO ₂ /O ₂ /SO ₂ /He | 1.1 | 9.8 | 1.4 |
| | 0.20:1 | 3.3 | 2.2 |
| | 0.05:1 | 1.4 | 3.6 |

3.6 DeSOx Mechanism

It was performed SOx removal tests in the presence of CO₂ in modified alumina (Li-V/Al₂O₃) with and without coke. The ultimate objective is to evaluate the lithium - vanadium - Alumina as a multiadditive for FCC process which would promote the reaction RB and removal of SOx at same time. The profile of the thermogravimetric analysis was divided into four steps:

- 1st. Weight loss by pretreating in helium for 30 min;
- 2nd. Mass gain by capturing SO₂ at 725 °C;
- 3rd. Weight loss in the transition stages (in helium);
- 4th. Weight loss to reduce the H₂S.

As expected, the deposition of coke on the catalyst surface considerably reduces the SO₂ capture step, which occurs in the regenerator. Regarding to the presence of CO₂ was not observed an important modification of weight percent. CO₂ introduction into FCC regenerator does not affect DeSOx mechanism. Coke presence affected Li-V/Al₂O₃ made, particularly on SO₂ capture step.

Table 3.4 Results of the thermogravimetric analysis of DeSOx tests for the catalyst Li-V/Al₂O₃ with and without DX coke supported on the surface.

| | Atmosphere | 1 st (wt%) | 2 nd (wt%) | 3 rd (wt%) | 4 th (wt%) |
|---|--|--------------------------|--------------------------|--------------------------|--------------------------|
| Li-V/Al ₂ O ₃ | SO ₂ /O ₂ /He | -5.1 | 8.6 | -8.7 | -0.4 |
| | SO ₂ /O ₂ /CO ₂ /He | -5.8 | 8.1 | -8.3 | 0 |
| Li-V/Al ₂ O ₃ ^{DX} | SO ₂ /O ₂ /He | -7.0 | 4.6 | -8.1 | -0.4 |
| | SO ₂ /O ₂ /CO ₂ /He | -11.6 | 7.9 | -7.2 | -1.0 |

4. Conclusion

Vanadium-lithium-alumina catalyst is an efficient additive for performing the regeneration of a spent catalyst under FCC conditions in CO₂ rich atmosphere regardless the presence of O₂. Moreover RB reaction seems to be less affected by the type of coke on this catalyst.

RB reaction was favoured in an ensemble containing vanadium-lithium-alumina and coke. It proceeded by forming CO and oxygenated species in the coke, that is followed by CO formation and CO₂ that sequentially reacts producing more CO, increased by the CO/CO₂ ratio, largely. Moreover oxygen undergoes mobility between additive and spent USHY improving its regeneration. The additive effect was considered efficient up to 0.10 part of additive to 1 parts of USHY.

Account an industrial application of the process was analyzed the effect of SO₂ introducing for the RB reaction through isotopically labelled tests (¹³CO₂). The presence of sulfur compounds in the coke affects only slightly the performance of the reaction RB. Finally, by DeSOx tests, it was observed that the SOx removal was not affected with CO₂ presence.

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