Coke steam reforming in FCC regenerator: A new mastery over high coking feeds

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ABSTRACT

One of the crucial problems of processing residual feeds in the FCC is their high coking tendency, which limits their use in the FCC and requires them to be mixed with lighter feeds to be processed in conventional FCC units. A step-out improvement of the FCC process to use in processing heavy feeds is presented, where the heat balance in the unit is maintained by removing the high coke-on-catalyst by a combination of coke combustion and reforming, i.e., coke steam reforming (CSR) in the regenerator. This option enables using feeds with more than 10% Conradson Carbon while still maintaining the possibility to control the heat balance in the unit without using partial combustion or catalyst coolers. Although the Equilibrium catalyst has little CSR activity, we have found that hydrotalcite materials, besides having an excellent catalytic cracking selectivity for heavy feeds, also have significant CSR activity. We have demonstrated that CSR can be performed together with combustion at conditions found in the FCC regenerator so that the regenerator temperature remains within traditional limits despite higher coke-on-catalyst, and the coke on the catalyst is nearly completely removed. While the reaction rate at higher temperatures seems to obey first order, steam reforming coke removal kinetics at lower (750 °C) temperatures seem more complex due to the heterogeneous nature of coke.

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1. Introduction

The upgrading of low value, high boiling point fractions of crude oil into lower boiling point hydrocarbons, which can be used in the production of higher value fuels such as gasoline, diesel and kerosene, is an important aspect of crude oil refining. Therefore, a number of hydrocarbon coking and cracking processes have been developed in order to achieve this aim [1]. Such processes are becoming increasingly important in the exploitation of heavy crude oil sources, such as tar sands and shale oils, and also in processing heavy crudes that are extracted from mature and declining oil wells. Heavy crude oils usually carry more contaminants than regular crude oils, resulting in a decrease over the years of the quality of the feedstocks that are processed in FCC [1–3]. Processing of such feeds will require new cracking catalysts containing zeolites with larger pores with smaller crystallites or even zeolite free catalysts. Recent publications have shown existing methodologies that pave the way towards "Ab initio" design and synthesis of new zeolites structures [4–7]. The authors use their own work and sometimes pioneering work on computational design of zeolite frameworks [6,7] together with the synthesis, guided by organic structure directing agents and the support of high throughput techniques to draw the map towards the synthesis of zeolites. In particular, these heavy

feedstocks have a larger amount of Conradson Carbon, which leads to higher coke yields during the cracking process [8–10]. A certain amount of coke is necessary in the FCC process to maintain the unit heat balance and temperature since the combustion of coke gives the heat necessary to vaporize the feed and compensate for the endothermic heat of reaction. The system self-regulates by adjusting the catalyst circulation rate in the unit (heat transferred to the reaction side from regeneration) which in turn influences the feed conversion (heat demand) and then coke yield [11]. Yet with feeds with high Conradson Carbon, it has been shown that a significant part of this Conradson Carbon will deposit thermally on the catalyst with little relation to conversion. A rule of thumb usually used is that 65% of CCR is deposited on the catalyst, but factors from 58% to 100% have been observed depending on the feed [8]. Thus, for high CCR feeds, the coke yield in the unit rises and the regenerator temperature cannot be fully controlled through the catalyst circulation rate alone, leading to regenerator temperature runaway. The amount of feed with high coking tendency, which can be processed in an FCC unit (essentially the amount of Conradson Carbon to be processed), is therefore strongly limited. Dilution with oils having lower coking potential, for example feedstocks with lower Conradson Carbon values, is usually used to process heavy feeds with high Conradson Carbon. It should be noted that there are other factors that may also limit the amount of feed with high Conradson Carbon that can be processed in an FCC unit, as these feeds may also carry larger amounts of contaminants such as metals, basic organonitrogen molecules and acids. Besides controlling the coke yield in the unit

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through catalyst circulation rate, there are other options that allow stabilizing the unit temperature by modifying the heat balance [11]:
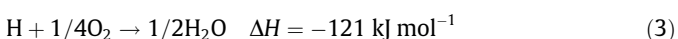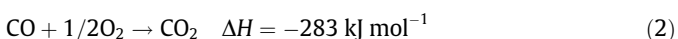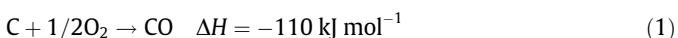
- Removing heat directly from the regenerator using catalyst coolers.
- Using a lean oxygen supply such that only partial combustion of the coke occurs to produce carbon monoxide (CO). The CO produced can be further combusted in a separate reactor to produce CO_2 and additional heat [12,13] without causing catalyst or unit damage.

Yet these processes have some disadvantages as the amount of removable heat is limited or the catalyst is not completely regenerated. Also, most of today's FCC units are not equipped with catalyst coolers or a CO boiler.

Besides combustion, coke can be removed from the catalyst surface by other means: for example, in some coking processes, a part of the coke is removed by steam reforming [14]. An additional advantage is that hydrogen is produced in the reaction, thus transforming low-value coke into high-value hydrogen instead of heat. The temperatures necessary to achieve this operation in the absence of a suitable catalyst are in the range of 850–950 °C, which is higher than the tolerance of the FCC catalyst and the actual metallurgy of FCC regenerators. Therefore, for application of coke steam reforming in the FCC unit, it is critical that catalysts active for steam reforming under FCC regenerator conditions are identified and studied. Some [15,16] have claimed being able to remove a portion of the coke from an FCC catalyst at temperatures between 540 and 650 °C, but to date no commercial application has followed. An alternative to the use of large amounts of water would be to use carbon dioxide to remove the coke-on-catalyst [17,18]. Yet the proposed catalysts to perform the coke reforming under conditions compatible with FCC regenerator have not been proven to be effective during the catalytic cracking of hydrocarbons. We have investigated the removal of coke-on-catalyst through the use of steam at several temperatures, adjusting water pressure and contact time to have measurable conversions. After evaluating the coke steam reforming activity of standard Equilibrium and other catalysts, we have found that some catalysts that are active in the catalytic cracking of hydrocarbons also have a significant activity in coke steam reforming under conditions that make it compatible with FCC regenerator conditions.
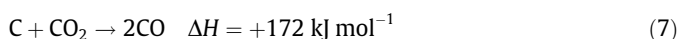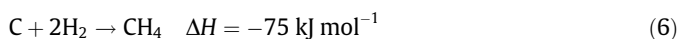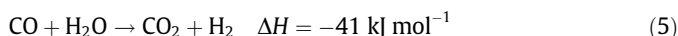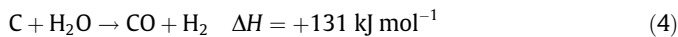
2. Reforming of coke-on-catalysts with steam or carbon dioxide: thermodynamics and influence on the regenerator heat balance

A number of reactions happen in the FCC regenerator, with different reaction heats and, thus, different impacts on the heat balance. While S and N are also present in small amounts in the coke to be burned in the FCC regenerator, we will discard their influence on the heat balance for purposes of this discussion and will limit our study to C and H. Accordingly, we have considered the following reactions:

$$C + 1/2 O_2 \rightarrow CO \quad \Delta H = -110 \text{ kJ mol}^{-1} \tag{1}$$

$$CO + 1/2 O_2 \rightarrow CO_2 \quad \Delta H = -283 \text{ kJ mol}^{-1} \tag{2}$$

$$H + 1/4 O_2 \rightarrow 1/2 H_2O \quad \Delta H = -121 \text{ kJ mol}^{-1} \tag{3}$$

Heats of reactions have been calculated on the basis of solid and gaseous reactants. Note that the coke is usually represented by CH_x, with $x \approx 0.8$, so the fraction of heat emitted by the hydrogen present in coke represents approximately 20% of the heat released in the regenerator in full combustion.

With the presence of significant water and hydrogen pressure in the regenerator, there are a number of other reactions that are promoted, namely steam reforming, water–gas shift (WGS) and methanation.

$$C + H_2O \rightarrow CO + H_2 \quad \Delta H = +131 \text{ kJ mol}^{-1} \tag{4}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H = -41 \text{ kJ mol}^{-1} \tag{5}$$

$$C + 2H_2 \rightarrow CH_4 \quad \Delta H = -75 \text{ kJ mol}^{-1} \tag{6}$$

$$C + CO_2 \rightarrow 2CO \quad \Delta H = +172 \text{ kJ mol}^{-1} \tag{7}$$

The thermodynamic equilibrium dependence on temperature for reactions 4–7 is presented in Fig. 1. The Gibbs free energy (ΔG) for each reaction

$$A + bB \rightarrow cC + dD \tag{8}$$

is related to the reaction equilibrium constant through:

$$K_{eq} = \frac{[C]^c [D]^d}{[A][B]^b} = e^{\frac{-\Delta G}{RT}} \tag{9}$$

and the logarithm of the equilibrium constant K_{eq} for reactions 4–7 has been plotted in Fig. 1 vs. temperature. A lower Gibbs free energy in Fig. 1 means that the equilibrium is displaced toward the product side of the equilibrium as written in reactions (4)–(7), and a higher value for ΔG shifts equilibrium to the reactant side. The Gibbs free energy for equilibrium is calculated per mole of C or CO on the reactant side of the equilibrium. The carbon reforming by steam or CO_2 is not favored by thermodynamic equilibrium below 650 °C. Meanwhile, methanation equilibrium is not favored above 650 °C, and WGS is only slightly favored at typical regenerator temperatures of 620–750 °C. It appears then that the thermodynamic equilibrium allows for a significant part of the coke to be converted above temperatures of 650 °C. Thus, in commercial applications, it is the reaction kinetics between 650 and 900 °C, which limit practical use of thermal steam reforming at these temperatures. Then, the use of a proper catalyst may allow reforming of a significant portion of the coke-on-catalyst even at temperatures near 700 °C.

As an example, we calculated the equilibrium carbon-on-catalyst concentration for several temperatures making some assumptions for a hypothetical regenerator atmosphere where combustion and reforming products are mixed. The equilibrium constant is directly obtained from the Gibbs free energy of the reforming reaction.

We can assume for this example that 1/3 of the coke is reformed, while the other 2/3 are combusted (this proportion would be in the range of the adequate reforming/combustion ratio to maintain an optimal heat balance as explained below). We can also assume a final concentration of 10% water in the flue gas (similar to current FCC operation) and a total pressure of 3 bars. Considering only coke steam reforming (no parallel reaction) and full combustion, this would lead to the following volume percent in the regenerator atmosphere: 7.5% CO and H_2, 15% CO_2, 10% water and 60% nitrogen. We can then calculate the equilibrium concentration of carbon-on-catalyst. The results of the calculation are presented in Table 1, together with the corresponding equilibrium constant for temperatures from 600 to 750 °C. The carbon concentration has been calculated as carbon-on-catalyst, in weight percent of carbon by weight of catalyst, assuming a catalyst density of 500 kg/m³ for the regenerator dense bed. It appears that under these conditions, and assuming that the carbon concentration on the catalyst entering the regenerator will be between 1% and 2.5% for the conversion of feeds with high CCR, the coke conversion may be significant above a regenerator temperature of 650 °C (0.61% on catalyst at equilibrium, so conversion at equilibrium
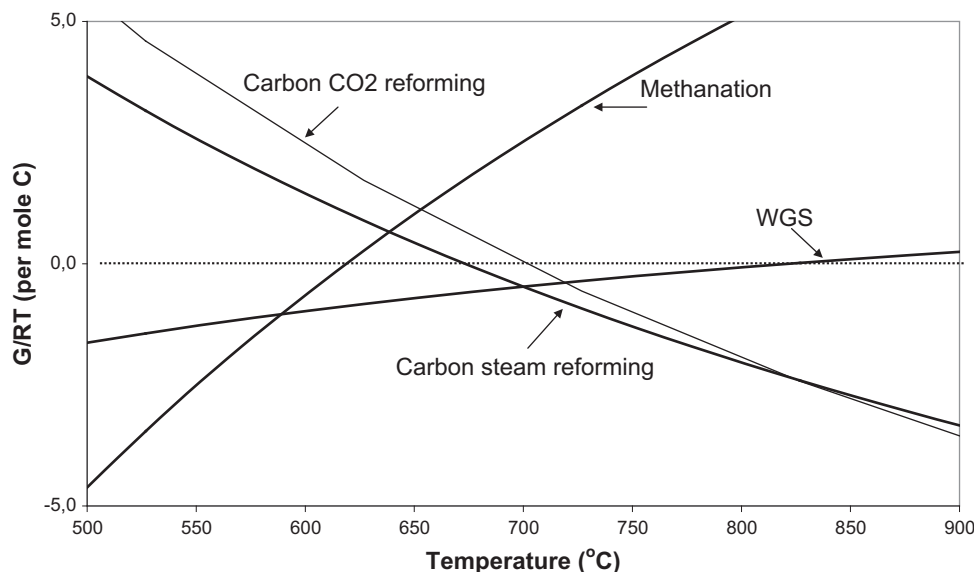
Fig. 1. Gibbs free energy for several reactions vs. temperature.

Table 1
Equilibrium coke concentrations CoC^{eq} under model atmosphere for combined coke steam reforming and combustion at several temperatures.

Temperature (K/°C)	$K_{steam\ reforming}$	CoC^{eq}, wt.% on cat.
900/627	0.41	0.99
925/652	0.67	0.61
950/677	1.07	0.38
975/702	1.66	0.25
1000/727	2.62	0.16
1025/752	3.75	0.11

would be 39–75% depending on initial coke-on-catalyst) and may be close or superior to 90% at temperature above 730 °C.

The occurrence of steam reforming in the FCC regenerator has a large influence on the heat balance as this prevents a part of the coke from being combusted, and moreover, the reforming reaction is endothermic. We have made a simple mass and heat balance on the FCC regenerator to check for the impact of increased steam reforming on the amount of coke to be combusted in order to maintain the heat balance. Here, we assume that one part of the coke is removed by full combustion and another part by steam reforming followed by WGS, thus forming CO_2 and H_2. We also assume that the H_2 is not combusted by working with an amount of air significantly lower than that necessary to burn all the coke, so that all air is consumed within the regenerator bed. The final result would be an atmosphere with H_2, CO_2 and N_2. The calculation assumes a combustion heat of 514 kJ/mol of coke (that includes the heat of combustion of C and H contained in coke), a reforming + WGS heat of −90 kJ/mol of coke (endothermic) and a temperature increase in the regenerator of 230 °C (from 500 to 730 °C). As shown in Fig. 2, doubling coke-on-catalyst by the use of heavy feeds would require that 1/3 of the coke-on-catalyst be steam reformed to maintain the same heat generation in the regenerator.

The use of steam reforming is expected to be associated with the use of feeds with high Conradson Carbon. If we assume in our heat balance that a clean feed with zero Conradson Carbon (CCR) would give 5.0% coke yield at CTO 5.5 (typical FCC figures) and that 65% of the Conradson Carbon goes to coke, then we can make an estimation of the coke-on-catalyst as a function of feed CCR and thus the amount to be reformed compared with a zero CCR feed. We can also include a calculation of the increase in air

blower capacity needed compared with the base case. As can be seen in Fig. 3, with feeds from 5% to 20% CCR, an amount of coke from 25% to 40% has to be reformed so that the heat balance is maintained, while air blower capacity will be increased from 30% to 100%. While the increase in air blower capacity needed is substantial, this is much less than the increase from 75% to 260% capacity needed if all coke would have to be burned.

3. Materials and methods

3.1. Catalysts

A simulated FCC commercial Equilibrium catalyst (Ecat) was used in this study with the properties listed in Table 2a. This catalyst was obtained from a fresh, microsphere, commercial FCC catalyst which was then steam deactivated at 816 °C during 4 h and used in a Davison Circulating Riser (DCR) pilot plant. This catalyst does not carry appreciable amounts of metals other than 1% Lanthanum used for stabilization. It has low levels of Ni and V. Metal-impregnated catalysts (metal = La, Ce, Zn, Mn) are obtained by wet impregnation of the aforementioned Ecat catalyst with aqueous nitrate solutions of the desired metal. For impregnation with Ti, a butoxide precursor was used. The wet impregnated catalysts are then calcined at 550 °C for 3 h. The hydrotalcite materials were prepared by a standard co-precipitating procedure using two solutions [19]. The first solution contained $Mg(NO_3)_2·6H_2O$ and $Al(NO_3)_3·9H_2O$. The second solution contained NaOH and Na_2CO_3 in the adequate concentration to obtain the total precipitation of aluminum and magnesium and to fix the pH at a value of 13. Both solutions were added, while vigorously stirring, at a total flow-rate of 1 ml/min. Metal concentration in the first solution is calculated so that the concentration of Mg + Al is 1.5 mol/l, and the molar ratio Mg/Al is 3 in the final solution. The gel was aged for an hour at room temperature, then filtered and washed with distilled water until the pH was 7 and carbonate was not detected in the filtrate. The recuperated solid was calcined at 550 °C for 3 h and subsequently treated with steam at 750 °C for 5 h to simulate hydrothermal deactivation. The resulting catalyst has an area of 110 m^2/g and a pore volume of 0.37 cm^3/g. The powdered catalyst is then shaped into 0.4–0.6-mm pellets before testing in a fixed bed. The resulting catalyst particles were subjected to a number of coking/
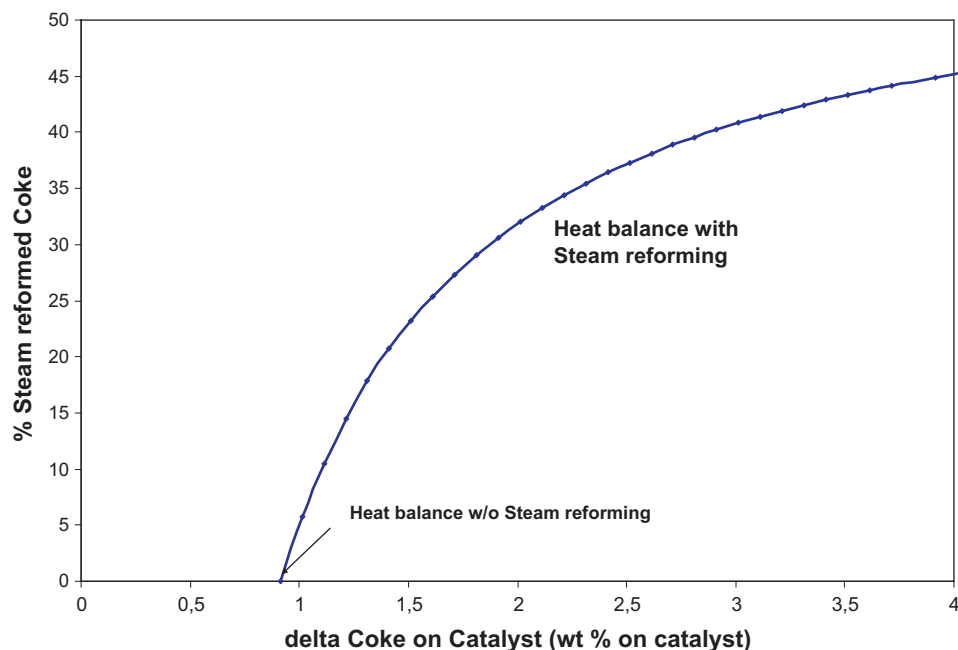
Fig. 2. Relation between the fraction of coke to be steam reformed with increasing coke-on-catalyst to maintain heat balance in the FCC regenerator. Calculations are made assuming catalyst inlet temperature of 500 °C and regenerator temperature of 730 °C, with vapor and steam entering at 200 °C in the regenerator.
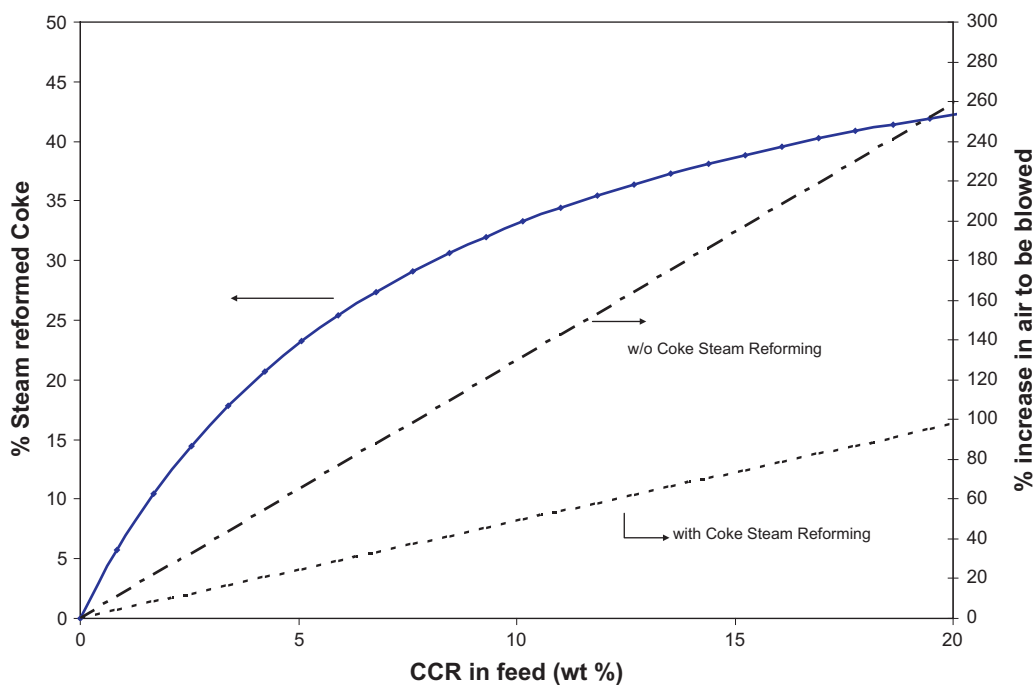

Fig. 3. Fraction of coke to be steam reformed vs. Conradson Carbon in feed. Comparison of increase in air blower capacity with and w/o steam reforming.

Table 2a
Catalyst properties. Catalysts were steamed at 750 °C for 5 h with 1 bar steam.

	CatA	Hydrotalcite material
Rare earth content (wt.%)	1.0	–
Unit cell size (nm)	2.430	–
% of zeolite in catalyst	24	–
BET surface area (m²/g)	297	110
Micropore area (m²/g)	183	–
Pore volume (cm³/g)	0.34	0.37

steam reforming cycles during this study as the same catalyst particles were reused to perform several reforming activity measurements at different operating conditions and/or with different feeds. It was verified that the steam reforming activity of the steam-treated hydrotalcite sample coked with VGO did not vary significantly after 5 reaction/regeneration cycles. Regeneration is performed with air at 540 °C and lasts 3 h. A certain amount of SO_x are formed during regeneration, depending on sulfur content of the feedstock and the catalyst.

3.2. TPD-MS

3.2.1. Protocol and apparatus

These experiments have been carried out in an AutoChem 2910 Analyzer connected in series with a ThermoStar GSD 300 T Mass spectrometer. He is used as carrier gas and is saturated with water at 22 °C, which results in a water partial pressure of 2.6 kPa. A mass of 0.3 g of coked sample is used for each experiment. The temperature ramp is set at 10 °C/min until reaching a plateau at 750, 800 or 900 °C depending on the experiment, and the temperature at the plateau is maintained for approximately 10 h. Total experiment duration is 38,000 s. The sample is purged with carrier gas saturated with water for at least 30 min before the temperature ramp begins so that the system is allowed to stabilize. The respective signals at masses of $m/z = 2$, 16, 18, 28 and 44, which correspond to the main masses associated with hydrogen, methane, water, CO and CO_2, respectively, are recorded. Water also gives a secondary mass at $m/z = 16$ which adds to the methane signal.

3.2.2. Kinetic data extraction from MS signal

Coke steam reforming reaction rate is extracted from the Mass Spectrometer data signal. The MS signal at $m/z = 44$ is proportional to CO_2 concentration, while the signal at $m/z = 28$ is proportional to CO concentration plus a small contribution from CO_2 concentration (11% of main peak at $m/z = 44$) at the outlet of the TPD reactor. Thus, a signal proportional to CO and CO_2 molar flow can be obtained from MS signal at m/z 28 and 44.

A mass balance in the TPD reactor on coke on the catalyst, with N_c being the number of moles of coke in the TPD reactor gives:

$$dN_c/dt = (R_{reforming} + R_{Boudouard} + R_{methanation})V_R \qquad (10)$$

where R_j the reaction rate for the corresponding reforming, methanation or Boudouard reactions, respectively, by reactor volume (V_R) unit. Methanation is highly unfavorable at temperatures above 700 °C, and combined with the very low local pressure of hydrogen, the contribution of this reaction to the removal of the coke on the catalyst is negligible. Due to the very low local partial pressure of CO_2 (at least two orders of magnitude lower than the water concentration), the contribution of the Boudouard reaction to the coke conversion under these conditions can also be ruled out. Thus, we can deduce that the change in the number of moles of carbon N_c on the catalyst during the experiment can be approximated by

$$dN_c/dt \approx (R_{reforming})V_R \qquad (11)$$

And the total amount of moles of coke removed during the reforming operation of duration τ can be calculated as:

$$N_c(\tau) - N_c(0) = \int_0^\tau R_{reforming}(t)V_R dt \qquad (12)$$

Elemental analysis of the coked samples can be performed before and after the reforming operation to quantify the total mass (and then moles) of carbon removed during the operation.

Assuming no O_2, CO or CO_2 at the inlet and no accumulation, a mass balance performed on CO and CO_2 on the TPD reactor gives:

$$F_{CO}^{outlet} = (R_{reforming} - R_{WGS} + 2 * R_{Boudouard})V_R \qquad (13)$$

$$F_{CO2}^{outlet} \approx R_{WGS}V_R \qquad (14)$$

where F_i^{outlet} is the molar flow of i at the reactor outlet. As stated before, the reaction rate for the Boudouard reaction will be very small compared with the reforming rate under these operating conditions.

Thus, combining (13) and (14), we obtain:

$$F_{CO}^{outlet} + F_{CO2}^{outlet} \approx R_{reforming}V_R \qquad (15)$$

The molar flow of CO_2 can be monitored directly from the MS signal ($m/z = 44$). In the case that the CO_2 signal is found to be much smaller than the CO signal, then the WGS reaction rate is assumed to be much smaller than steam reforming reaction rate, the molar flow of CO is then directly proportional to the signal at $m/z = 28$ and the reforming rate is approximated as

$$F_{CO}^{outlet} \approx R_{reforming}V_R \qquad (16)$$

The integral of the MS signal, being proportional to the molar flow of CO (plus CO_2 if present), is also proportional to the integral of reaction rate with time and then related to the amount of coke removed during the experiment as indicated by relation (12). Thus, the MS signal can be normalized in terms of moles of carbon removed from catalyst by time unit, allowing the calculation of the instantaneous steam reforming reaction rate.

3.3. Coke steam reforming in fixed bed

A fixed bed reactor derived from a MAT unit is used for Coke Steam Reforming tests. One gram of coked catalyst is loaded; plus 2 grams of Carborundum® (CSi) acts as a preheater for steam. The reactor is then heated as fast as possible to the reaction temperature (750–770 °C) with a ramp of typically 40 °C/min in 40 ml/min nitrogen flow, so thermal aging of the coke is limited. When the temperature is stabilized, 0.2 ml/min of water is injected. Nitrogen is co-fed to regulate water partial pressure. A minimum flow of 40 ml/min of nitrogen is maintained to ensure that the reaction products are entrained to the collection section. Water is condensed in a trap at the exit of the reactor. Gases are collected in a gas bag. Reaction time is 20 min, unless otherwise specified. After the reaction time, water injection is stopped, and the system is flushed with 80 ml/min of nitrogen for 5 min and collected with the reaction gases. Then, the remaining coke on the catalyst is determined either by Elemental analysis (in this case the sample is cooled down and the solid recovered) or by burning the remaining coke and determining the amount of CO_2 emitted during combustion. In this second option, the coke is burned with a 100 ml/min air flow for 45 min and the emitted CO_2 quantified by an online IR analyzer.

3.4. Sample coking

The coke on the catalyst was deposited using a fixed bed reactor and performing catalytic cracking of a hydrocarbon feed following a modified ASTM-D-3907-86 method. Catalytic cracking was performed at a temperature of 803 K and a time-on-stream (TOS) of 30 s. Three grams of catalyst was loaded to the reactor, and the mass ratio of catalyst to oil feed injected (usually called the CTO ratio) was 3, which corresponds to a weight hourly space velocity (WHSV) of 40 h^{-1}. Before each experiment, the system was purged with a 30 cm^3/min N_2 flow for 30 min at the reaction temperature. Catalytic cracking was performed by injecting the hydrocarbon feed at a rate of 2 g/min during 30 s. After reaction, stripping of the catalyst was carried out for 15 min using a N_2 flow of 40 cm^3/min. During the reaction and stripping steps, the liquid products were collected in separate glass receivers located at the exit of the reactor, which were maintained at 283 K. Meanwhile, the gaseous products were collected in a gas buret by water displacement. Immediately after the stripping step, the reactor is cooled, and the coked sample is recuperated from the reactor. Hexadecane, a regular vacuum gas oil (VGO) and an Atmospheric Resid (AR) have been used as feeds to obtain coked samples. VGO has a Conradson Carbon (CCR) of 0.2 wt.%, while AR has a CCR of 8 wt.%. Properties of VGO and ATR are listed in Table 2b.

Table 2b
Feed properties.

	VGO	ATR
Density (15 °C)	0.91	0.94
Conradson carbon, wt.%	0.2	7.8
Sulfur wt.%	1.6	3
Ni	0.2	n/a
V	0.4	n/a
ASTM D1160 (°C)		
30% off	414	495
50% off	436	527
70% off	459	569
90% off	512	>600

4. Results

4.1. TPD-MS results and influence of the temperature on FCC equilibrium catalyst

The mass spectrometry signal obtained in steam reforming of an Equilibrium catalyst coked with VGO is presented in Fig. 4. The signals obtained with the same catalyst coked with *n*-hexadecane or AR feeds are very similar, so the reaction mechanism appears to be similar for all feeds.

The $m/z = 18$ signal that corresponds to water shows:

- a peak at 50 °C which corresponds to the dehydration of the sample,
- a slight increase beginning at 4000 s or 600 °C which corresponds to the dehydration of Brönsted sites,
- a decrease beginning at 4800 s or 700 °C, with a minimum at the end of the temperature ramp (900 °C) which corresponds to the maximum water consumption rate by coke steam reforming.

The $m/z = 16$ signal is formed by contributions from both methane and water. The peak at 50 °C is due to water. The peak that appears at 600 °C (4000 s, Fig. 4) is due to methane and is correlated with a peak for hydrogen. The hydrogen and methane emissions

from coked catalyst have already been observed during stripping [20] or preheating of coked catalysts at temperatures above 600 °C before further processing [21]. The emissions of methane and hydrogen from coke have nearly stopped when the second emissions begin at 700 °C and represent only a tiny fraction of the total coke-on-catalyst (<3%).

The $m/z = 28$ signal, which corresponds to CO (no nitrogen in atmosphere, little CO_2), shows an increase starting at 700 °C till the end of the temperature ramp and then decreases once the final plateau temperature has been reached. This emission is correlated with a large H_2 emission, and very little CO_2 emission as shown by the $m/z = 44$ signal. The coke reforming rate increases sharply with temperature from zero at 700 °C to maximum at 900 °C and then decreases with the decreasing coke-on-catalyst while temperature is maintained constant. We can also deduce that the coke removal proceeds entirely through steam reforming and that there is little water–gas shift with this catalyst.

The $m/z = 2$ signal, which corresponds to hydrogen, exhibits a very similar shape, with an additional shoulder beginning at 3800 s or 600 °C.

Reaction rates for steam reforming of samples coked with *n*-hexadecane, Vacuum Gasoil and an Atmospheric Resid have been calculated using the procedure described in Section 3.2.2. and are shown in Fig. 5a. Reaction rate is expressed as coke-on-catalyst (CoC) percent removed per second. The temperature ramp is the same for all samples: 10 °C per minute till 900 °C. The relative reaction rate rank is clearly

$$r_{nC16} < r_{VGO} < r_{residue}$$

4.2. Kinetics of steam reforming from TPD experiments

While a large number of articles and reviews exist on the gasification of coal, thermally or with catalysts [22,23], very little literature refers to the gasification of coke deposited on catalysts like silica–alumina and zeolites. One reference [24] considers coke gasification in the range 810–870 °C, under 1 bar of steam (water partial pressure was maintained constant). Coke was obtained via reacting an Atmospheric Resid with catalyst at 482 °C for 24 h,
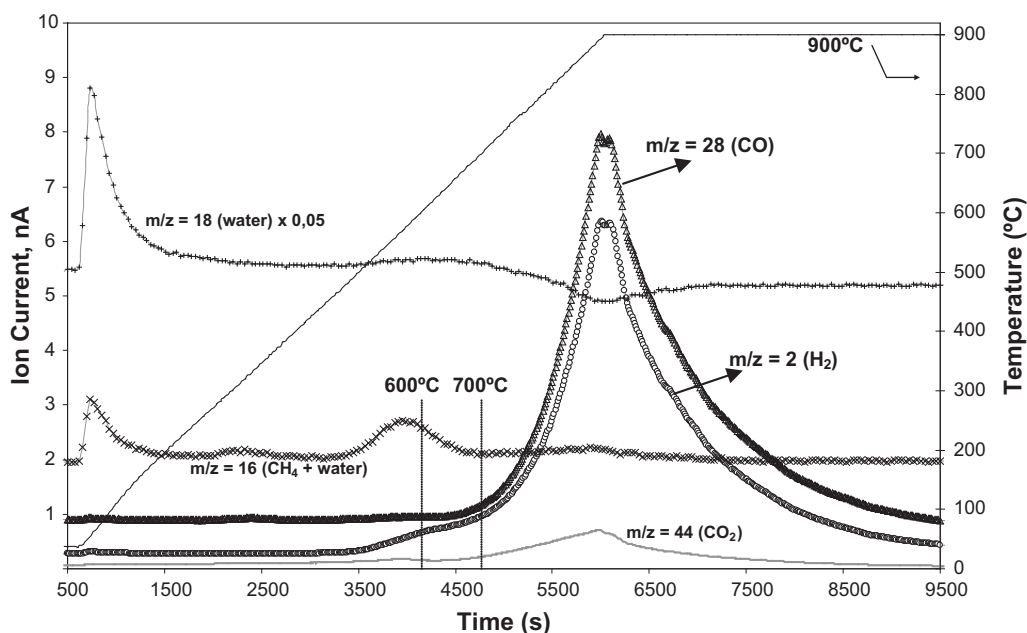

Fig. 4. m/z signals obtained from the processing of a coked sample in the presence of water in a TPD-MS unit. Ecat samples coked with VGO. m/z at 2 and 28 are shifted 0.3 and 0.8 nA, respectively.
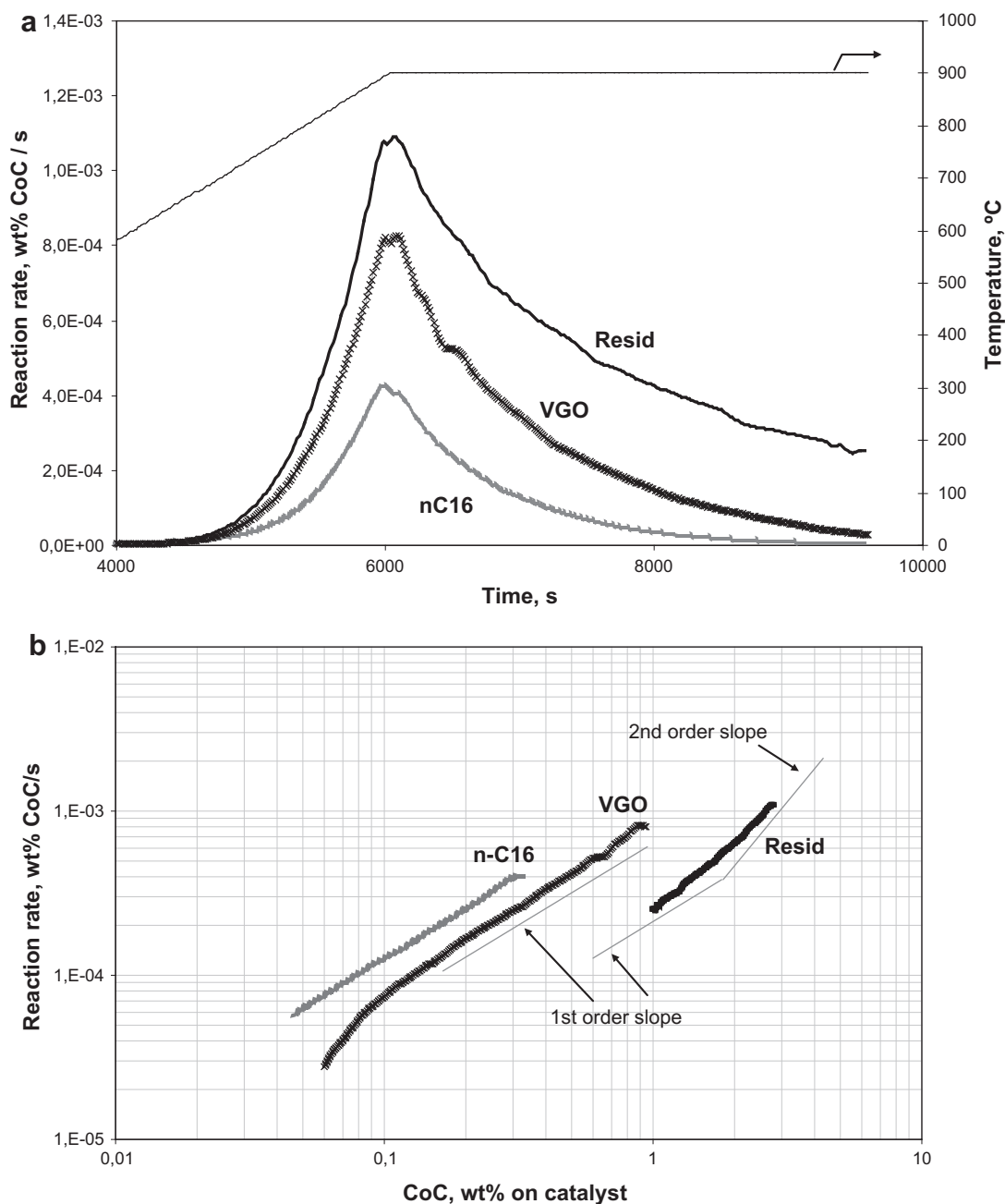
Fig. 5. (a and b) Variation of reaction rate with time (a) and plot of kinetic data: log of reaction rate vs. log of coke-on-catalyst (b). Catalyst sample has been coked with nC16, VGO, and a residue feed, respectively.

resulting in a coke content between 5% and 10% wt of the catalyst. This coke was more dehydrogenated (2% H in coke) than a coke formed in a catalytic cracker (typically 6–8%). Data fit well with a first-order reaction rate against coke-on-catalyst.

A reaction similar to coke steam gasification is the combustion of coke on the catalyst. This reaction has been extensively studied [25–29]. It has been shown that, in most cases, the kinetics of coke combustion at temperatures of 500–600 °C follow with first-order kinetics, even considering over 80% coke removal in less than 5 min [25]. Some diffusion limitations have been shown to occur with particles of larger diameter (1.2–2 mm). In this case, a model including first-order kinetics and intraparticle diffusion allowed for a very good simulation of the results, independent of the experimental conditions and particle size [26]. Metcalfe [29] observed that, for coke-on-catalyst higher than 1 wt.%, the reaction rate

tended to follow a first-order reaction rate, while for lower carbon contents it tended to adjust to a second-order reaction rate. Thus, a variable order for reaction rate was proposed, with first-order reaction rate at high coke-on-catalyst and a higher order of reaction with lower coke-on-catalyst. Reaction order was 2 for a coke-on-catalyst of 1%.

A practical way to determine reaction order is to plot the log of reaction rate vs. the log of coke-on-catalyst. The reaction rate data used in the analyses are those which are collected from the moment the temperature of the TPD reaches the constant plateau temperature. At this point, a certain amount of coke has been already removed, which represents about 5–10% of the initial coke-on-catalyst. Initial coke-on-catalyst for the considered samples is 0.55%, 1.35% and 3.4% for samples coked with *n*-hexadecane, VGO and AR, respectively. Fig. 5b shows this plot for catalysts

coked with these three different feeds, with a final plateau temperature at 900 °C. Coke formed from nC16 or VGO reforms at 900 °C with a first-order reaction rate, while coke formed from resid seems to reform with a reaction order of 2 above 2 wt.% coke-on-catalyst and a first-order reaction rate for coke lower than 1.5 wt.% coke-on-catalyst. The kinetic rate constant for a first-order reaction rate (coke-on-catalyst lower than 1.5 wt.%) can be deduced form Fig. 5b, and they rank as:

$$k_{nC16} > k_{VGO} > k_{residue}$$

which means that the coke formed by heavier feeds is harder to reform than the coke from lighter feeds. Values are 1.3×10^{-3}, 8×10^{-4} and 2.5×10^{-4} s^{-1} for nC16, VGO and resid, respectively. Yet the overall reaction rate can be higher with resids due to the higher amount of coke-on-catalyst.

The same log–log representation of the reaction rate vs. coke-on-catalyst has been used to represent the results obtained when reforming at different temperatures ranging from 700 to 900 °C of a sample coked with VGO (Fig. 6). With the exception of low values of coke-on-catalyst for the 900 °C sample, the reaction rate is first order over the whole range of coke-on-catalyst values investigated. However, at lower temperatures, while a first-order rate is observed for coke contents below 0.8 wt.%, the first portion of the coke seems to be reformed under a different reaction order that gets higher with lower temperature. The rate constant determined at each temperature from the part of the data that obeys a first-order reaction rate allows for the calculation of an activation energy assuming that:

$$k = A_0 e^{(-Ea/RT)}$$

In this way, an activation energy of 239 kJ/mol has been obtained (Fig. 7), which indicates that diffusion limitations can be ruled out.

4.3. Steam reforming under realistic conditions

The very low water pressure during the TPD experiments is not representative of a typical FCC atmosphere, which may contain up
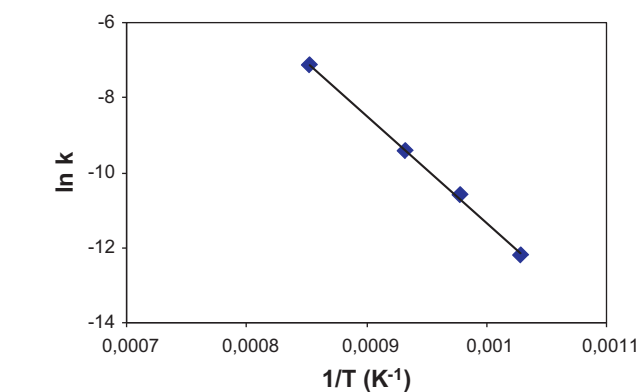

Fig. 7. Temperature dependence of rate constant.

to 10–15% water. This, combined with a total pressure of 2–3 bars, results in a water pressure of ≈30 kPa in the regenerator. Thus, we performed experiments in a fixed bed with 50–90 kPa of water, a temperature of 750 °C and 20 min time-on-stream. While these conditions are somewhat more drastic than actual FCC regenerator operating conditions, we have applied them to promote more understanding of the CSR reaction.

Results of these tests are presented in Table 3. The coke conversions obtained are low, in the range 7–12%, allowing us to conclude that under FCC regenerator operating conditions, it is possible to assume that no significant portion of the coke-on-catalyst can be removed by steam reforming with an Equilibrium catalyst. Thus, the Equilibrium catalyst needs to be modified, or a proper additive has to be added, to enhance the reforming reaction rate.

4.4. Improving the steam reforming by impregnation of Ecat with metals

A number of metals and rare earths have been impregnated on an Equilibrium catalyst in an attempt to improve the steam reforming rate. When doing this, the effect on the catalytic
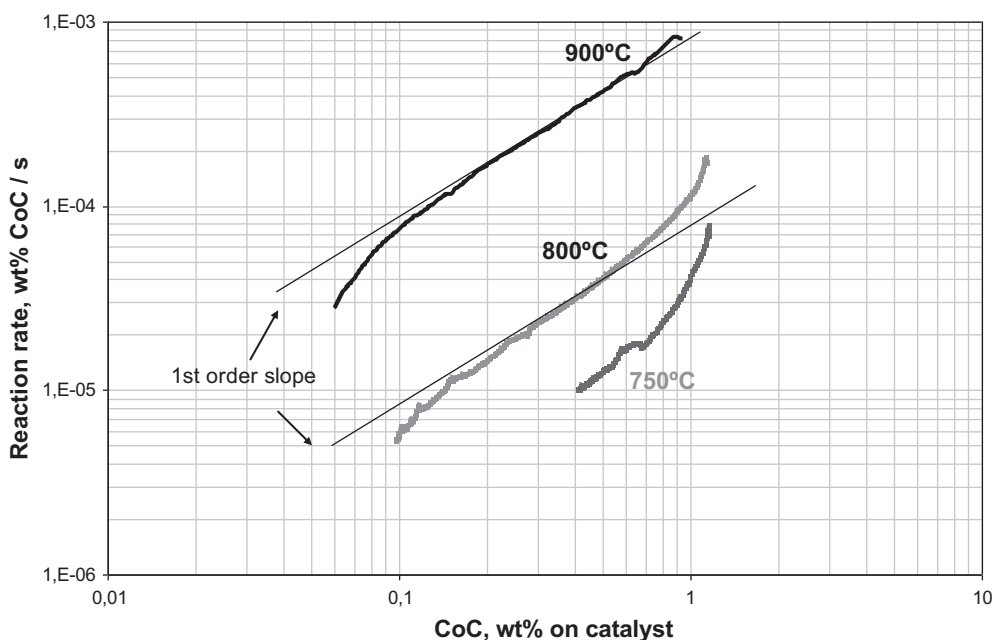

Fig. 6. Plot of kinetic data: log of reaction rate (in coke-on-catalyst percent per second) vs. log of coke-on-catalyst (CoC). Catalyst sample was coked with VGO. Temperature ramp of 10 °C to a plateau at 750, 800 or 900 °C.

Table 3
Steam reforming experiments in fixed bed, 750 °C and 20 min time-on-stream.

Catalyst	CatA	CatA	CatA
Feed for coking	VGO	VGO	Residue
Water pressure, kPa	90	50	90
Coke conversion	12	7	9
Carbon balance			
CO	9.0	6	7
CO_2	2	<0.5	1
CH_4	1	1	1
H_2/CO molar	2.1	2.2	1.6

Table 4
Ecat impregnated with metals. Hydrogen and coke yield change at 67% conversion in catalytic cracking. Changes in reforming rate constant when compared to Ecat.

Impregnated metal	Metal content, wt.%	Catalytic cracking		CSR
		H_2 yield change	Coke yield change	K
–	0	Base	Base	Base
La	1.28	−30%	+20%	Base
Ce	1.52	+100%	+30%	+50%
Zn	2.00	+500%	+60%	+140%
Ti	2.48	+100%	+20%	+20%
Mn	2.13	−10%	−10%	+50%

cracking activity and selectivity to the main products (gases, gasoline and LCO) has to be studied. Thus, depending on the element added, there may be a significant effect on hydrogen and coke selectivity. In Table 4, the increase in hydrogen and coke yield at a conversion of 67 wt.% is presented. Also, the coke steam reforming rate constant for the part of reforming that obeys a first-order reaction rate is determined by the procedure described above and compared to the rate constant for the base Equilibrium catalyst.

In agreement with the well-known effects of increased La on FCC catalysts on hydrogen and coke yields [30], impregnation with La decreases hydrogen yield and increases coke yield. Meanwhile, the coke steam reforming rate remains the same as for the base Ecat.

The impregnation with Ce, Zn, Ti and Mn at loadings in the range of 1.5–2.5% leads to an increase in the coke steam reforming

rate, as shown in Fig. 8. A rate constant was deduced from the linear part of the curves, where the reaction is first order, and the influence of metal on the rate constant is ranking:

Ti < Mn ≈ Ce < Zn

It has to be noted that a significant part of the coke is removed at a reaction rate with higher order respect to coke-on-catalyst. The presence of metal on the catalysts has significant effects on hydrogen and coke yields. While Mn has nearly no effect on the selectivity of catalytic cracking, hydrogen and coke yields are increased with the other impregnated metals in the ranking from less to more harmful:

Ti < Ce < Zn

Thus, we can deduce from the above findings that doping with Ce or Mn would be a preferred option for improving the steam reforming rate.

In summary, impregnation of Ecat with certain metals allows for increasing the steam reforming reaction rate 1.5–2.5 times. While this is a significant improvement, when compared to the low conversion obtained under more realistic water pressure conditions with Equilibrium catalyst, the reforming reaction rate needs to be further improved by using other types of catalysts.

4.5. Steam reforming with hydrotalcite in TPD-MS

Hydrotalcite-based materials have been identified as possible additives to catalytic cracking, improving the selectivity to diesel as well as diesel quality by lowering the content of aromatics in middle distillates [31]. Thus, we have tested this material as a potential steam reforming catalyst. The use of hydrotalcite may result in changes in catalyst activity compared with traditional FCC catalysts, and the operation may be significantly different and oriented to the maximization of middle distillates.

A sample of hydrotalcite was coked with a VGO, and the coked catalyst was reacted with diluted steam in TPD-MS with the procedure described earlier. MS data with time are presented in Fig. 9 and expanded to the 5000–12,000 s time range. In agreement with what we observed for FCC Ecat, an emission of methane and hydrogen is observed during the ramp which peaks at 600 °C and then
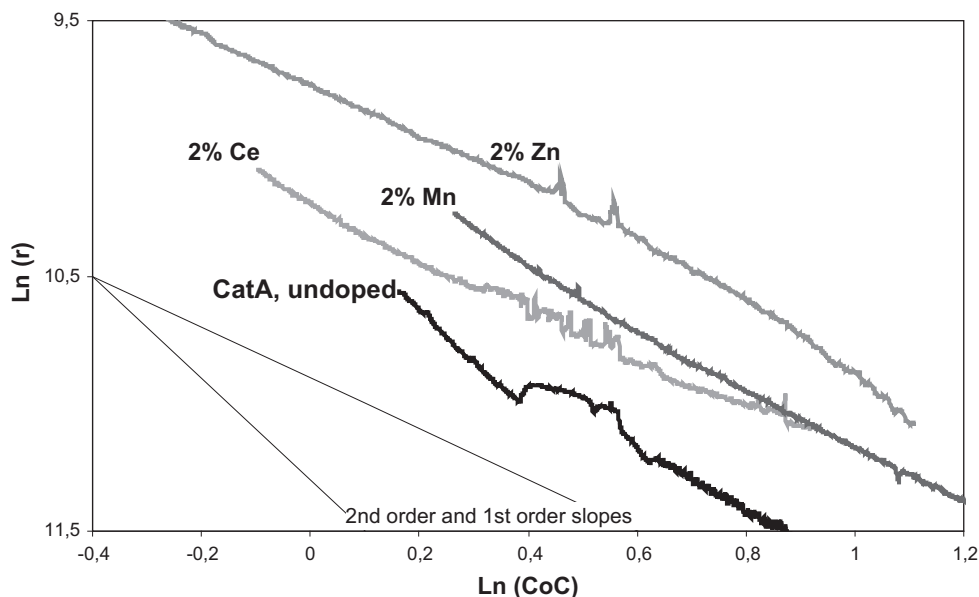

Fig. 8. Plot of kinetic data: log of reaction rate (in coke-on-catalyst percent per second) vs. Log of CoC (in percent on catalyst), determined through TPD experiments for metal-impregnated Ecat.
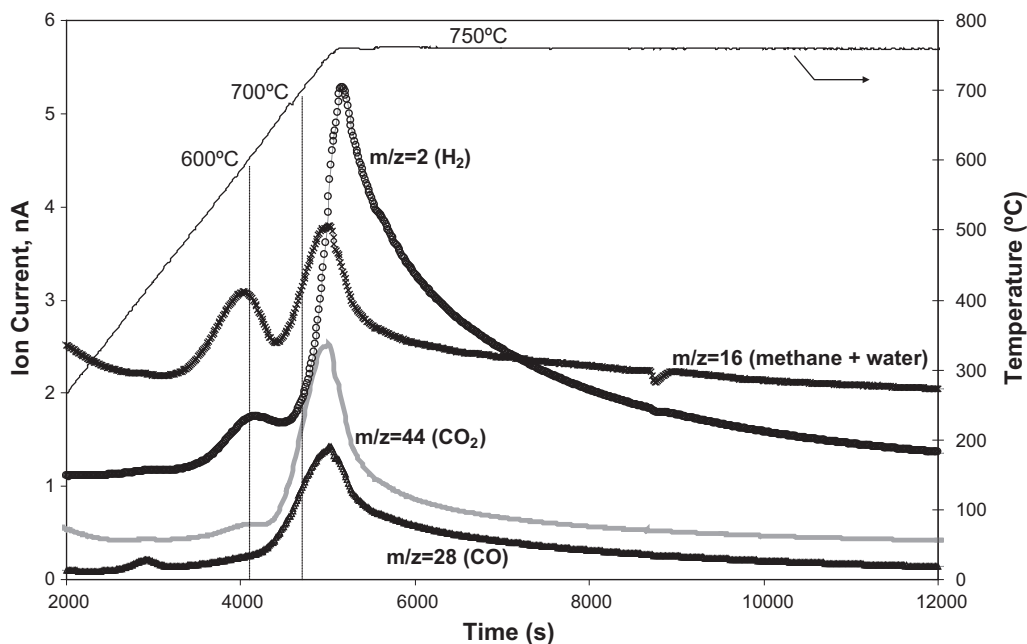
Fig. 9. m/z signals obtained from the processing of a coked sample in the presence of water in a TPD-MS unit. Hydrotalcite sample coked with VGO. m/z at 2 and 44 are shifted 0.3 and 1 nA, respectively.

rapidly decreases, which corresponds to dehydrogenation and demethylation of the coke. Then, the CO emission begins, but it can be observed that this emission starts at 650 °C, i.e., 50 °C lower than with Ecat, and that it is accompanied by an emission of hydrogen (due to coke reforming) but also by a significant emission of CO_2 and methane. Thus, with this catalyst, coke steam reforming occurs together with water–gas shift and some methanation.

A coke removal reaction rate can be deduced from the MS signal using the same procedure as described earlier. It can be seen in Fig. 10a that the coke removal rate is much higher than for the Equilibrium catalyst. Plotting reaction rate vs. CoC (Fig. 10b) reveals that the coke removal from hydrotalcite seems to follow a second-order reaction rate for coke contents between 0.2 and 0.8 wt.% coke-on-catalyst. The fraction below 0.2% coke-on-catalyst seems difficult to reform, while the fraction above 0.8% coke-on-catalyst is reformed at much higher rate. All this indicates that the coke on the hydrotalcite-derived material is of a heterogeneous nature and that it may exist as different types of coke reforming at different rates. Indeed, the shape of the curve depicting the remaining coke-on-catalyst on hydrotalcite at times higher than 20,000 s (Fig. 10a) indicates that there is a fraction of about 20% of the coke-on-catalyst which is reformed much slower than the rest of the coke. In order to extract kinetic data on reforming rate of the other 80% of the coke, we can drop this refractory 20% fraction from the total amount of coke so that the reaction rate measured corresponds to the fraction of coke which can be effectively reformed under these conditions. In Fig. 11 is presented the plot of the reaction rate vs. the calculated coke-on-catalyst (CoC) performing the correction discussed above. As happens with Equilibrium catalyst, the reforming rate of coke fraction below 0.8 wt.% obeys first-order kinetics. The rate constant deduced from Fig. 11 gives $1.8 \times 10^{-4}\,\mathrm{s}^{-1}$, which is roughly seven times higher than that of the Equilibrium catalyst.

4.6. Steam reforming with hydrotalcite-derived materials in a fixed bed reactor

The steam reforming of coked hydrotalcite (HT) samples under fixed bed conditions is presented in Table 5. Compared with steam

reforming of coke on Equilibrium catalyst at 750 °C and 20 min time-on-stream (data in Table 3, second and fourth column), the coke conversion on the hydrotalcite sample is considerably higher, with either VGO (64% for HT vs. 12% for Ecat) or AR (50% for HT vs. 9% for Ecat) used as a feed for coking. Also, the H_2/CO ratio is significantly higher with HT than with Ecat (5–7 vs. 2), which implies that the HT sample is able to perform the water–gas shift reaction. As expected, the H_2/CO ratio decreases with increasing temperature as dictated by thermodynamic equilibrium (Fig. 1). The conversion obtained with coke made from resid is lower than with coke with VGO at the same conditions, which agrees with the results obtained with TPD-MS. As temperature increases from 700 to 770 °C, a conversion increase in coke from 15 to 50 wt.% can be obtained. These conversions are in the range needed to maintain the FCC heat balance when feeds with high coking tendency are used, as described in Section 2. While the operating conditions necessary are still somewhat high for a typical FCC regenerator, they are much closer to them than they are to typical thermal steam reforming conditions.

4.7. Simultaneous Steam reforming and combustion

In Section 2, we assumed that the coke steam reforming was performed together with combustion and that the coke-on-catalyst has to be removed nearly completely to restore catalytic cracking activity. In order to prove that both operations can be carried out simultaneously in the regenerator, a mixture of diluted air and water was fed on a sample of coked hydrotalcite material loaded in the fixed bed which has been coked previously during the catalytic cracking of a residue with a CCR of 8 wt.%. In addition, a test was conducted with the same flow of diluted air but without water. Note that the total amount of air fed has been calculated so that only a portion of the coke can be removed by combustion. Results are presented in Table 6 and compared to the steam reforming experiment carried at the same temperature of 770 °C and the same time-on-stream of 20 min (Table 5, last column). The conversion obtained by feeding air only is 45%, while the conversion feeding water only is 50%. Considering that the two reactions proceed in parallel, we should obtain a total conversion of
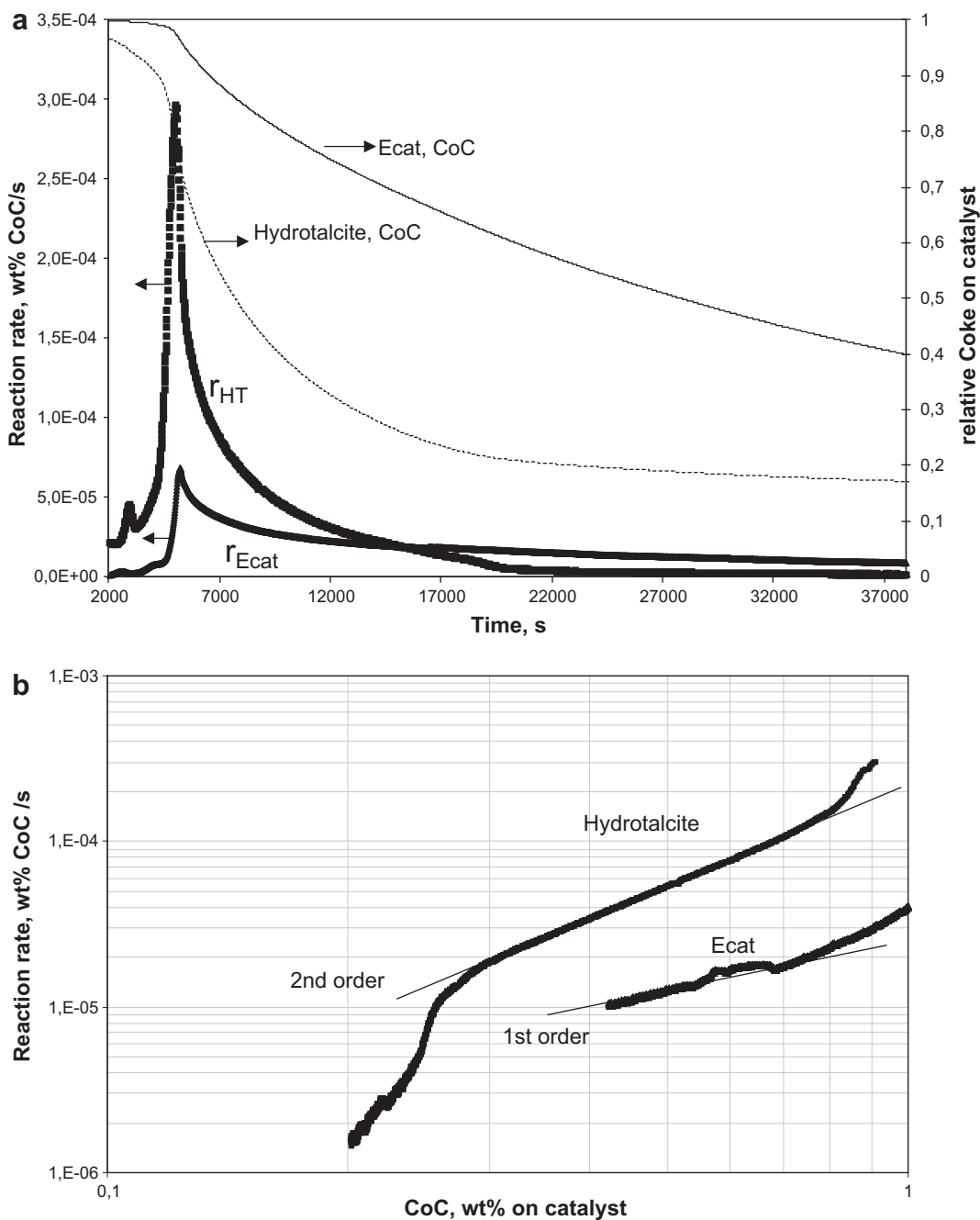
Fig. 10. (a and b) Variation of coke-on-catalyst (CoC) and reaction rate with time (a) and plot of kinetic data: log of reaction rate vs. Log of CoC. Hydrotalcite and Ecat coked with VGO.

72.5%, while the actual conversion was 84%. The presence of large amounts of water during combustion may help to increase conversion through combustion as less oxygen is used to combust CO into CO_2, and thus, more oxygen is available to combust coke into CO.

5. Conclusions

An important barrier to the processing of residual feedstocks with high Conradson Carbon is their high coking tendency that exceeds the heat management capacity of the FCC unit. This can be overcome by performing the endothermic coke steam reforming together with coke combustion in the regenerator, so that the catalyst can be regenerated while the regenerator temperature is

maintained at reasonable levels. A heat balance around the regenerator has shown that 25–40% of the coke-on-catalyst has to be removed though steam reforming with feeds containing 5–20% CCR in order to maintain the regenerator temperature within the usual range for FCC operation. Typical FCC catalysts have very low activity in steam reforming, but the impregnation with select metals increases the steam reforming rate 50–150%. We have found that hydrotalcite has a steam reforming activity several times higher than FCC catalyst. This creates the possibility to perform steam reforming along with combustion to completely regenerate the cracking catalyst under operating conditions that are not very far from typical FCC conditions, and in any case, under much milder conditions than for thermal steam reforming. The steam reforming reaction has been found to be a first-order reaction over an FCC
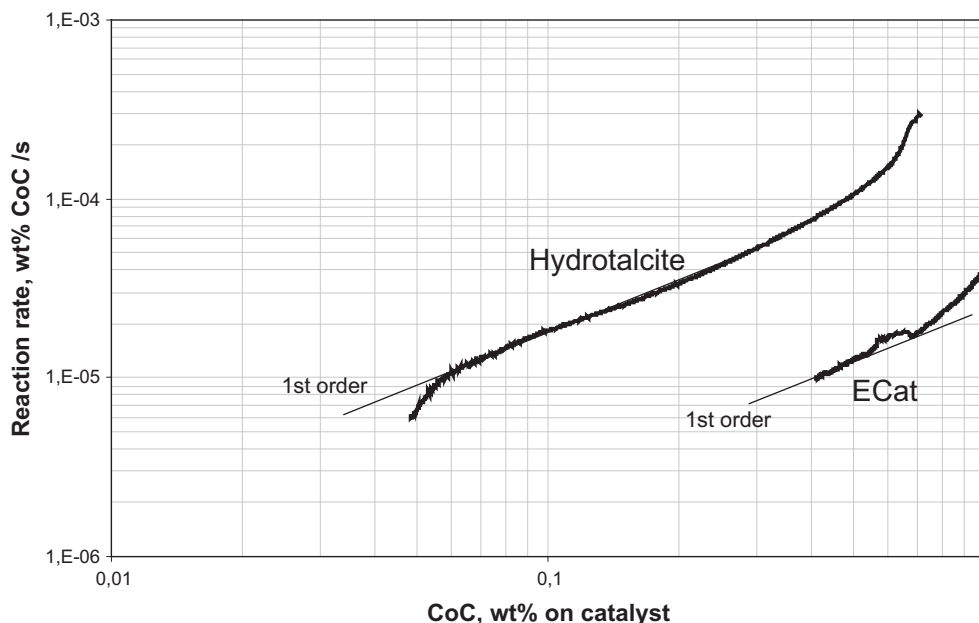
Fig. 11. Log of reaction rate r_C vs. Log of coke-on-catalyst (CoC) for hydrotalcite compared with Ecat. Hydrotalcite reaction rate has been corrected taking into account a 0.2 wt.% coke-on-catalyst fraction that is difficult to reform.

Table 5
Conversion and selectivity results for steam reforming experiments in fixed bed with hydrotalcite, 20 min time-on-stream, 90 kPa water partial pressure, several temperatures and feeds. coke-on-catalyst (CoC) before the experiment is also reported.

Feed for coking	VGO	Resid	Resid	Resid
Temperature	750	700	750	770
Water pressure, kPa	90	90	90	90
Initial CoC, wt.%	1.2	3.8	3.8	3.8
Coke conversion, wt.%	64	15	33	50
Yields, vol.%				
CO	13	4	10	16
CO_2	43	10	22	33
CH_4	8	1	1	1
H_2/CO molar	5	7	6	5

Table 6
Simultaneous coke steam reforming and combustion with hydrotalcite catalyst. All testing performed at 770 °C and 20 min time-on-stream while feeding a gas mixture containing water and/or air.

	Combined CSR and combustion	CSR only	Combustion only
Water partial pressure, kPa	90	90	–
O_2 partial pressure, kPa	0.6	–	0.6
Coke conversion	84	50	45
Carbon yields, wt.%, normalized			
CO	21	16	9
CO_2	62	33	36
CH_4	1	1	0
H_2/CO molar	2.7	5.4	–

catalyst at high temperatures (>800 °C). On a hydrotalcite or FCC catalyst at lower temperatures (<800 °C), the reforming reaction rate expression is more complex, and only a fraction of the coke is reformed with a first-order reaction rate. The heterogeneous nature of coke makes necessary a realistic simulation under regen-

erator working conditions at laboratory scale to properly assess the amount of coke removed by reforming.

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