Applied Catalysis A: General 353 (2009) 223–227

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Processing of resid–VGO mixtures in FCC: Laboratory approach

Alejandra Devard, Gabriela de la Puente, Francisco Passamonti, Ulises Sedran *

Instituto de Investigaciones en Catálisis y Petroquímica (INCAPE, FIQ, UNL-CONICET), Santiago del Estero 2654, 3000 Santa Fe, Argentina

ARTICLE INFO

Article history:
Received 4 June 2008
Received in revised form 27 October 2008
Accepted 28 October 2008
Available online 5 November 2008

Keywords:
Catalytic cracking
Resid
Fuels
Catalyst evaluation

ABSTRACT

In order to validate a new method for the evaluation of resid in the laboratory, the conversion of a mixture of 10% of an ATR resid with a FCC VGO feedstock was assessed with two equilibrium catalysts of the conventional and resid type at 550 °C and contact times up to 25 s, and compared with the conversion of the base VGO and ATR under the same conditions. The experiments were performed in a batch, fluidized bed CREC Riser Simulator laboratory reactor. Under these circumstances, the overall conversions of the mixture were not very different from those of the base VGO in the case of the resid catalyst, but increased up to 5% points with the conventional and more active catalyst. For a given conversion level, the yields of the main hydrocarbon groups like dry gas, LPG and gasoline did not change significantly, and were consistent with the reactivity of the pure reactants (VGO and ATR), that showed essentially the same selectivities. The higher coking trend of the ATR was observed moderately in the case of the most active catalyst. The most important changes were noticed in the composition of the various products; for example, with both catalysts, the gasoline cuts produced by the ATR–VGO mixture were less aromatic and more olefinic than those obtained with the pure VGO. It was shown in this new laboratory method that in order to achieve realistic results in the evaluation of the addition of resid to a FCC feedstock, it is necessary to consider simultaneously the mixture intended, the proposed catalyst and the operative conditions.

1. Introduction

The refinery process of catalytic cracking of hydrocarbons (FCC) is facing new trends and demands as a consequence of its versatility and efficiency to transform low value hydrocarbons into products of high value and use [1]. The increasing restrictions about fuels composition, the social calls to decrease the environmental impact of petroleum processing and use, and the economy of refining, together with the increasing interaction with petrochemistry, lead to important changes in the process.

At present, worldwide, the steady decrease in fuel oil consumption and the extremely high cost of crude motivate the increasing utilization of residual hydrocarbon cuts in FCC units [2] that are added to conventional feedstocks namely vacuum gas oils (VGO). Resids enclose a broad range of feeds, such as atmospheric (ATR) or vacuum (VTR) distillation tower bottoms, deasphalted oil or aromatic extracts [3]. The inclusion of resid in FCC feedstocks is not a new approach, but a rather regular operative strategy; however, the proportions of resid into VGO have been increasing steadily and most of FCC technology licensors developed processes that are able to cope with full-resid feedstocks [4,5]. Moreover, if some of the various processes that can handle and convert resids into more attractive products, such as hydrocracking, coking, solvent deasphalting or FCC, are considered, FCC may result the most convenient in many cases [6].

Resids are different from conventional VGO feedstocks in their higher content of catalyst contaminant metals such as Ni, V, Na and Fe, of polynuclear aromatics that are strong coke forming compounds and of sulfur and nitrogen heteroatom species that contribute to SO_x and NO_x emissions and to sulfur-containing hydrocarbons in the products [2]. Resid components average very high molecular weights over 1000 g gmol^{-1} [7] that boil above 530 °C. They have a high content of naphthenics, aromatics, resins and asphaltenes [7] and their chemical structure is extremely complex [8]. It is a consequence that resids have a large CCR Conradson carbon index, above 2, which means that the coking potential is high.

Resid processing in FCC generates demands of fundamental knowledge, such as the specific reactivity of the particular residual cut, and requires a close evaluation of catalysts and feedstocks. Indeed, usually the particular characteristics of resids call for higher thermal levels to achieve convenient conversions, and the catalysts must obey a number of conditions, such as (a) higher thermal and hydrothermal resistance; (b) higher contaminant

---

* Corresponding author. Tel.: +54 342 452 8062; fax: +54 342 453 1068.
E-mail address: usedran@fiq.unl.edu.ar (U. Sedran).

0926-860X/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcata.2008.10.036

metals tolerance; (c) minimum coke yield; (d) good relationship between catalytic and thermal bottoms conversion and (e) minimum intraparticle mass transfer limitations. Under these conditions, and also considering the particular operative approaches, certainly a given catalyst will not be the optimum choice in many cases; thus, custom-made catalysts are needed.

When added to conventional FCC feedstocks, and even though their properties differ substantially, it is not a common practice to evaluate resid conversion on purpose. Andersson and Myrstad [9] evaluated ATR resids by combining microactivity test (MAT fixed bed reactor) and pilot plant results. Besides the short contact time resid test (SCT-RT [10]), there are no specific laboratory techniques for the evaluation of residual feedstocks. Moreover, since for a given refinery it is usual to change the proportion of resid into VGO frequently, the procedure of resid catalyst evaluation and selection must take not only the resid and the conventional feedstock into account, but also the process conditions, thus adding a strong factor of complexity [11].

It is the objective of this work to define a new method to evaluate the impact of the addition of residual feedstocks to conventional VGO using experimental conditions close to those in the refinery and a CREC Riser Simulator reactor [12]. The soundness of the method will be analyzed through the comparison of the performances of two equilibrium commercial FCC catalysts, of the resid and conventional types, in the conversion of an atmospheric resid from a naphthenic crude added to a VGO FCC feedstock.

2. Experimental

The conversion experiments were performed in a batch fluidized bed laboratory unit with internal recirculation, the CREC Riser Simulator reactor [12] that was specifically designed for FCC studies; additional descriptive details of the setup can be found in, e.g., Ref. [13]. Reaction temperature was 550 °C, reaction times ranged from 5 to 25 s and catalyst to oil ratio was 5.8, achieved with a catalyst mass of 0.8 g. Runs were performed with a VGO feedstock alone and mixed with 10 wt.% of ATR for each catalyst and every experimental condition. Mass balances in all the experiments closed to approximately 95%.

Two commercial FCC catalysts equilibrated in refineries that were named E-cat D (conventional type) and E-cat R (resid type), were used. Their properties are shown in Table 1. The residual feedstock, obtained from a naphthenic crude, is the bottom stream from an atmospheric distillation tower (ATR), its properties and those of the base VGO being shown in Table 2. Some experiments were performed with the ATR feedstock alone, using catalyst E-cat R, and the results were evaluated with the approach by de la Puente et al. [14].

Table 1
Catalyst properties.

Property	Catalyst	
	E-cat R	E-cat D
UCS[a] (nm)	2.427	2.423
Specific surface area[b] ($m^2\,g^{-1}$)	125.0	139.4
Zeolite content[c] (wt.%)	14.8	16.9
REO[d] (wt.%)	2.94	1.26
Fe (wt.%)	0.42	n.a.
Ni (wt.%)	0.51	0.40
V (wt.%)	0.58	0.27
AAI[e]	8.3	5.5

[a] Unit cell size, ASTM D-3942-85.
[b] BET method, N_2 adsorption.
[c] Johnson's method [23].
[d] Rare earth oxides.
[e] Akzo Accesibility Index.

Table 2
Properties of the feedstocks.

	VGO		ATR resid	
Density ($g\,cm^{-3}$)	0.916		0.954	
°API	22.3		16.2	
Sulfur (%)	2.03		1.4	
CCR (%)	0.11		8.11	
Total nitrogen (ppm)	1441		1650	
Iron (ppm)	2.4		28	
Nickel (ppm)	0.1		13	
Vanadium (ppm)	0.7		30	
Distillation (°C)	10%	361	Initial	295
	30%	408	10%	411
	50%	432	20%	449
	70%	456	30%	473
	90%	494	40%	500
			Final	514
			Yield	45.6%

Reaction products were analyzed on-line by conventional capillary gas chromatography. Coke was assessed by means of a temperature programmed oxidation method, in which carbonaceous materials are burnt off and later the carbon oxides formed are converted to methane and quantified by a FID detector. For every experiment it is possible to assess the yield of individual hydrocarbons or groups, and the following main groups were defined: dry gas (C1–C2), LPG (C3–C4), gasoline (C5–216 °C), LCO (216–344 °C), bottoms (compounds boiling over 344 °C) and coke. Conversion was defined as the sum of the yields of dry gas, LPG, gasoline and coke. Selectivities were calculated as the relationships between the corresponding yields and conversion.

3. Results and discussion

A VGO FCC feedstock was used pure and mixed with 10% of an ATR stream. The proportion of resid was considered as certainly representative of trials in refineries aimed at reducing the amount of residual streams but without altering significantly the FCC

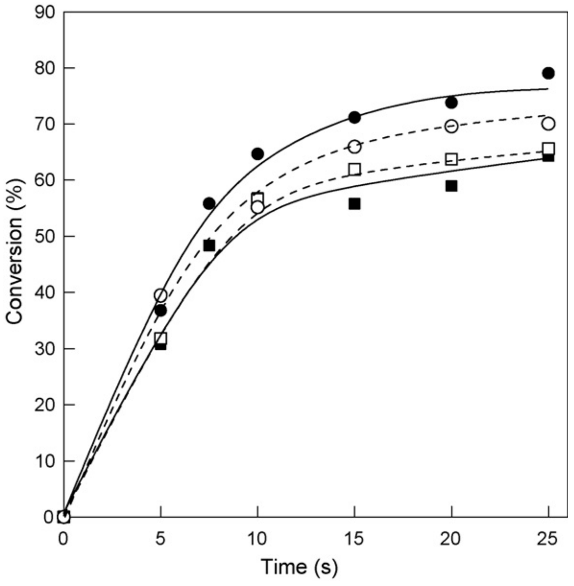

Fig. 1. Conversion of the ATR–VGO mixture (closed symbols, full lines) and pure VGO (open symbols, dashed lines) feedstocks over catalyst E-cat D (●) and E-cat R (■) as a function of time. Temperature: 550 °C.

operation. The conversions of the VGO alone and of the ATR–VGO mixture are shown in Fig. 1 as a function of reaction time for both catalysts. Since the CREC Riser Simulator reactor is a closed system, conversion increases steadily. The conversions observed are in the range of commercial values, although they were reached at reaction times longer than those in FCC units. It is clear that whatever the feedstock used, catalyst E-cat D, of the conventional type, is more active than catalyst E-cat R, that was developed for resid processing. This characteristic of the conventional catalyst is observed even though the unit cell size of the zeolite component, that is usually linked to zeolite activity, is smaller in this catalyst than that of catalyst E-cat R; however, the higher activity could be attributed to the higher zeolite content, the higher specific surface area, and the lower content of contaminant metals. The contribution by the rare earths to the performance of the catalysts is analyzed later in this paper.

However, it is to be noted that when the ATR is added to the VGO, the response of each catalyst is significantly different. In effect, in this case conversion for catalyst E-cat R is the same or slightly lower for a given reaction time, but conversion in the high activity catalyst E-cat D increases in about 5–6% points when reaction time is over 10 s. This could be the consequence of the higher reactivity of a fraction of the resid in relation to the VGO. Some hydrocarbon molecules in the resid, with higher molecular weight, could have long aliphatic chains in the aromatic rings, longer than those in the VGO, that would behave in FCC in a way similar to a more paraffinic, lighter feedstock [15,16]. The activity of the catalyst E-cat R would not be enough to exhibit this behavior with the mixture.

The yields of the main hydrocarbon groups obtained with both catalysts in the conversion of the VGO and the ATR–VGO mixture can be observed in Fig. 2. The addition of resid to the conventional feedstock, at least under these conditions and catalysts, does not produce significant variations in the yields and corresponding selectivities to the main groups. Thus, the differences that could be observed at a given reaction time, correspond to the lower or higher conversion of the mixture as compared to pure VGO. In the particular case of the more active catalyst E-cat D, a very slight decrease in the selectivity to gasoline can be observed when the resid is added, and the higher coke forming potential of the resid is perceived under the conditions used through a very slight increase in coke yields.

These results are consistent with observations of the reactivity of this resid (pure) at 550 °C on the same catalysts with a technique involving low reactivity solvents (the performance of catalyst E-cat D in the conversion of the resid was reported in a previous work [14]). It was shown that the resid alone can be converted above 75%, with selectivities to the main hydrocarbon groups that are very similar to those observed in the conversion of the VGO alone, as shown in Fig. 2. The yield curves show that in this particular case, with the ATR and the VGO from different crude sources, the yields still follow essentially the same trends, with the only exception of LCO, that is originally present in the VGO but not in the resid. The higher coking trend of the resid in this case would be the result of the higher conversions (refer to the higher coke selectivity at high conversions).

The properties derived from the different formulation of the catalysts reflect clearly in the comparison of the various product yields that are obtained on each of them. In effect, with both feedstocks, the most active catalyst E-cat D produces more dry gas and LPG, and less gasoline than catalyst E-cat R (refer to Fig. 2a and b). Another different characteristic between catalysts is that catalyst E-cat R, which was designed specifically to convert residual feedstocks, shows a better coke selectivity considering the poisonous metal content, a fact that is crucial to keep a proper energy balance in these operations with resid included.

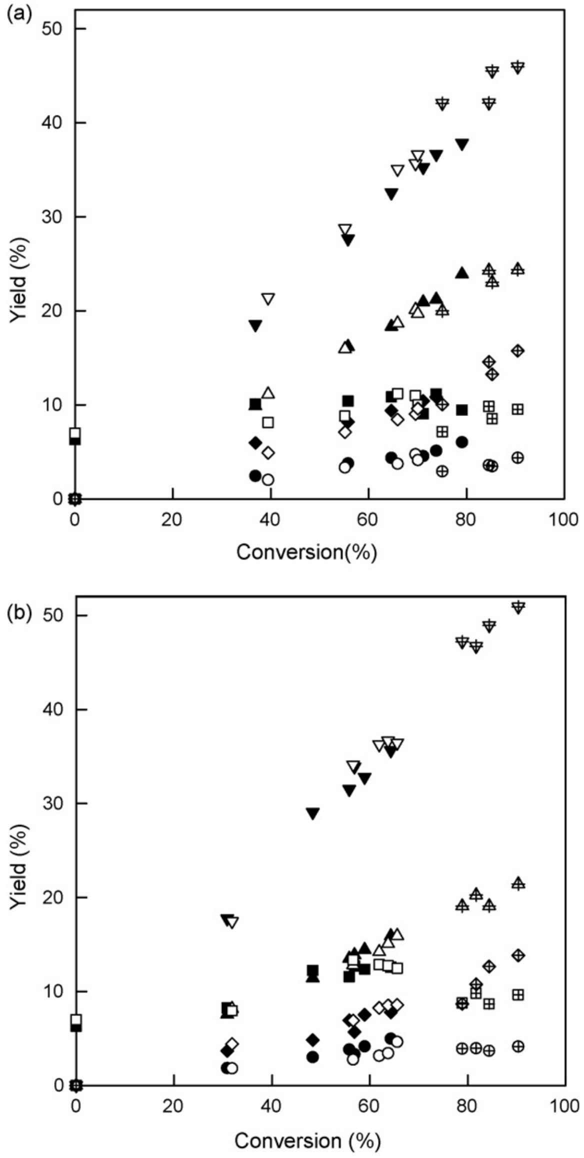

Fig. 2. Hydrocarbon yields as a function of the conversion of VGO, ATR–VGO mixture and ATR resid feedstocks. Temperature: 550 °C. (a) Catalyst E-cat D and (b) catalyst E-cat R. Symbols: open (VGO), closed (ATR–VGO mixture), + center (ATR resid); dry gases (●); LPG (▲); gasoline (▼); LCO (■); coke (◆).

For a given feedstock, the catalyst properties also reflect on the composition of gasoline, as can be observed in the comparison of Fig. 3a (catalyst E-cat D) and b (catalyst E-cat R). For both VGO and ATR–VGO mixture, it is evident that catalyst E-cat R, with lower hydrogen transfer ability, as a consequence of its high content of rare earth oxides, yields a gasoline with more olefins and less aromatics and isoparaffins than catalyst E-cat D [17]. Rare earths are considered crucial to improve hydrogen transfer properties, but if the load is above approximately 3%, like in the case of catalyst E-cat R, rare earth ions may form OH bridges between them, leading to a decrease in the catalyst acidity, below that expected from the hydrolysis of the individual cations [18]. Based on a large equilibrium FCC catalyst database, it has also been postulated that high accessibility catalysts, like E-cat R, with an Akzo Accesibility Index of 8.3, would show less hydrogen transfer than low accessibility catalysts [19].

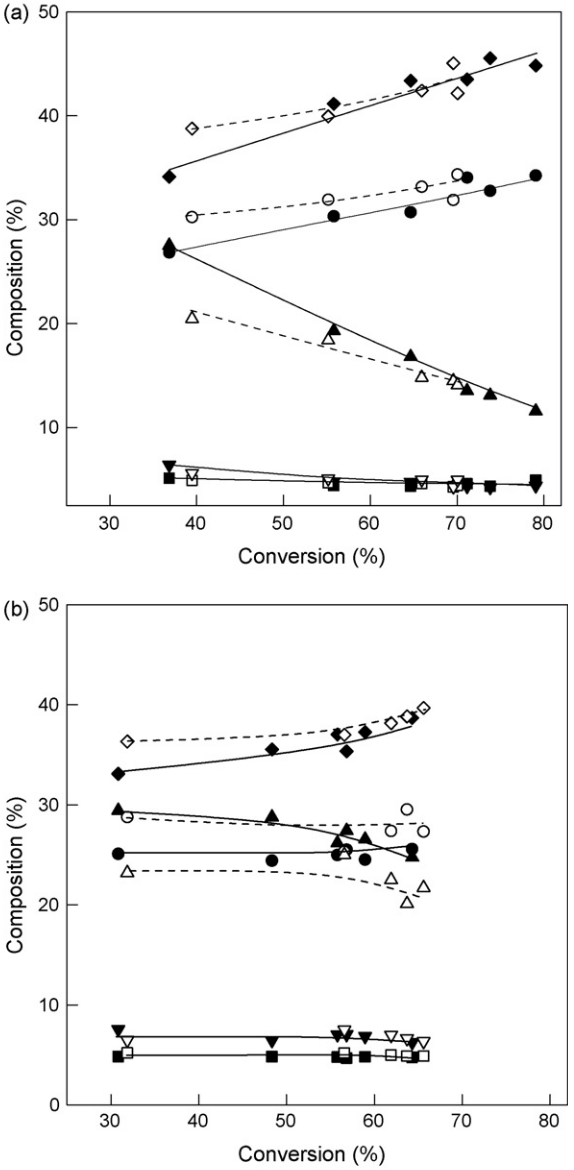

Fig. 3. Gasoline composition as a function of the conversion of VGO (open symbols, dashed lines) and ATR–VGO mixture (closed symbols, full lines) feedstocks. Temperature: 550 °C. (a) Catalyst E-cat D and (b) Catalyst E-cat R. Symbols: aromatics (◆); i-paraffins (●); olefins (▲); *n*-paraffins (■); naphthenics (▼).

Table 3

Overall and LPG isobutane selectivity and C4 and C5 group olefinicity in the conversion of the VGO, the ATR and their mixture. Temperature 550 °C. Conversion: 65%.

	Catalyst					
	E-cat D			E-cat R		
	VGO[a]	ATR–VGO[a]	ATR[a,b,c]	VGO[a]	ATR–VGO[a]	ATR[a,c]
iC4 selectivity (%)	9.0	8.8	7.1	5.2	5.2	5.6
iC4/LPG	0.31	0.31	0.26	0.23	0.21	0.24
C4 = /C4total	0.33	0.34	0.45	0.48	0.51	0.53
C5 = /C5total	0.29	0.30	0.48	0.40	0.47	0.53

[a] Feedstock.
[b] From Ref. [14].
[c] Conversion 75%.

The most important effect of this particular addition of resid to VGO can be observed in the comparison of the composition of the gasoline cuts, that determines its quality. In effect, it can be seen in Fig. 3 that when resid was added to VGO, changes are more perceptible in the case of the resid catalyst E-cat R (Fig. 3b), where the content of olefins in gasoline increased significantly, and the proportions of aromatics and isoparaffins decreased, in the whole range of conversions. These observations are coincident with those in commercial and fluidized bed laboratory ACE units [16], where the conversions of pairs of VGO and resid from the same crude (paraffinic and naphthenic, respectively) were compared. It was confirmed in that work that, independently from the conversion level, the gasoline obtained from the resid is less aromatic than that from the VGO. This fact was considered the consequence of the occurrence of heavy aromatic hydrocarbons with long aliphatic substituting chains that confer the resid a more paraffinic-like behavior, as compared to the VGO. The same changes in gasoline composition after adding resid to a lighter feedstock (increase in olefinicity, decrease in aromatic character) were also observed when using an ATR–LCO mixture [20]. In the case of catalyst E-cat D, the addition of resid produced changes in the gasoline composition with the same trends as those observed on catalyst E-cat R, but that are only significant at low conversion levels below 55%, that is, far from usual refinery values. On the contrary, Arandes et al. [21] observed an increase in the concentration of aromatics in gasoline when cracking a mixture of 20% ATR in VGO that was justified based on dealkylation of heavy aromatics.

The more significant effect of the addition of the resid on the composition of the gasoline that is observed on catalyst E-cat R can be explained on the fact that this catalyst, given its higher accessibility, would adsorb components from the resid more extensively than catalyst E-cat D. As a consequence, the reduction of the density of paired sites would be more important and impact more significantly on hydrogen transfer, given its dependence on that surface property [22], and reflect on the higher yields of olefins in gasoline. These matters are also confirmed by the higher selectivities to C4 and C5 olefins when the ATR is cracked over catalyst E-cat R, as shown in Table 3.

This type of study is also useful to determine the yield of particular hydrocarbons as, for example, isobutane, or C4 or C5 olefins that can be used as raw materials for other processes. It can be seen in Table 3 that the ATR forms more light olefins than the VGO over the two catalysts; however, this fact is again extended to the mixture only in the case of catalyst E-cat R.

The set of observations about yields, selectivities and group compositions produced with the ATR and the VGO alone, as well as with their mixture, over these catalysts strongly suggest that the impact of the addition of a resid cannot be evaluated with information from the base reactants only, but the proposed mixture must be analyzed. Similarly, besides using different techniques, Andersson and Myrstad [9] concluded that the same feed as used in commercial units should be used in the evaluation of resid catalysts.

4. Conclusions

The impact of using mixtures of resids and conventional FCC feedstocks can be evaluated properly in the laboratory by using a CREC Riser Simulator reactor. The experiments under conditions close to those of the commercial operation revealed the characteristics of each of the two commercial equilibrium catalysts (resid and conventional types) used, thus providing validity. The use of a realistic amount of ATR resid in the mixture imposed slight changes in the yields of the main hydrocarbon groups. This behavior was consistent with the own reactivity of the pure resid, that showed selectivities to the main hydrocarbon groups very similar to those with the pure VGO and, consequently, with their mixture. However, overall conversion was different for each catalyst: the most active one (conventional) increased conversion of the mixture as compared to pure VGO, while the resid catalysts showed essentially the same levels. The most important changes were observed in the compositions of products, as the gasoline cut, that became less aromatic and more olefinic in nature, or the light olefins, with particularities according to the catalysts' formulations.

In order to achieve realistic results in the laboratory evaluation of the addition of resid to a FCC feedstock, the comparison with the conversion of the resid and the VGO alone under similar conditions showed that it is necessary to consider simultaneously the mixture intended, the proposed catalyst and the operative conditions.

Acknowledgements

This work was performed with the financial assistance of University of Litoral (Santa Fe, Argentina), Secretary of Science and Technology, Proj. CAID 2005 #01-07; CONICET, PIP 6285/05 and the National Agency for Scientific and Technological Promotion, PICT2005 14-32930.

References

[1] P. O'Connor, Stud. Surf. Sci. Catal. 166 (2007) 227–251.
[2] R.H. Harding, A.W. Peters, J.R.D. Nace, Appl. Catal. A: Gen. 221 (2001) 389–396.
[3] U. Alkemade, S. Paloumbis, Stud. Surf. Sci. Catal. 100 (1996) 339–354.
[4] C.R. Marcilly, R.R. Bonifay, Arab. J. Sci. Eng. 21 (1996) 627–652.
[5] S. Tan, P. Satbhai, PTQ (Winter) (1999) 47–51.
[6] G. Phillips, PTQ (Spring) (2002) 93–99.
[7] J.R.D. Nee, P.A. Diddams, S.S. Paloumbis, PTQ (Summer) (2001) 37–41.
[8] W.S. Letzsch, A.G. Ashton, Stud. Surf. Sci. Catal. 76 (1993) 441–498.
[9] S.-I. Andersson, T. Myrstad, Stud. Surf. Sci. Catal. 166 (2007) 13–29.
[10] K.Y. Yung, P. Imhof, M. Baas, American Chemical Society FCC Symposium, Boston, MA, August 18–22, 2002. Petroleum Chemistry Division Reprints 47, (2002), pp. 281–288.
[11] M. Mitchell, J.F. Hoffman, H.F. Moore, Stud. Surf. Sci. Catal. 76 (1993) 293–338.
[12] H.I. de Lasa, U.S. Patent 5,102,628 (1992).
[13] F.J. Passamonti, G. de la Puente, U. Sedran, Ind. Eng. Chem. Res. 43 (2004) 1405–1410.
[14] G. de la Puente, A. Devard, U. Sedran, Energy Fuel 21 (2007) 3090–3094.
[15] A. Corma, L. Sauvanaud, Stud. Surf. Sci. Catal. 166 (2007) 41–54.
[16] W.R. Gilbert, C.A. Baptista, A.R. Pinho, Stud. Surf. Sci. Catal. 166 (2007) 31–39.
[17] F.J. Passamonti, G. de la Puente, U. Sedran, Ind. Eng. Chem. Res. 46 (2007) 9269–9273.
[18] F. Lemos, F. Ramoa Ribeiro, M. Kern, G. Giannetto, M. Guisnet, Appl. Catal. 39 (1988) 227–238.
[19] S. Foskett, Catal. Courier 69 (Autumn) (2007) 10–13.
[20] G. de la Puente, A. Devard, U. Sedran, in: Proceedings of the XV Congreso Argentino de Catálisis and IV Congreso de Catálisis del Mercosur, La Plata, Buenos Aires, Argentina, November 12–16, 2007, ID-157.
[21] J.M. Arandes, I. Torre, M.J. Azkoiti, J. Ereña, J. Bilbao, Energy Fuels 22 (2008) 2149–2156.
[22] G. de la Puente, U. Sedran, Chem. Eng. Sci. 55 (2000) 759–765.
[23] M.F.L. Johnson, J. Catal. 52 (1978) 425–431.