# Study of promoters to Reverse Boudouard reaction under regeneration step conditions of FCC process

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**ABSTRACT**

The fluid cracking catalytic process (FCC) contributes with about 30% of the total $CO_2$ emissions in a refinery. The possibility to react $CO_2$ and coke (Reverse Boudouard reaction) during the spent catalyst regeneration using a rich atmosphere in $CO_2$ and $O_2$, instead of air, can mitigate $CO_2$ emissions and, simultaneously, produce CO for sequential uses. In this work, alumina catalysts modified by both alkali and alkaline earth metals in presence or not of vanadium were prepared, with the purpose of finding promoters for this reaction.

Therefore, it was shown that this goal was achieved by an alumina catalyst modified with lithium and vanadium under normal regeneration temperatures, i.e. in the range of 690 to 720ºC, with the best efficiency among all catalysts, verifying a great synergy between lithium and vanadium. This synergy is noticed by comparing the values of average conversion during the first five minutes of reaction in $^{13}CO_2/O_2/He$ atmosphere of $Li-V/Al_2O_3$ and $Li/Al_2O_3$. At 720ºC, the first catalyst attained a value of 39% while the second attained only 6%. The first formed product was $^{13}CO$, followed by $^{12}CO$ and then by $^{12}CO_2$. The $^{12}CO$ was formed by both RB reaction and by burning the coke with $O_2$. Considering the amount of coke produced in FCC units, we notice that this process could be performed in a $CO_2/O_2$ atmosphere.

Keywords: $CO_2$, FCC, Coke, Vanadium, Lithium, Reverse Boudouard reaction
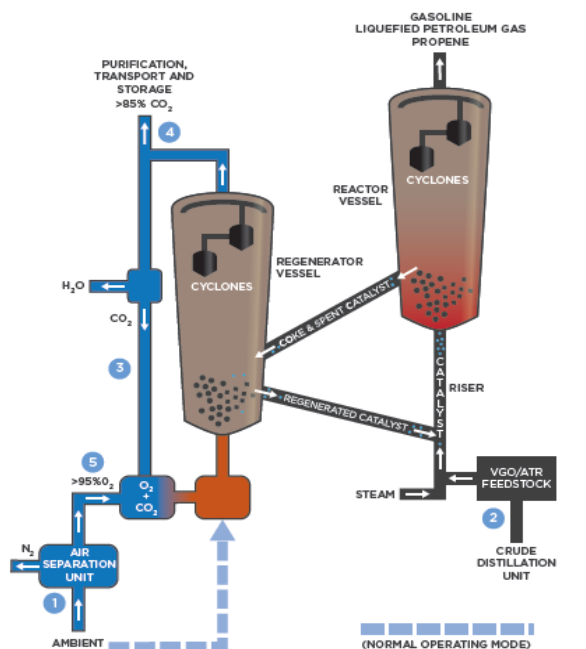
## 1. Introduction

The industry quick development in the second half of the twentieth century led to a serious decline of planet's ecological situation. A major problem has been the combustion of hydrocarbons, which during the last few decades caused a significant increase of carbon dioxide in atmosphere, it's the main greenhouse gas. Currently, less than 1% of total $CO_2$ production by anthropogenic sources is recycled [1] and the concentration of this gas is about 400 ppm. Although there are measures to reduce $CO_2$ emissions, it is estimated that, if there is no additional effort by the major emitting countries, this situation will become worse [2]. This makes the study of new technologies to reduce $CO_2$ emissions increasingly important.

The Fluid Catalytic Cracking (FCC) is one of the most important processes in a refinery and its objective is converting vacuum gasoil from atmospheric or vacuum distillation in high added value products, such as gasoline. The process consists mainly of three steps: reaction, separation, and catalyst regeneration. In the reaction step, there is the formation of coke (6-

10%) [3] in the catalyst being related to the processed load quality, i.e., lower quality results in larger quantity of coke formed. This coke leads to catalyst deactivation. However, it is easily regenerated from combustion reactions, releasing large quantities of pollutants, mainly carbon dioxide. It is estimated that this process is responsible for about 15-30% of the total carbon dioxide emissions in a refinery. Because of the need to restrict emissions of this gas various studies have been carried, especially in FCC catalyst regeneration step. Recently it was proposed to use pure oxygen instead of air ("oxy-firing process"), where it is mixed with recycled $CO_2$ from flue gases and this reaction mixture is used in the regeneration stage of the FCC catalysts [4]. This strategy would enable the transformation of $CO_2$ to CO, which can subsequently be converted into various products, such as hydrogen by water-gas shift reactions, methanol, dimethyl ether or hydrocarbons as well, significantly reducing the $CO_2$ emissions from those FCC units. The project is showed in Figure 1.

The reaction between $CO_2$ and coke, known as

for this work. The global RB reaction: $C+CO_2 \rightarrow 2CO$, is very endothermic, between 160 to 200 $kJ.mol^{-1}$, however the partial reaction (Scheme 1a) is slightly exothermic or endothermic [5] [6]. In this reaction, in addition to CO are formed species of oxidized coke (coke-O). This oxidized coke will be decomposed and lead to the formation of CO and $CO_2$, Scheme 1b, though, this reaction is very endothermic, since it involves the decomposition of functional groups formed on the surface of the oxidized coke [5]. Consequently for this process the use of $O_2$ is required to cause the decomposition of these groups. The oxidized coke burning with $O_2$, represented by the Scheme 1c, will provide the necessary energy, since this is a very exothermic reaction [7].

Scheme 1a: $CO_2$ + coke → CO + coke-O
Scheme 1b: Coke-O → $CO/CO_2$
Scheme 1c: Coke-O + O2 → $CO/CO_2$
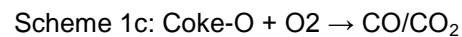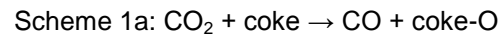
**Scheme 1.** Reaction steps in FCC catalyst regeneration in an atmosphere rich in $CO_2$ and $O_2$.

Following this idea, M. Pereira and collaborators [1] [8] [9] proposed that the regeneration stage of the FCC catalyst may be divided into two regeneration steps to a better performance of the reaction RB, according to Figure 2.
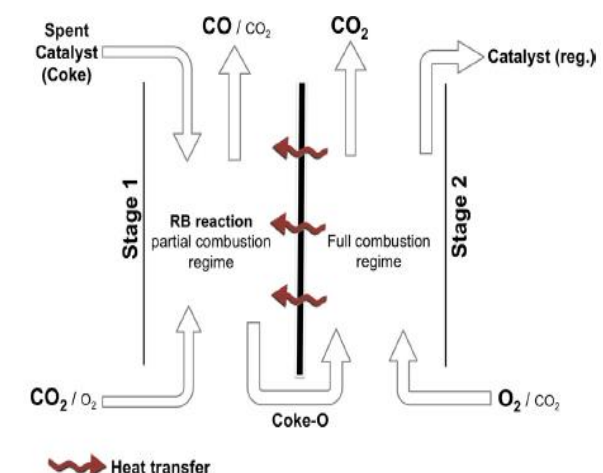


Reverse Boudouard reaction (RB) serves study

Figure 1. Simplified diagram of an FCC unit using pure O2 instead of air in the regeneration reactor [4].



Figure 2. Two stage FCC regeneration with diathermic wall [9].

Several studies have been done to promote the reaction between coke and $CO_2$ [10] [11]. Group I and II elements are excellent promoters for this reaction, for taking into account the acidity of the $CO_2$ molecule and the basicity of these metals, they are able to create basic sites on alumina for carbon dioxide adsorption thereby promoting their reaction with the coke. As regards the vanadium, it is widely used as a catalyst for oxidative dehydrogenation reactions in the presence of $O_2$ and $CO_2$. The mobility along the constituents of the catalyst can be used in favor of RB reaction, since the catalyst can be formed *in-situ* during the regeneration of the spent catalyst. Herein, we explore the RB reaction over alumina modified by alkali (Li, Na, K) and alkaline-earth (Mg, Ca, Ba) metals, with and without vanadium [12].

## 2. Experimental

### 2.1. Catalyst preparation

#### 2.1.1. Support preparation

The precursor alumina exhibited the boehmite structure, according to X-ray diffraction pattern (JCPDS 74-1895).

The preparation of modified alumina was carried out by performing a physical mixture of alumina and aqueous solution of chlorides salts of lithium, sodium, potassium, magnesium, calcium and barium. The amount of group I and II chloride salts in the mixture was determined to obtain a 5 wt.% final mixture in alumina. After drying, the modified support was obtained by the calcination at 800°C for 20 hours in air with a heating rate of 5°C/min. The catalysts were named as $Li/Al_2O_3$, $Na/Al_2O_3$, $K/Al_2O_3$, $Mg/Al_2O_3$, $Ca/Al_2O_3$ and $Ba/Al_2O_3$. Additionally, a pure alumina sample was prepared to use as comparison.

#### 2.1.2. Vanadium addition

Vanadium was introduced by incipient wetness impregnation using an aqueous solution of vanadyl acetylacetonate ($VO(C_5H_7O_2)_2$, 95%, Aldrich). The supports already impregnated by group I and II metals were placed in contact with the aqueous solution of vanadium precursor in a rotary evaporator at 60ºC under reduced pressure for 2 hours. Finally, drying was carried out in an oven at 120°C for a period of approximately 12 hours. After drying, the samples were calcined at 600°C for 3 hours with a heating rate of 5°C/min. The catalyst preparation was performed to set up a loading of 1 wt.% of vanadium on all supports and the catalyst were named as $V/Al_2O_3$, $Li$-$V/Al_2O_3$, $Na$-$V/Al_2O_3$, $K$-$V/Al_2O_3$, $Mg$-$V/Al_2O_3$, $Ca$-$V/Al_2O_3$ and $Ba$-$V/Al_2O_3$.

#### 2.1.3. Catalyst coking

For coke formation, the prepared catalysts were impregnated with vacuum gas oil (VGO) at a proportion catalyst/VGO of 2:1. In order to facilitate the dissolution of VGO was used n-hexane (99%, Vetec) as solvent. The coking was carried out in a quartz reactor under nitrogen flow of 60 mL/min. The reactor was introduced into a preheated oven at 530°C and the reaction occurred during 15 minutes.

#### 2.1.4. Catalyst characterization

The textural characterization was carried out by nitrogen adsorption on an ASAP 2020 Micromeritics analyzer. The implementation of this technique involved a step where gas was removed from the samples at a temperature of 220°C for 4 hours. The specific surface area was determined through the BET (Brunauer-Emmett-Teller) method and pore volume and pore diameter distribution were calculated form the $N_2$ adsorption curve using the BJH (Barrett-Joyner-Halenda) method.

The X-ray diffraction (XRD) patterns were obtained using a Rigaku Ultima IV diffractometer. This equipment uses CuK radiation (1.542 Å), voltage 40 kV and 20 mA current. The measurements were performed according to a variation of the angle 2θ

Table 1. Catalysts textural properties. Metal and coke amount.

| Catalysts | Metal (wt.%) | $S_{BET}$ (m²/g) | Coke (wt.%) | Catalysts | Metal (wt.%) | $S_{BET}$ (m²/g) | Coke (wt.%) |
|---|---|---|---|---|---|---|---|
| $Al_2O_3$ | - | 127 | 3,0 | $V/Al_2O_3$ | nd | 122 | 7,0 |
| $Li/Al_2O_3$ | 1,5 | 48 | 1,9 | $Li-V/Al_2O_3$ | 1,7 (Li) 0,9 (V) | 46 | 3,9 |
| $Na/Al_2O_3$ | 2,5 | 131 | 2,3 | $Na-V/Al_2O_3$ | 2,7 (Na) 0,9 (V) | 134 | 5,1 |
| $K/Al_2O_3$ | nd | 149 | 2,6 | $K-V/Al_2O_3$ | nd | 148 | 5,4 |
| $Mg/Al_2O_3$ | 1,8 | 110 | 6,0 | $Mg-V/Al_2O_3$ | 1,6 (Mg) 0,9 (V) | 112 | 5,4 |
| $Ca/Al_2O_3$ | 3,7 | 104 | 4,1 | $Ca-V/Al_2O_3$ | 3,2 (Ca) 0,8 (V) | 105 | 5,5 |
| $Ba/Al_2O_3$ | nd | 138 | 3,0 | $Ba-V/Al_2O_3$ | nd | 134 | 6,0 |

between 5° and 80° using a 0.02° step with a 10°/s.

Inductively coupled plasma/optical emission spectrometry (ICP-OES) was used to determinate the global composition of group I and II elements, as well as the vanadium in catalysts. This technique was held in an external laboratory. Lithium and vanadium surface amount was determined by X-ray photoelectron spectroscopy (XPS) in order to compare with the ICP results and try to conclude the lithium and vanadium location in the catalyst. The XPS technique was performed in a ThermoScientific Escalab model 250 XI equipment with monochromatic AlKα X-ray with a pressure of approximately $1 \times 10^{-9}$ mbar.

The amount of coke in the spent catalysts was determined through thermogravimetric analysis in a Netzsch TG-IRIS equipment. Initially, the sample was heated under a $N_2$ flow from 35°C to 250°C with a heating rate of 10°C/min and the temperature was maintained at 250°C for 30 min. After this time, the sample was heated to 700ºC under a synthetic air flow, and then the temperature was maintained at 700°C for another 30 min.

### 2.3. Catalyst regeneration

The regeneration of spent catalysts was studied by various catalytic tests under different atmospheres. In all cases the formed gases were monitored by a Mass Spectrometer.

However, the amount of alkali or alkaline earth metal presents values lower than expected, but

The first catalytic tests were performed under three different atmospheres (pure He, 5%$O_2$/He, 10%$CO_2$/He) and are important to evaluate the performance of the catalysts and thus conclude what will be the best catalyst for promoting RB reaction. Initially, the sample was heating from 25ºC to 1000ºC at a heating rate of 10ºC/min under flow of 60 mL/min in those three different atmospheres.

Afterwards, tests were conducted in an atmosphere of $^{13}CO_2$(1.9%)/He and $^{13}CO_2$ (1.9%)/$O_2$(0.8%)/He in order to differentiate the RB reaction products in the regeneration step of the catalyst. These have only been performed for catalysts that have obtained a better performance in the initial tests. In this second test, the spent catalysts were heated from 25ºC to the reaction temperatures (690, 720, 760 and 800ºC) at a heating rate of 10ºC/min under a He flow of 60 mL/min. Reaching the desired temperature, the atmosphere is changed to start the reaction which took place during 5 min. In this step, it was used a flow of 30 mL/min.

## 3. Results and discussion

### 3.1. Catalyst characterization

Textural properties and metal and coke amount of all used catalysts are presented in Table 1.

The amount of vanadium in all catalysts are within the expected range, i.e., about 1 wt.%. this can be explained by the high time (20 hours) in the calcination step, and also by the used

temperature, 800°C. This temperature is higher than the melting point of the promoters salts [13].

BET surface area is similar for all the catalysts except for lithium catalysts. The results suggest that there was a change in the alumina structure when modified with lithium. Some catalysts have a BET surface area higher than the support, which may be indicative that alumina without metal addition has transited to another crystalline phase. All catalysts showed a type IV isotherm profile, which are characteristic of mesoporous adsorbents.

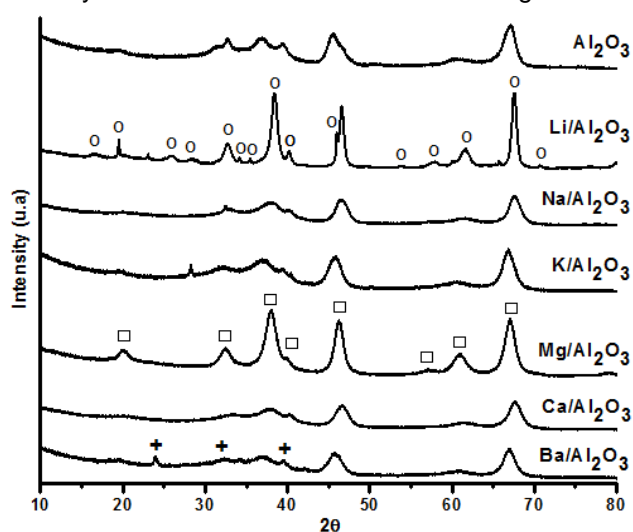XRD diffraction patterns of support and all catalyst without vanadium are shown in Figure 3.



Figure 3. XRD diffraction patterns of support and all catalysts without vanadium. (O-LiAl$_5$O$_8$, □- MgAl$_2$O$_4$, +- BaCl$_2$).

The catalyst Li/Al$_2$O$_3$ showed the formation of the LiAl$_5$O$_8$ compound during calcination (appropriately identified in Figure 3) and this compound adopts a spinel type structure. In the XRD diffractogram of the catalyst Mg/Al$_2$O$_3$ was observed the presence of MgAl$_2$O$_4$ compound, also known as spinel. To Ba/Al$_2$O$_3$ peaks at angles 23°, 33° and 39° are respective to the metal precursor salt, BaCl$_2$. Compared with the diffractogram of pure alumina, which has a mixture of γ and δ-phase, the Na/Al$_2$O$_3$, K/Al$_2$O$_3$, Ca/Al$_2$O$_3$ and Ba/Al$_2$O$_3$ present only the γ phase of alumina. This phenomenon is due to the alkali

and alkaline-earth metals, which enhance stability of the alumina against phase transition and loss of specific surface area [14] [15]. Because of this, the alumina does not turn into the δ phase.

XRD diffraction patterns of catalyst with vanadium are quite similar, however, by adding vanadium to Ba/Al$_2$O$_3$ caused the characteristic BaCl$_2$ salt diffraction peaks disappearance [16].

XPS was carried out for Li/Al$_2$O$_3$, Li-V/Al$_2$O$_3$ and V/Al$_2$O$_3$ catalysts. V/Li ratio measured by XPS in Li-V/Al$_2$O$_3$ catalyst was 0,03 while the same ratio based on ICP results was 0,5. Thus, it is possible to conclude that only a small portion of vanadium was in surface.

The amount of coke determined by thermogravimetric analysis showed that the catalysts with vanadium form more coke, except for the catalyst modified by magnesium. The alumina catalysts modified with lithium are those with a smaller amount of coke. This can be explained by the fact that those catalysts present a smaller area. Thus, in general, a smaller area implies a reduction in active sites of the alumina and hence a lower coke formation.

## 3.2. Coke characterization

The tests under pure He, allowed to investigate the nature of coke by thermal desorption, and by analyzing the CO and CO$_2$ formation profiles. For catalysts without vanadium, the CO profiles are very similar to the support profile, with a peak appearance in a temperature range of 800 to 875°C. The profiles for catalysts with vanadium are identical to V/Al$_2$O$_3$, where they exhibit a first peak in a temperature range of 773 to 840°C and a second between 890 and 990°C. These peaks are in a temperature range of highly stable compounds, such as carboxylic compounds and quinones [17]. The CO$_2$ profile for catalysts without vanadium begins to form between 450°C and 850°C, and presents two peaks at 595°C and 755°C. Those peaks are related to decomposition of lactones. For catalysts with vanadium the profiles begins to form at about 265°C to 760°C
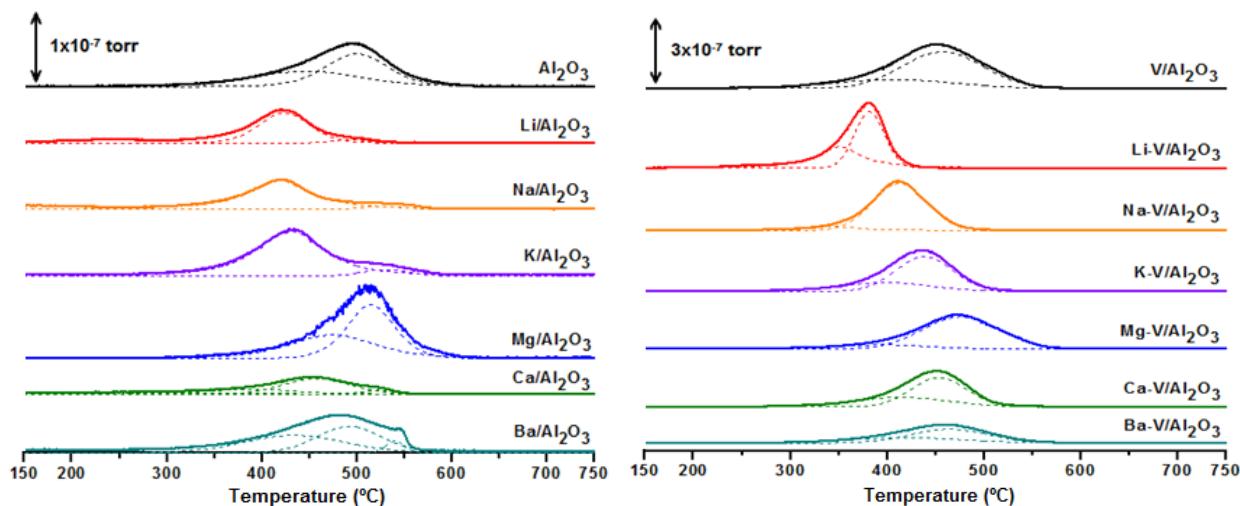
Figure 4. $CO_2$ profiles and $CO_2$ profiles deconvolution (dotted) for support and all spent catalysts in a 5%$O_2$/He atmosphere.

with a single peak at 616ºC, which is also related to lactones. Also, the catalysts modified by lithium, sodium and calcium and with or without vanadium have a first peak at a temperature range of 175 at 250ºC. This may be related to adsorption on metal sites.

### 3.3. Spent catalyst regeneration

### 3.3.1. Regeneration in $O_2$/He atmosphere

The $CO_2$ profiles during the regeneration of spent catalyst in 5%$O_2$/He atmosphere are shown in Figure 4. Notice that CO profiles are quite similar to $CO_2$ profiles, and they are not showed. In all spent catalysts, the $CO_2$ profile was composed by different peaks. On alumina modified by alkali metals the $CO_2$ formation occurred at lower temperatures than pure alumina and catalyst with alkaline-earth metals.

However, when vanadium is added it is clearly seen that $CO_2$ formation is promoted because it occurs at lower temperatures. For instance, Li-V/$Al_2O_3$ catalyst, which is the one that presents a lower temperature for $CO_2$ formation had a reduction of this temperature by approximately 40°C when compared to Li/$Al_2O_3$, and it indicates that Li-V/$Al_2O_3$ is a powerful oxidation catalyst.

### 3.3.2. Regeneration in $CO_2$/He atmosphere

The CO profiles during the regeneration of spent catalysts in 10%$CO_2$/He atmosphere are shown in Figure 5. Notice that for pure alumina and Mg/$Al_2O_3$ catalyst are the only where the CO is still being formed when the temperature reaches 1000°C. On all others catalysts the CO formation occurs at lower temperatures and exhibit three main CO formation peaks. For alkali metals the first peak appears at 730-750ºC, the second at 780-820ºC and the third at 840-870ºC. For alkaline-earth metals, except Mg/$Al_2O_3$ the first peak occurs at 780-800ºC, the second around 850ºC and the third around 890ºC.

However, on catalysts modified with vanadium it is possible to observe the effect of vanadium, which favors CO formation at temperatures below those observed in catalysts without the addition of this metal, shifting the profiles for lower temperatures. Just like for catalysts without vanadium, CO formation exhibit three peaks. For alkali metals the first peak appears at 725-740ºC, the second at 775-810ºC and the third at 810-850ºC. For alkaline-earth metals, except Mg/$Al_2O_3$ the first peak occurs at 725-760ºC, the second around 815ºC and the third around 865ºC.
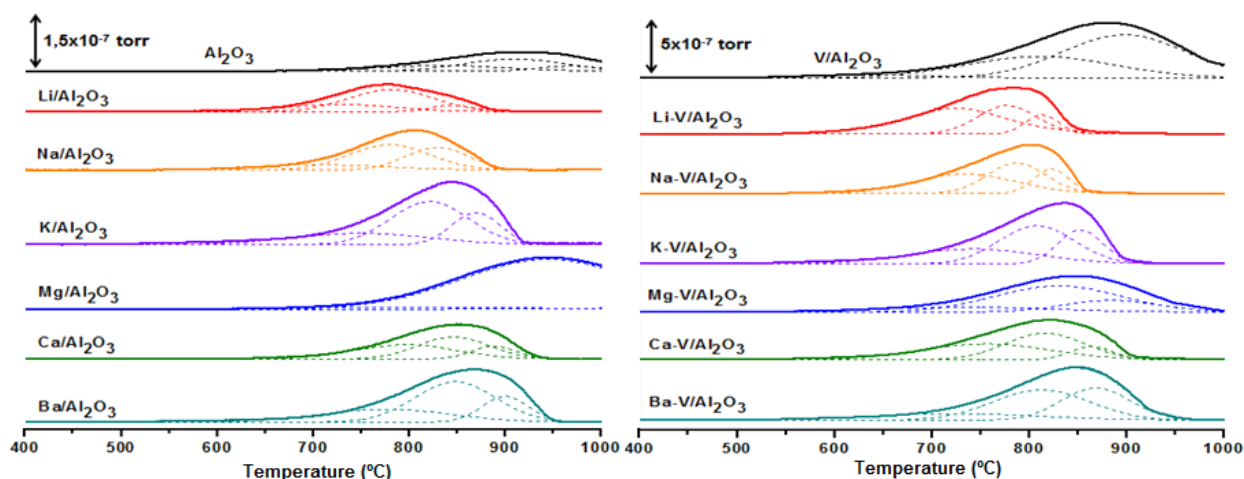
Figure 5. CO profiles and CO profiles deconvolution (dotted) for support and all spent catalysts in a 10%CO2/He atmosphere.

From these results, it is clear that the catalysts modified with alkali metal reaction promoters are better than those modified with alkaline earth metals, and the catalyst $Li-V/Al_2O_3$ is what provides the best results. This is because it is the catalyst whose profile is shifted to lower temperatures, with a maximum peak of 778ºC, thus enabling temperatures close to the catalyst regeneration step of FCC process. So this should be the best catalyst for promoting reverse Boudouard reaction.

### 3.3.3. Reverse Boudouard reaction

For a detailed study of reverse Boudouard reaction, this reaction was carried out at four different temperatures (690, 720, 760 and 800ºC) using $^{13}CO_2/O_2/He$ and $^{13}CO_2/He$.

The conversion during the first five minutes of reaction and conversion results of the average catalyst modified with lithium and vanadium are presented in Figure 6 and Table 2, respectively.

The $^{13}CO_2$ conversion was estimated by the total amount of $^{13}CO$ formed, i.e., using the following equation: $^{13}CO/(^{13}CO+^{13}CO_2)$.

Comparing 1B and 2B profiles it is possible to observe the pronounced effect of synergy between lithium and vanadium, which results in an average conversion of 33% to $Li-V/Al_2O_3$ and only 6% to $Li/Al_2O_3$.
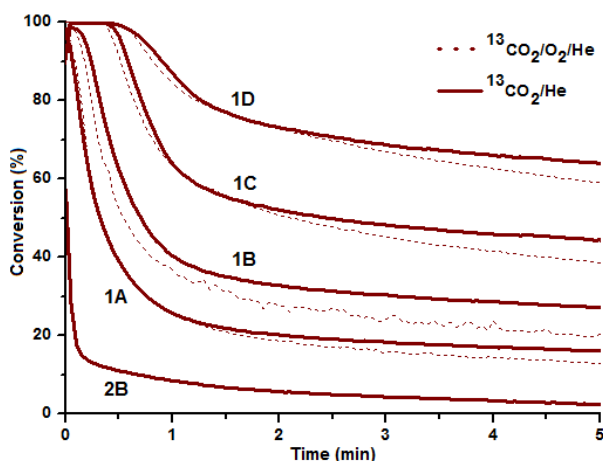


Figure 6. $^{13}CO_2$ conversion into $^{13}CO$ using $^{13}CO_2/O_2/He$ (dotted) and $^{13}CO_2/He$ (continuous) atmospheres for two catalysts: 1-$Li-V/Al_2O_3$ and 2-$Li/Al_2O_3$ and to four temperatures: A-690ºC, B-720ºC, C-760ºC and D-800ºC.

Table 2. Average conversions for RB reaction of $Li/Al_2O_3$ and $Li-V/Al_2O_3$ catalysts.

| Catalyst | T (ºC) | Atmosphere | Average conversion (%) |
|---|---|---|---|
| $Li/Al_2O_3$ | 720 | $^{13}CO_2/O_2/He$ | 6 |
| Li-V/Al_2O_3 | 690 | $^{13}CO_2/O_2/He$ | 23 |
| | 690 | $^{13}CO_2/He$ | 25 |
| | 720 | $^{13}CO_2/O_2/He$ | 33 |
| | 720 | $^{13}CO_2/He$ | 39 |
| | 760 | $^{13}CO_2/O_2/He$ | 55 |
| | 760 | $^{13}CO_2/He$ | 58 |
| | 800 | $^{13}CO_2/O_2/He$ | 74 |
| | 800 | $^{13}CO_2/He$ | 76 |

Actually, the catalyst $Li-V/Al_2O_3$ is very effective in promoting the reaction of $CO_2$ with coke in both atmospheres. But the important fact is that the $CO_2$ conversion is poorly affected by the presence of $O_2$, since the continuous and dotted profiles are quite similar.

Furthermore, the results suggest that those profiles are relatively closer with increasing of temperature, by comparing the results of the 1B and 1D profile. Another important point is the behavior of $CO_2$ conversion throughout the reaction time. At temperatures up to 720ºC, conversion decreases rapidly at low reaction times. The reduction of the initial activity is less obvious for higher temperatures (800ºC). On the other hand, nowadays, the FCC units can't work



Figure 7. $^{12}CO$, $^{13}CO$, $^{12}CO_2$ and $^{13}CO_2$ profiles for RB reaction using an atmosphere of $^{13}CO_2/O_2/He$ for the catalyst of $Li-V/Al_2O_3$ at a temperature of 760°C.



Figure 8. $^{12}CO$ profiles for the catalyst of $Li-V/Al_2O_3$ in the first 5 minutes of reaction using an atmosphere of $^{13}CO_2/O_2$ and $^{13}CO_2/O_2/He$.

at this temperature range (800ºC), but in the future, units can be designed and catalysts can operate in these conditions. However, in normal regeneration temperature (720ºC), the catalyst is also effective.

To illustrate the products of RB reaction in the $Li-V/Al_2O_3$ catalyst, the profiles $^{12}CO$, $^{13}CO$, $^{12}CO_2$ and $^{13}CO_2$ at temperature to 760°C and $^{13}CO_2/O_2/He$ atmosphere are shown in Figure 7.

The results showed that $^{13}CO$ is the primary reaction product, followed by $^{12}CO$. After a short delay (in the case of the catalyst $Li/Al_2O_3$ this delay is not so evident) appears the $^{12}CO_2$ and simultaneously the concentration of $^{13}CO_2$, the latter product, due to a decreased reaction with coke, i.e., the $^{13}CO_2$ not converted.

To distinguish the effect of oxygen with carbon dioxide, the $^{12}CO$ formation profiles are presented in Figure 8, for two temperatures, 760°C and 720ºC and for $^{13}CO_2/O_2/He$ and $^{13}CO_2/He$ atmospheres. It was concluded that the $^{12}CO$ formation is higher in the atmosphere containing oxygen, as expected, but also is formed a considerable amount of this product in the reaction of coke with $^{13}CO_2$ without the presence of oxygen. This result indicated that the catalyst can promote the activation of $CO_2$ in the presence of $O_2$. The difference between the $^{12}CO$ profiles suggests that part of CO was originated in the reaction of the coke with the $^{13}CO_2$, so, both oxidizers contribute to $^{12}CO$ selectivity.

Taking into account the results of the reactions for $Li-V/Al_2O_3$ catalyst it is possible to suggest a reaction mechanism. First, there is the activation of $CO_2$. XPS results indicated that only a small amount of vanadium is in the surface, so, it is suggested that $CO_2$ is activated near vanadium, and of course, near the coke and lithium. In the reaction between $CO_2$ and coke is formed $^{13}CO$ and species of oxidized coke (coke-O), as presented by Scheme 1a. This oxidized coke could release surface mobility oxygen that form $^{12}CO$ or may react with oxidized coke to form $^{12}CO_2$. The second formation of $CO/CO_2$ (Scheme 1b) is very endothermic, since it involves the decomposition of the functional groups of coke
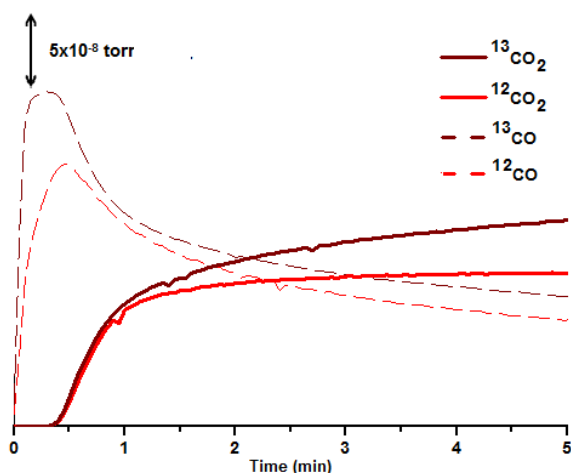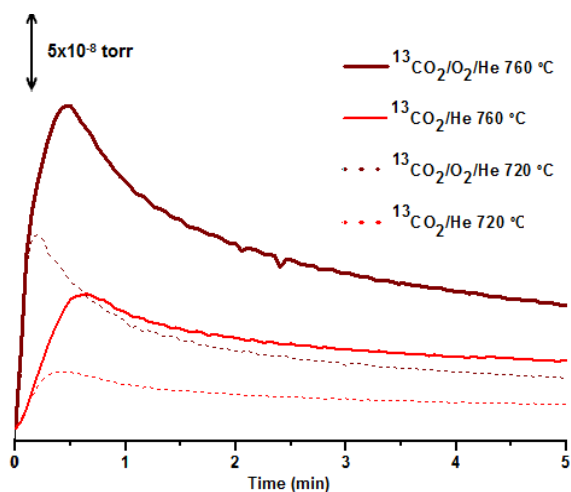
surface. However, the reaction between $O_2$ and oxidized coke is very exothermic, (Scheme 1c) thus, providing the energy necessary for the decomposition of the functional groups. Therefore, in terms of a real case the amount of CO produced could be controlled by the ratio between the amount of additive and catalyst and by the composition of the $CO_2/O_2$ atmosphere admitted to the reactor, making it possible to maintain the unit under stable thermal conditions.

## 4. Conclusions

The RB reaction could be performed in $CO_2/O_2$ atmosphere and under FCC regeneration conditions. This approach can largely contribute to $CO_2$ emissions reduction on these units. Alumina modified by groups I and II elements could be used to attain this goal, particularly when modified by both vanadium and lithium. These two metals showed a synergism that largely favored the $CO_2$ and coke reaction. This synergism is observed by comparing $^{13}CO_2$ conversion profiles of Li-V/Al$_2$O$_3$ and Li/Al$_2$O$_3$, which results in a 33% average conversion for Li-V/Al$_2$O$_3$ and 6% to Li/Al$_2$O$_3$. It was also concluded that the first product observed for these reactions was $^{13}CO$ followed by $^{12}CO$, and then the $^{12}CO_2$. The formation of $^{12}CO_2$ is being disadvantaged at higher temperature in comparison to CO formation.

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