Catal Lett (2009) 130:86–92
DOI 10.1007/s10562-009-9911-4

Catalytic Cracking of Heavy Olefins into Propylene, Ethylene and Other Light Olefins

R. Le Van Mao · A. Muntasar · H. T. Yan · Q. Zhao

Received: 12 January 2009 / Accepted: 17 February 2009 / Published online: 4 March 2009

Abstract Hybrid catalysts developed for the thermo-catalytic cracking of liquid hydrocarbons were found to be capable of cracking C_4^+ olefins into light olefins with very high combined yields of product ethylene and propylene (more than 60 wt%) and C_2–C_4 olefins (more than 80 wt%) at 610–640 °C, and also with a propylene/ethylene weight ratio being much higher than 2.4. The olefins tested were heavier than butenes such as 1-hexene, C_{10}^+ linear alpha-olefins (LAO) or a mixture of LAO. The hydrogen spillover effect promoted by the Ni bearing co-catalyst, contributed to significantly enhancing the product yield of light olefins and the on-stream stability of the hybrid catalyst.

Keywords TCC-type hybrid catalysts · Cracking of heavy olefins · Effect of hydrogen spillover on product yields and coke deposition

1 Introduction

Light olefins, particularly the high-volume produced ethylene and propylene, are the backbone of the petrochemical industry [1]. Ethylene and propylene are experiencing continuous growth due to a sustained worldwide demand. However, in recent years, propylene is booming on the demand site [2], so that the industry has to move this intermediate from the state of by-product of the hydrocarbon steam cracking (SC) into that of one of the main products. Thus, several processes are being used for an increasing production of propylene, such as propane dehydrogenation, olefin metathesis and mostly (modified) fluid catalytic cracking (FCC).

The thermo-catalytic cracking process (TCC) of various liquid hydrocarbon feedstocks (naphthas, gas oils) has been recently developed with the main objective to produce ethylene and propylene, the product propylene/ethylene weight ratio being higher than that obtained by the conventional steam cracking [3–6]. In addition, the TCC process shows some other important technical and environmental advantages (lower reaction temperatures and less carbon deposition on the reactor walls) [5, 6].

The most recent version of the TCC catalysts possesses a hybrid configuration that comprises of a main component and a co-catalyst [5, 6]. The role of the main catalyst component is to crack large hydrocarbons of the feed over the cracking sites provided by the (Mo–P) species while the resulting smaller molecules are subsequently cracked onto the (ZSM-5) zeolite acid sites [5]. The co-catalyst contains a noble metal (Pt or Pd) or Ni being dispersed on a very hydrothermally stable support [5–7]. The role assigned to the co-catalyst is to prevent or slow down the currently rapid formation of coke due to the cracking reaction at such relatively high temperatures. It has been seen that if a rigid and compact network of two “ideally sparse” nano-sized particles could be created by using bentonite clay for instance as binding/pressurizing agent, some reaction intermediates would be transferred from one particle to the other, in virtue of the “pore continuum” concept [5, 6, 8–13]. In many reactions (particularly aromatisation, cracking of paraffins and hydrogenation [5–15]), the involved reaction intermediates are “in situ produced” hydrogen species.

R. Le Van Mao (✉) · A. Muntasar · H. T. Yan · Q. Zhao
Industrial Catalysis Laboratory, Department of Chemistry and Biochemistry, Concordia University, 7141 Sherbrooke West, SP 275-09, Montreal, QC H4B 1R6, Canada
e-mail: lvmao@alcor.concordia.ca

Particularly in the present study, the co-catalyst contains an active surface capable of promoting the hydrocarbon steam-reforming (Ni, for instance [6]). Thus, some hydrogen species are produced and they can be spilt-over onto the surface of the main acidic component. These hydrogen spilt-over (HSO) species, once in contact with the acidic sites, can control the formation of coke precursors (and finally, coke), thus enhancing the on-stream stability of the hybrid catalyst [5, 6]. However, these (HSO) species are predominantly active on acidic sites located at the external surface (and the pore openings) of the ZSM-5 zeolite particles [16]. It is to note that the phenomena of hydrogen spillover are well proven [17–20, and references]; however, the nature of these species are still a matter of controversy. In addition, the amount of these super-active and in situ formed hydrogen species is generally very small but their action is quite distinguishable from that of molecular hydrogen that may be present in the reaction medium [6].

The main objective of this paper is to show the capability of the TCC-type hybrid catalysts to efficiently crack olefinic hydrocarbons into propylene and other light olefins, as also suggested in our recent patent application [21].

We have chosen to investigate the cracking of (C_4^+) heavy olefins because they are the main by-products of two industrial processes of great interest, as shown in the following:

(1) *methanol-to-olefins*: Essentially, synthesis gas that can be first produced from natural gas or other solid raw materials (biomass or coal, by gasification) can be then converted into methanol. Olefins are subsequently produced using zeolite or zeolite-type materials via a process called MTO (methanol-to-olefins or MTO, which was developed by Mobil oil [22–24]). However, some olefins heavier than C_4 are also produced in significant amounts, so that it is advantageous to crack further these olefins into lighter olefins (ethylene and propylene). This is the reason why, in the new pilot plant built by Total (France) in Feluy, Belgium [25, 26], the UOP/Total cracking process (OCP) is being integrated into the main MTO process (UOP/Hydro). It is to note that methanol (and its alcohol derivatives) is a viable alternative to always problematical and dwindling energy resources based on fossil fuels [23, 24], because methanol can be produced from a variety of raw materials such as natural gas, coal and biomass via technologically feasible processes.

(2) *cracking of C_{10}^+ olefins*: The synthesis of C_4–C_{20} linear alpha-olefins (LAO) by dimerization/oligomerization of ethylene has become a topic of a considerable amount of fundamental and applied investigations because of growing demand as co-monomers with ethylene, plasticizers and detergents [27–29]. Since the demand for C_4–C_{10} LAO being used for the production of branched linear low-density polyethylene, poly-alpha-olefins, synthetic lubricants and additives for high-density polyethylene, is growing much faster than that of LAO in the C_{12}^+ range (used to produce surfactants) [28], some of the latter ones may be available for further conversion into more valuable chemicals or intermediates. Thus cracking of these C_{12}^+ olefins into light olefins using TCC-type hybrid catalysts was proposed [21].

2 Experimental

2.1 Preparation of the Hybrid Catalyst

The procedure used was similar to that described in references [5, 6].

2.1.1 Main Catalyst Component

About 50 g of HZSM-5 (powder, acid form, silica/alumina molar ratio = 50, purchased from Zeochem, Switzerland) were added to a solution that was composed of 25.0 g of lanthanum nitrate hydrate (strem chemicals) in 500 mL of deionized water. The suspension, gently stirred, was heated to 80 °C for 2 h. After filtration, the obtained solid was washed on the filter with 500 mL of water, then dried at 120 °C overnight and finally activated at 500 °C for 3 h. This material was called La-HZSM-5.

A solution of 5.52 g of ammonium molybdate hexahydrate (Aldrich) in 89 mL of 2.3 N H_3 PO_4 in water was homogeneously impregnated onto 40.02 g of La-HZSM-5. The solid was dried at 120 °C overnight and finally activated at 500 °C for 3 h.

Its chemical composition was as follows: MoO_3, 8.0 wt%; La_2O_3, 2.5 wt%; phosphorous, 4.1 wt%; and zeolite, balance.

2.1.2 Co-Catalyst

A mixture of 2.59 g of nickel nitrate hexahydrate (strem) in 20 mL of deionized water and 0.036 g of ruthenium acetylacetonate (Strem) in 25 mL of methanol, was homogeneously impregnated onto 20.0 g of yttria-stabilized alumina aerogel (Y-AS) [5]. After drying at 120 °C overnight, the solid was activated at 500 °C for 3 h. Its chemical composition was: nickel, 2.5 wt%; ruthenium, 0.05 wt%; and Y-AS, balance.

Because the TCC-type hybrid catalysts were used in this work at relatively high temperatures and in the presence of steam, both the main zeolite bearing components and the co-catalysts (thus, their support, the yttria-stabilized alumina aerogel, Y-AS) were thoroughly investigated and found to be thermally and hydrothermally stable in the reaction conditions used [7].

2.1.3 *Preparation of the Final Hybrid Catalyst*

This hybrid catalyst, HYB, was obtained by extruding with bentonite clay (Aldrich) the solid mixture of the main component (M-Cat) particles and the (Co-Cat) ones, in the following proportions: M-Cat, 65.6 wt%; Co-Cat, 16.4 wt%; bentonite (binder), 18.0 wt% [6]. The final catalyst was dried in air at 120 °C overnight and activated at 700 °C for 5 h. The resulting extrudates were mechanically strong, ensuring thus a stable hybrid (M-Cat/Co-Cat) configuration.

The reference catalyst, REF, was obtained by extruding M-Cat with the co-catalyst support (Y-AS). The resulting extrudates were also dried in air at 120 °C overnight and activated at 700 °C for 5 h.

2.2 Catalyst Characterization

The techniques used for the characterization of the HYB and REF catalysts include: atomic absorption spectroscopy (chemical composition), BET total surface area and pore size by nitrogen adsorption/desorption, surface acidity (density of acid sites and their distribution in terms of strength) by NH_3 adsorption/TPD and by using a pH meter equipped with an-ion selective electrode (ISE) [30], and thermogravimetric analysis (TGA) and differential analysis (DTA), as reported elsewhere [5, 6]. In particular, these thermal analyses were carried out in a PL Thermal Sciences model STA-1500 apparatus, and the results were used to assess the amount of bound species and/or coke deposited onto the catalyst surface. The flow rates of argon (Ar, inert gas) and air (oxidative gas) were set at 20 mL/min. The rate of the temperature heating was set at 10 °C/min. This combined TGA/DTA system is particularly useful for simultaneously observation of weight changes and reactions/phase changes occurring in the bulk or the surface of the sample being investigated.

2.3 Experimental Set-up and Testing Procedure

The experimental set-up and testing procedure were similar to those previously reported [5, 6]. Liquids—namely, hydrocarbon feed and water—were injected into vaporizers using two infusion pumps. Steam and vaporized hydrocarbons were thoroughly mixed, and the resulting gaseous mixture was sent into a quartz tubular reactor (length = 140 cm, OD = 1.5 cm, and ID = 1.2 cm), heated in a tubular furnace with three heating zones [6].

Product liquid and gaseous fractions were collected separately, using a system of condensers. These fractions were analyzed using the gas chromatographic methods as reported in the previous paper [6].

The testing conditions used were as follows: total weight hourly space velocity (WHSV), 3.0 h^{-1}; catalyst weight, 5 g; steam/feed weight ratio, 0.5; reaction temperature, 615–630 °C.

The yield of product *i* was expressed as the number of grams of product *i* recovered by 100 g of hydrocarbon feed injected (wt%).

It is important to note that the experimental error usually observed on calculated product yields was ±0.2 wt%.

Long-term testing of catalysts, in the context of a university research laboratory, was designed as follows. A first run was performed with the hydrocarbon feed for 5 h. Then the feed was stopped while the heating and the flow of steam were kept unchanged till the next day. Another run of 5 h was carried out, and then the hydrocarbon feed was stopped for 24 h, and so forth. At the end of the second run, the time on stream (TOS) was 10 h and the heating time of the catalyst bed was 29 h.

Finally, a series of tests was carried out with a C_{10}–C_{18} linear alpha-olefins, MIX-LAO, whose composition was as follows (in wt%): 1-decene, 38.9; 1-dodecene, 26.2;1-tetradecene, 17.0; 1-hexadecene, 11.0; 1-octadecene, 6.9.

3 Results and Discussion

Table 1 reports the main physico-chemical characteristics of the HYB and REF catalysts and their components. The used catalysts (10 h of TOS) after regeneration in air at 600 °C overnight did not show any significant change in terms of surface area and surface acidity. In Table 2 are reported the distribution of the acid sites in terms of acidity strength for various powders used for the preparation of the hybrid and reference catalysts.

As shown in Table 2, the incorporation of the (Mo-P) species onto the ZSM-5 particles (for the production of the M-Cat) shifted the distribution of zeolite acid sites to the weaker (acid) strength region while the incorporation of Ni (and Ru) species onto the Y-AS (for the preparation of the Co-Cat) did not significantly change the total density of acid sites or their distribution. Because of the weakness of the acid sites of the Y-AS and the Co-Cat, their contribution to the catalytic cracking should be negligible.

In the formulation of the Ni bearing Co-Cat, Re or Ru was incorporated in very small amounts [6] because it was found that the presence of the second metallic oxide contributed to the thermal stability of the co-catalyst. The same

Table 1 Main physico-chemical characteristics of the HYB and REF catalysts, and their components

	Form	SiO_2/Al_2O_3	Surface area (m^2/g)		Surface acidity (10^{-3} mol/g)
			Micropores	Large pores	
H-ZSM-5	Powder	59	262	141	0.51
Y-AS	Powder	0	0	291	0.27
M-Cat	Powder	57	178	47	0.43
Co-Cat	Powder	0	29	218	0.25
HYB	Extrudates	NA	102	96	0.32
REF	Extrudates	NA	116	115	0.33

NA not applicable

Table 2 Distribution of acid sites in terms of their strength (referred to the powder form)

	Acid sites density (10^{-3} mol/g)	Acidity strength (distribution in %)	
		Weak [w] + medium	Strong
H-ZSM-5	0.51	29	71
Y-AS	0.27	100 [w]	0
M-Cat	0.43	55	45
Co-Cat	0.25	100 [w]	0
Bentonite[a]	0.00	0	0

[a] Used for the preparation of the final extrudates, surface area lower than 0.5 m^2/g

observation was previously made with the Pd-Sn bearing co-catalyst [5]. The effect of the second metal on the behaviour of bimetallic catalysts has been investigated for many reactions and has resulted in various interpretations [31]. Thus, an ongoing study of the stabilizing effect of Re or Ru on the Ni supported on Y-AS used as co-catalyst in the TCC process, led to the preliminary result that “doped” Ni kept its original dispersion much better than the “undoped” form during the successive steps of reaction and catalyst regeneration. It is to note that TCC hybrid catalysts are being used at relatively high temperatures (715–725 °C) [5, 6].

3.1 Thermo-catalytic Cracking of C_6–C_{10} Linear Alpha-olefins

Cracking of paraffinic hydrocarbons over acidic catalysts is usually assumed to start with the formation of carbocations and then to go through carbenium ions as crucial reaction intermediates, which decompose via beta-scission into olefins and (smaller) carbenium ions [32]. If olefinic feeds are used, the catalytic reaction requires lower temperatures (in fact, 610–640 °C). However, because many reactions can take place simultaneously (C–C bond cleavage, dealkylation, isomerization, etc.), the yields of wanted products (propylene, ethylene, and other light olefins) and the catalyst on-stream stability should be of primary concern for a process scientist. Knowing the beneficial effect of the co-catalyst in the TCC process, we wanted to verify first this fact by comparing the performance of the hybrid catalyst (HYB) with that of the REF sample in the cracking of a heavy olefin.

Figure 1 shows the catalytic behaviour (product C_2–C_4 olefins yield, Y_{LO}) versus the time on-stream (TOS) and heating time (HT) of the HYB catalyst in the presence of 1-hexene as feed. This figure also reports the data obtained with the REF sample, tested in the same reaction conditions.

With the HYB sample, the yield in these light olefins remained constant for at least 15 h as TOS or 53 h as HT while that of the REF catalyst underwent a slow but noticeable decay from the beginning. In addition, the level of conversion to light olefins with the hybrid catalyst was always significantly higher than that of the REF sample (Fig. 1).

The TGA/DTA analyses (Table 3) showed that, while the combustion temperatures (analyses performed in air)

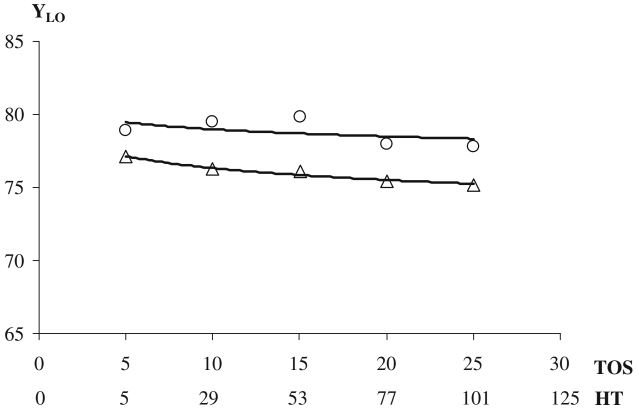

Fig. 1 Catalytic performance of HYB (O) and REF (Δ) (Y_{LO} in wt%) versus time on-stream (TOS in h) and heating time (HT in h) in the cracking of 1-hexene. Reaction parameters (See Sect. 2)

Table 3 Tabulated results for the DTA/TGA analysis of the used reference (REF) and the used hybrid (HYB) catalysts in various environments

Parameter	REF		HYB	
	Ar	Air	Ar	Air
Weight loss (wt%)	15.6	17.2	9.5	9.3
Temperature (°C)	750	530	730	528
Assumed type of reaction				
DTA[a]	TD	COMB	TD	COMB

Desorption of adsorbed water is not reported herein. Reaction parameters: same as in Fig. 1

[a] TD (moderately exothermic), thermal decomposition; COMB (highly exothermic), combustion

were almost equal for the two samples (528–530 °C), the weight losses were 9.3 and 17.2 wt% for the used HYB and REF, respectively (after 25 h, TOS).

Under inert atmosphere (Ar), "adsorbed" species underwent thermal decomposition, as expected, at much higher temperatures (730–750 °C) for both samples. However, the used HYB and REF samples behave differently under the influence of high temperature: (a) the weight loss observed with the (used) HYB sample (Ar atmosphere) was 9.5 wt%, corresponding to almost the weight loss of the same sample upon combustion of the sorbed/deposited species on the catalyst surface (9.3 wt%). (b) the used REF catalyst showed a weight loss of 15.6 wt% in Ar flow, that represented a significant difference with a weight loss of 17.2 wt% recorded for the same sample in air ($\Delta = 1.6$ wt%).

Thermal decomposition (in Ar flow) is assumed to involve firmly chemisorbed species, i.e., coke precursors and not the coke itself. Thus, the difference in weight loss between the combustion and the thermal decomposition of these species recorded during the TGA/DTA analyses of the reference sample REF, represented the amount of coke deposited onto the surface of that catalyst. This means that the co-catalyst (of the HYB sample) was playing its role of "cleaning or preventing the formation" of coke, confirming thus the results obtained in previous investigations [5, 6, 16, 21].

All these results (Fig. 1; Table 3) constitute another evidence of the positive effect of the hydrogen spillover species in the catalytic reactions where the HYB sample containing the Ni bearing co-catalyst was used.

In Table 4 are reported in column 1 the catalytic data of the hybrid catalyst in the conversion of 1-hexene over the hybrid catalyst (all data recorded at TOS = 10 h). The total yield in light olefins (C_2–C_4 olefins) was circa 80 wt% while the yield in "ethylene + propylene" was higher than 60 wt%. The product "propylene/ethylene" weight ratio was as high as 3.5.

It is to note that from the definition of yield given in paragraph 2.3 (Experimental set-up and testing procedure) and from the data reported in Table 4 it is clear that the conversion is 100% for all the reagents.

Table 4 Catalytic results obtained with various olefinic feeds over the hybrid catalyst, HYB

Feed	1-hexene		1-tetradecene	1-hexadecene	1-octadecene	MIX-LAO
Column number	1	2[a]	3	4	5	6
Product yield (wt%)						
Hydrogen	2.0	1.9	2.1	2.1	2.1	2.1
Methane	2.2	2.4	1.3	1.2	1.1	1.0
C2-C4 paraffins	2.2	4.8	3.2	3.3	2.4	3.6
Ethylene	13.6	19.5	19.1	18.3	16.5	19.1
Propylene	47.5	39.7	44.8	45.1	47.5	46.8
n-butenes	5.7	5.0	14.4	16.2	19.7	13.1
Isobutene	13.0	12.0	2.7	0.9	0.0	1.7
1,3-butadiene	0.5	0.2	0.4	0.4	0.5	0.3
C5–C9 (non-aromatics)	8.4	6.3	7.9	7.5	7.1	7.6
BTX aromatics	4.7	8.5	4.0	4.6	3.1	4.3
Other liquid products	0.3	0.6	0.4	0.5	0.3	0.5
Ethylene + propylene	61.1	59.2	63.9	63.4	64.0	65.9
Propylene/ethylene	3.5	2.0	2.4	2.5	2.9	2.5
C2–C4 olefins[b]	79.8	76.2	81.0	80.5	83.7	80.7

Second day of reaction, total TOS = 10 h, total heating time, HT = 29 h, reaction temperature = 630 °C. (615 °C for MIX-LAO, column 6)

[a] Performance of the reference sample (REF) tested in the same conditions as the HYB (column 1)

[b] Not including 1,3-butadiene

3.2 Thermo-catalytic Cracking of C_{10}^+ Linear α-olefins

Table 4 also reports the catalytic data obtained with C_{10}^+ LAO (1-tetradecene and higher, columns 3–5). Irrespective of the molecular length, the product yields in "ethylene + propylene" and in C_2–C_4 olefins were significantly higher than 60 and 80 wt%, respectively. It is to note that with increasing molecular length of the feed, the production of isobutene decreased rapidly while that of n-butenes increased steadily.

The "propylene/ethylene" product weight ratios were always higher than 2.4, suggesting that at the reaction temperature used (630 °C), the catalytic cracking promoted by the acid sites of the ZSM-5 was much more effective than the thermal cracking, favouring thus a higher production of propylene [22, 33–35]. It is also to note:

(1) an exceptionally higher production of isobutene when the feed was a shorter olefin (1-hexene, column 1). Such result was in agreement with the conclusion of Buchanan [35] who observed the prevalence of cracking (over other catalytic reactions promoted by zeolite acid sites, including skeletal isomerization) for longer olefins (and paraffins); and.
(2) low yields in heavy liquid products for all the feed olefins.

Figure 2 reports the variations of the product "Ethylene + Propylene" and C_2–C_4 olefins yields as functions of the time on-stream (TOS) and heating time (HT) observed with the mixture of linear alpha-olefins, MIX-LAO (see composition in the Experimental section) over the HYB catalyst (Table 4, column 6). After 5 runs of 5 h each, extended over a period of 101 h heating time, these yields did not show any significant decrease, suggesting an interesting on-stream stability that was already observed with the same hybrid catalyst on petroleum naphthas or gas oils [5, 6]. Such on-stream stability was assigned to the effect of the hydrogen-spilt over species produced on the surface of the co-catalyst [5, 6, 10, 12, 16]. It is to note that such transfer of the active hydrogen species from the co-catalyst surface to that of the main catalyst component, was only possible because the configuration of the hybrid catalyst obeyed to the concept of "pore continuum". It is also to note that the product propylene/ethylene ratio (wt/wt) was equal or higher than 2.4 (Table 4, columns 3–6).

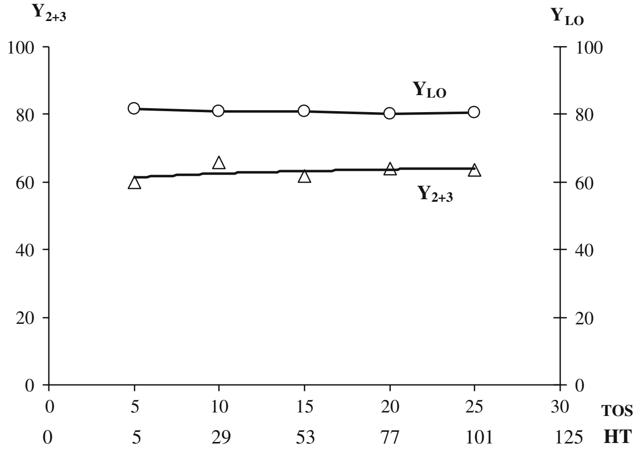

Fig. 2 Product yields in "ethylene + propylene" (Y_{2+3}) and C_2–C_4 olefins (Y_{LO}) (in wt%) vs. time on-stream (TOS) and heating time (HT) (in h) over the HYB catalyst. The MIX-LAO was used as feed (reaction parameters: as in Table 4, column 6)

This series of tests was carried out at a relatively short time on-stream. However, the obtained results actually anticipated those of ongoing investigations regarding the long-term "on-stream" stability of the TCC-type hybrid catalysts in such conversion.

3.3 Hybrid Catalyst (HYB) vs. Reference Catalyst (REF)

Table 4 reports the catalytic performances of the HYB (column 1) and the REF (column 2) catalysts, that allow us to make the following interpretations.

(1) The production of hydrogen was not significantly different for these two catalysts, suggesting that the amount of spilt-over hydrogen species, in situ produced, was very small. In addition, in the outstream of the HYB catalyst (but not in that of REF sample), some CO_2 (much less than 0.1 wt%) was detected, thus denoting the occurrence of the steam-reforming (and subsequent water–gas shift reaction) over the Ni bearing co-catalyst. These observations were coincident with those of previous works [5, 6].
(2) The yields of C_2–C_4 light olefins and of (propylene + ethylene) were higher for the HYB catalyst.
(3) There was less coke deposition onto the HYB surface (Table 3).
(4) The propylene/ethylene product ratio was much higher for the HYB catalyst. This suggests that the coked REF sample in which the fouling process was more severe, had less acid sites available for cracking (beta-scission), thus favouring other side-reactions (thermal cracking, etc.).

4 Conclusions

This work carried out with the TCC-type hybrid catalysts has shown that it was possible to crack heavy olefins (heavier than butenes) into light olefins with very high combined yield of product ethylene and propylene (more than 60 wt% at 610–640 °C). At those temperatures, the observed propylene/ethylene weight ratio was 3.5 for 1-hexene and equal or higher than 2.4 for C_{10}^{+} linear alpha-olefins (LAO and their mixture, also called MIX-LAO). The hydrogen spillover (HSO) effect due to the Ni bearing co-catalyst, was very beneficial both in terms of yield (in light olefins) and on-stream stability. DTA/TGA data showed a significant reduction of the coke formed on the HYB catalyst surface.

Finally, the use of the TCC-type hybrid catalysts in a (fixed-bed or fluidized-bed [34]) reactor integrated into processes such as the MTO or the ethylene oligomerization can provide a higher production of propylene, as well as other light olefins.

Acknowledgments The authors thank the Natural Sciences and Engineering Research Council of Canada (NSERC) and Valeo Management for their financial support.

References

1. Chauvel A, Lefebvre G (1989) In: Petrochemical processes, vol. 1. Technip (Paris) (ed), pp 117
2. Plotkin JS (2005) Catal Today 106:10
3. Le Van Mao R, Melançon S, Gauthier-Campbell C, Kletnieks P (2001) Catal Lett 73:181
4. Melançon S, Le Van Mao R, Kletniek P, Ohayon D, Intem S, Saberi MA, McCann D (2002) Catal Lett 80:103
5. Le Van Mao R, Vu NT, Al-Yassir N, François N, Monnier J (2006) Top Catal 37:107
6. Le Van Mao R, Vu NT, Al-Yassir N, Yan HT (2008) Ind Eng Chem Res 47:2963
7. Al-Yassir N, Le Van Mao R (2008) Can J. Chem 86:146
8. Le Van Mao R (1999) Micropor Mesopor Mat 28:9
9. Le Van Mao R (1988) US Pat. 4732881
10. Le Van Mao R, Al-Yassir N, Nguyen DTT (2005) Micropor Mesopor Mat 85:176
11. Al-Yassir N, Le Van Mao R, Heng F (2005) Catal Lett 100:1
12. Al-Yassir N (2007) Ph.D. thesis, Concordia University, Montreal
13. Le Van Mao R, Yao J, Dufresne L, Carli R (1996) In: Dooley K, Price G (eds) Gallium-loaded zeolites. Catal Today 31:24
14. Le Van Mao R, Yao L, Dufresne LA, Carli R, Ragaini R (1993) In: Inui T, Fujimoto F, Uchijima T, Kasai M (eds) New aspects of spillover effects in catalysis. Elsevier, Amsterdam, p 143
15. Maret D, Pajonk GM, Teichner SJ (1983) In: Pajonk GM, Teichner SJ, Germain JE (eds) Spillover of adsorbed species. Elsevier, Amsterdam, p 215
16. Yan HT, Le Van Mao R (Nov. 2008) Catal Lett (submitted)
17. Curtis Conner W Jr, Falconer JL (1995) Chem Rev 95:759
18. Hassan A, Fujimoto K, Tomishige K, Kusakari T, Akasaka A (2003) In: Studies in surface science and catalysis, vol. 138. Elsevier, pp 39
19. Baeza P, Villarroel M, Avila P, Agudo Lopez, Delmon B, Gil-Llambias FJ (2006) Appl Catalysis A: General 304:109
20. Ueda R, Kusakari T, Tomishige K, Fujimoto K (2000) J Catal 194:14
21. Le Van Mao R, PCT/CA 2008/001163, Int. filing date: 17 June 2008, Priority date: 18 June 2007
22. Stocker M (1999) Micropor Mesopor Mat 29:3
23. Kiel FJ (1999) Micropor Mesopor Mat 29:49
24. Olah GA, Goeppert A, Prakash GKS (2006) In: Beyond oil and gas, the methanol economy, Wiley
25. Groupe Total, Press release (October 1st, 2008) and CEN, (October 13, 2008) p 21
26. Vermeiren W, Nesterenko N, Appl. No WO2008EP52816 20080310, publication no WO2008110530 (A1) (2008-09-18) assigned to Total Petrochemicals Res Feluy (BE)
27. Skupinska J (1991) Chem Rev 91:613
28. Speiser F, Braustein P, Saussine L (2005) Acc Chem Res 38:784
29. Yang P, Yang Y, Zhang C, Yang X-J, Hu H-M, Gao Y, Wu B (2009) Inorg Chim Acta 362:89
30. Le Van Mao R, Al-Yassir N, Lu L, Vu NT, Fortier A (2006) Catal Lett 112:13
31. Hagen J (2006) In: Industrial catalysis, a practical approach, Wiley, Weinheim, p 151
32. Kieboom APG, Moulijn JA, Sheldon RA, Van Leeuwen PWNM (1999) In: Van Santen RA, Van Leeuwen PWNM, Moulijn JA, Averill BA (eds) Catalysis: an integrated approach. Elsevier, Amsterdam, p 33
33. Dehertog WJH, Froment GF (1991) Appl Catal. 71:153
34. Wan J, Wei Y, Liu Z, Li B, Qi Y, Li M, Xie P, Meng S, He Y, Chang F (2008) Catal Lett 124:150
35. Buchanan JS (2000) Catal Today 55:207