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Catalytic Compatibility of Methanol with Petroleum Naphtha in Mixed Feeds Used in the Thermal-Catalytic/Steam-Cracking (TCSC) Process for the Production of Propylene and Ethylene

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Abstract In the thermal-catalytic steam-cracking (TCSC) of “naphtha–methanol” mixtures, the increasing presence of methanol in the feed significantly modified the kinetics of the catalytic cracking. The gradual and significant decrease of the apparent activation energy with increasing methanol concentration in the mixed feed was attributed to the effect of intensive interactions between the two types of molecules: hydrocarbons and methanol. The addition of methanol into petroleum naphtha feed, up to 25 wt%, did not significantly change the catalytic performance of the TCSC hybrid nano-catalyst, suggesting that this catalyst could create at such relatively low methanol concentrations, a certain compatibility between the feed components.

Keywords Thermal-catalytic steam-cracking · Hybrid nano-catalyst · “Naphtha–methanol” mixed feeds · Feed compatibility · Kinetic study

1 Introduction

Ethylene and propylene, two important petrochemical intermediates, are mainly produced by steam cracking of various hydrocarbon feedstocks [1]. Because the yield of propylene in steam cracking is usually low and the worldwide demand for this light olefin is continuously increasing, the need of propylene can be covered by other processes such as propane dehydrogenation, olefin metathesis and, primarily, catalytic cracking (FCC).

The thermal-catalytic/steam-cracking (TCSC), also formerly named (SDCC or selective deep catalytic cracking, TCC or thermo-catalytic cracking) [2–6], has been developed in our laboratory to selectively produce propylene and ethylene from the same hydrocarbon feeds as in steam-cracking. The TCSC process, which combines the (mild) thermal cracking (TC) with the acid cracking promoted by a zeolite-based catalyst, can provide very high yields of light olefins with a propylene-to-ethylene weight ratio much higher than 1.0 while operating at temperatures much lower than those used in the steam cracking technology. Most of the catalysts used in the TCSC process are in the hybrid configuration, i.e., they are comprised of two porous components with relatively high surface area: an acidic zeolite based component and a co-catalyst capable of exerting a specific physical–chemical effect on the overall catalytic reaction. In this work, the (Zn–Pd) co-catalyst shows strong activities of (hydrocarbon) steam reforming (and water–gas shift). A “pressurizing” binder is used to firmly hold the two types of particles together within the hybrid catalyst extrudates. Some hydrogen species, produced by the co-catalyst surface, can be transferred to the zeolite surface using the experimentally proven effect of “pore continuum” [7, 8]: these “hydrogen spillover” species show some very significant cleaning effect on the coke precursors formed and still adsorbed on the zeolite acid sites [2, 4–6].

In recent years, results of the cracking reaction over ZSM-5 type zeolite that was carried out with “hydrocarbons–alcohol” mixed feeds were reported: methanol and hydrocarbons [9], methanol and *n*-hexane [10], methanol and *n*-butane [11], methanol and 1-butene [12], ethanol and *n*-hexane [13]. Two papers on the TCSC of mixtures of gas oil and a short chain alcohol (and particularly methanol) [14], and of light naphtha and methanol [15], were already published by our group.

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In this work, we would like to investigate the cracking behavior of the mixed feed "light naphtha–methanol" over the (Zn–Pd) hybrid catalyst in various operating conditions. Particularly, the effects of the steam dilution on the conversion, product selectivity and coke deposition would be carefully observed in two specific situations: TC and overall catalytic (thermal + catalytic) cracking. In addition, by measuring some kinetic parameters such as the apparent activation energy, we would like to answer the question that was raised in our previous works [14, 15]: when mixed with the light naphtha hydrocarbons, does methanol incorporate itself into the cracking "hydrocarbon pool" or react merely by itself as in steam (thermal) cracking?

2 Experimental

2.1 Preparation of the Hybrid Catalyst

The preparation of the hybrid catalyst followed the same procedure as described in our previous work [15]. Thus, the final hybrid catalyst resulted from the extrusion of two porous components by using bentonite clay as "pressurizing" binder: the main component was the H-ZSM-5 zeolite and the co-catalyst, an yttria-stabilized alumina aerogel loaded with Zn–Pd [15].

Essentially, the hybrid catalyst was comprised of [15]:

(a) as main catalyst component (65.6 wt%), an acidic ZSM-5 zeolite, having the following characteristics: Si/Al ratio = 50, total BET surface area = 403 m^2/g;
(b) as co-catalyst (16.4 wt%), Zn–Pd loaded onto an yttria-stabilized alumina aerogel (Y-AS), having the following weight composition: Zn = 9.2%, Pd = 1.1% and Y-AS = balance;
(c) Bentonite clay (Aldrich, 18.0 wt%).

2.2 Catalyst Characterization

The hybrid catalyst and its components were characterized using the techniques as described in Ref. [15].

2.3 Experimental Set-Up and Testing Procedure

Light naphtha (named LN, supplied by Ultramar Corp., Quebec, Canada) had the following composition, in wt% [15]: *n*-alkanes (*n*-pentane, *n*-hexane and *n*-heptane) = 47.2, iso-alkanes (isopentane, isohexane) = 40.7, cyclohexane = 5.4, benzene = 6.0 and heavier hydrocarbons (C_8^+) = 0.7.

The feed components, namely, naphtha LN, in one infusion pump, and methanol (pure reagent, Aldrich) dissolved in water in another infusion pump, were injected into two vaporizers, respectively. The resulting vapors (hydrocarbons on one side, steam and vaporized methanol on the other side) were then thoroughly mixed in a (heated) homemade gas mixer. The resulting gaseous stream was then sent into a tubular reactor (quartz tube, 50 cm long, 1.5 cm in outer diameter and 1.2 cm in inner diameter). The temperatures were controlled and regulated by automatic devices that were connected to chromel–alumel thermocouples (set in the catalytic bed and in the preheating zone) and the heating furnace.

In the following, LN, 20 MeOH, 50 MeOH and MeOH, denote feeds of light naphtha, light naphtha mixed with 20 wt% of methanol, light naphtha mixed with 50 wt% of methanol, and pure methanol, respectively.

The testing conditions were as follows: temperature (of the catalyst bed) = 600, 615, 635, 650 and 670 ± 2 °C; total weight hourly space velocity (WHSV, related to naphtha or methanol, or naphtha + methanol) = 10–60 h^{-1}; steam/feed weight ratio (feed: all C-containing reactants in the feed) or R_{wf} = 0.5–2.0; catalyst weight = 2 g (1 g for study of steam dilution); duration of a run = 4 h.

Liquid and gaseous products were collected separately, using a system of condensers. The gas-phase components were analyzed using a Hewlett-Packard (HP) Model 5890 FID gas chromatograph that was equipped with a 30 m GS-capillary column (Agilent J&W Scientific), while the analysis of the liquid phase was performed using another HP gas chromatograph of same model but equipped with a HP-5 capillary column (Agilent J&W Scientific, 30 m).

The total conversion C_t was defined as the percentage of the weight of (all the components of) the organic feed (light naphtha and eventually methanol) converted into final products (and coke) as follows:

$$C_t = 100\%(W_i - W_f)/W_i$$

W_i and W_f being the weights of the all organic compounds of the feed (injected into the reactor) and the same organic compounds collected at the outlet of the reactor, respectively. Thus, the conversion is essentially referred to the consumption of reactants.

The product selectivity S_i was defined as the percentage of the weight of product i over the weight of all the reaction products collected.

In the following, C_{tc} and C_{tt} refer to the total conversion for TC and overall catalytic cracking (OC), respectively (see Sect. 2.4).

Several runs, carried out in the same reaction conditions (reproducibility of the testing method), showed that the data experimental error in this study was ±0.3%.

The WHSV was defined as the total flow-rate of C-containing reactants of the feed (expressed in g h^{-1}) divided by the catalyst weight (expressed in g), so that its unit was h^{-1}. Thus, the contact time ct (reciprocal of WHSV) was expressed in h.

The residence time rt, used in the study of the TC alone, was defined as the void volume of the catalyst (expressed in cm^3), divided by the total flow-rate of C-containing gaseous reactants of the feed (expressed in $cm^3\ s^{-1}$), so that its unit was second. It is to be noted that the void volume of the catalyst was assumed to be similar to that left by a packing of quartz beads with proper size. In such manner, the catalyst bed filled with these quartz beads showed almost the same void volume as that containing the real catalyst extrudates. The low surface area of these quartz beads (<0.2 m^2/g) was assumed not to be catalytically active. The value of the residence time rt used in this work ranged from 0.68 to 5.42 s.

2.4 Determination of the Apparent Activation Energy

As reported in our previous paper [15], there are two effects in the TCSC conversion: the TC (thermal cracking) and the OC. While the second effect includes that of the TC and the conversion due to the catalyst, it is possible to assess the TC effect if the reaction system is run without any catalyst [15]. Thus, the kinetics of TC was studied by varying the residence time, the contact time being nil. However, it is impossible to determine the effect of the sole catalytic cracking because in the reaction medium, products from TC might be adsorbed on the catalyst surface and thus undergo further conversion on these active sites. Therefore, kinetic data that bear the mention "overall catalytic cracking", refer to these two untied effects.

The following procedure was used to determine the apparent activation energy (Arrhenius equation) for both OC and TC [16].

Data of total conversion were plotted against corresponding values of contact time ct and residence time rt, respectively. By using the method of regression analysis based on a polynomial function for the best curve fitting, the following equations were found:

Thermal cracking: $C_{tc} = a + b\ (rt) + c(rt)^2 + d\ (rt)^3 + \cdots$

Overall catalytic cracking: $C_{tt} = e + f\ (ct) + g\ (ct)^2 + h\ (ct)^3 + \cdots$

- For TC, if the residence time rt = 0 (flow-rate of feed = 0), $C_{tc} = a = 0$.
- For OC, if the contact time ct = 0 (no catalyst), $C_{tt} = e$.

On the other hand, in order to give a full physical meaning to our data when using a curve fitting with a polynomial function, the power coefficient of such function must be as low as possible with the condition that the correlation factor is close to 1.00 (>0.95). It was observed that the polynomial functions for the plot C_{tc} versus rt and that of C_{tt} versus ct could be written as follows:

Thermal cracking: $C_{tc} = b(rt) + c(rt)^2$
(using power coefficient = 2). Thus:
$$C'_{tc}(\text{time derivative}) = b + 2c(rt) \tag{1}$$

Overall catalytic cracking: $C_{tt} = e + f(ct) + g(ct)^2$
(using power coefficient = 2). Thus:
$$C'_{tc}\ (\text{time derivative}) = f + 2g\ (ct) \tag{2}$$

C'_{tc} and C'_{tt} being the time derivative of the total conversion for TC and OC, respectively. Thus, they are equal to the respective rates.

It is usually more convenient to determine the initial rate for each category of reaction (rt and ct are both tending to zero), so that the coke deposited is almost nil and the measured rate is totally related to the formation of reaction products. Such assumption is fully supported by experimental data, as shown in the following example:

- Feed = light naphtha, reaction temperature = 635 °C, $R_{wf} = 2.0$: conversion of overall cracking (C_{tt}) = 5.73 wt%, that was equivalent to 2.86 g of reaction products collected for a run of 240 min (4 h); amount of coke formed on the hybrid catalyst (determined by TGA–DTA) in the same period of time (240 min) = 0.0041 g. Thus, the weight ratio of products to coke was = 700. This means that, in conditions used for this kinetic study (for having low conversions), the average rate of formation of products on the fresh catalyst surface was almost 700 times higher than that of coking. In other words, when the conversion was low (lower than 25 wt%, preferably lower than 15 wt%), the rate of formation of coke could be neglected in comparison with that of formation of products.
- In these conditions, the conversion based on the reaction products, experimentally determined, was almost equal to that based on the consumption of the organic compounds of the feed, as defined in Sect. 2.3.

Thus, the Eqs. 1 and 2 result simply in:Initial rate for thermal cracking: $r_o = \left[C'_{tc}\right]_o = b$, and for overall catalytic cracking: $r_o = \left[C'_{tt}\right]_o = f$.

Because the determination of the initial rate for each category of cracking reaction and for each temperature investigated in this study was carried out with the same concentration of organic reactants in initial conditions (the catalyst weight or the void volume, and the R_{wf}, being all held constant, only the flow-rate of organic reactants was varied), we can write that:

$$r_o = k_o \text{ (concentration)}$$

with k_o being the (initial) rate constant and assuming a first-order reaction. Thus, $r_o = k_o$ (constant).

By simply using the Arrhenius equation [16, 17]:

$$k_o = A \exp(-E_a/RT)$$

where A is the pre-exponential factor, E_a the (apparent) activation energy, T the absolute temperature of the reaction, and R is the ideal gas constant.

The apparent activation energy can be determined as follows:

$$r_o = \ddot{A} \exp(-E_a/RT) \quad \text{with } \ddot{A} = A(\text{constant}).$$

3 Results and Discussion

3.1 Combined Effect of Steam and High Temperature on the Textural Properties of the Zeolite Component

In order to show that the H-ZSM-5 zeolite component of the hybrid catalyst used in this work was resistant to the quite harsh operating conditions (mostly high temperature and with the presence of steam), we have reported in Table 1 the BET results of the fresh hybrid catalyst and the same, used/regenerated.

(a) Fresh catalyst: dried at 120 °C overnight and activated in air at 700 °C for 3 h.
(b) Used/regenerated catalyst: hybrid catalyst unloaded from reactor after a 4 h run at 635 °C, pure light naphtha, with the presence of steam ($R_{wf} = 0.5$), WHSV = 3.0 h^{-1}. After drying at 120 °C, the used catalyst was regenerated (de-coked) in air at 540 °C for 5 h.

It is to be noted that the yttria-stabilized alumina aerogel used as support for the co-catalyst, was very thermally stable [18].

The hybrid catalyst, during the first run and the subsequent regeneration, had actually experienced some decrease in terms of micropore surface area and volume (Table 1). However, testing of the regenerated catalyst did not show any significant loss of the catalytic activity (less than 2%, Table 1). This evidenced that there was some rearrangement of the internal surface of the zeolite component (as usually observed) occurring during this first cycle of run-regeneration, however such change did not significantly affect the overall catalytic performance of the hybrid catalyst in other following tests. The quite high resistance of the H-ZSM-5 zeolite to steam and high temperature used was also observed with gas oil feeds [5, 14]: thus, there were no serious phenomena of zeolite dealumination in the conditions used in this work.

3.2 Effect of Steam Dilution on the Reactivity of "Petroleum Naphtha–Methanol" Mixtures

In the hydrocarbon steam-cracking and related processes, steam plays an important role. It is a diluting agent for the vaporized feed and a retardant of coke formation. In the TCSC process, steam dilutes the organic feed and may contribute to some extent to the cleaning of the catalytic sites. In fact, with its strong affinity for the zeolite acid sites where cracking occurs, it can displace out some coke precursors before these latter species can undergo further conversion to coke. However, the "cleaning" effect of steam was extremely weak when compared to that of the hydrogen spillover species, the latter being purposely in situ produced: in fact, the weight of coke deposited on the hybrid nano-catalyst was only 25–30 wt% of that found on the reference catalysts (i.e. H-ZSM-5 based catalyst not having any co-catalyst with steam-reforming properties) [5].

3.2.1 Steam Dilution Effect on the Overall Catalytic Cracking

In the TCSC process, the steam dilution, $R_{wf} = 0.5$ is normally used for light naphtha and gas oil [2, 4–6, 14, 15]. Much higher R_{wf} values were used in the present work in order to assess the effect of a more important presence of steam in the feed. It was expected that the competitive sorption of water molecules for the acid sites depended on the affinity for protons of the reactant molecules.

The effect of steam (as represented by the "H_2O/organic feed" ratio or steam dilution factor, R_{wf}) on the activity (as

Table 1 Effect of high temperature and steam on the BET characteristics and catalytic performance of the hybrid catalyst

Catalyst	S_{tot}	S_{mic}	$S_{mes+lar}$	V_{mic}	C_{tt}	$S_{eth+pro}$
Fresh	279	169	110	0.070	56.8	29.5
Used/regenerated	277	157	120	0.066	55.9	29.4

S_{tot}, S_{mic} and $S_{mes+lar}$ (expressed in $m^2\ g^{-1}$) being the total surface area, the surface areas related to micropores and mesopores/larger pores, respectively; V_{mic} being the micropore volume (expressed in $cm^3\ g^{-1}$) (the pore distribution was determined by BJH adsorption method); C_{tt} and $S_{eth+pro}$ being the total conversion and selectivity to product ethylene + propylene, respectively (both expressed in wt%)

represented by the total conversion C_{tt}), shown in Fig. 1, can be summarized as follows.

(a) With “pure” light naphtha as feed, the increased presence of steam was very detrimental to the catalytic activity. In fact, the total conversion almost decreased by half when R_{wf} increased from 0.5 to 2.0.
(b) With “pure” methanol as feed, no large variation of the total conversion was observed.
(c) With “naphtha–methanol” mixtures, intermediary behaviors were observed.

All these phenomena were the manifestations of the competitive adsorption. Recently, it was shown that water molecules could adsorb on strong hydrophilic sites of a silica-rich zeolite and form water clusters [19]: could this be the reason for such competition in adsorption?

Nevertheless, while water molecules did not have much prevalence over methanol ones in terms of adsorption on the acid sites, they could however compete strongly with those of the naphtha hydrocarbons, so that less hydrocarbons adsorbed meant less cracking conversion. Thus, under the same conditions of testing but at higher values of R_{wf}, the total conversions (Fig. 1) obtained with mixed “naphtha–methanol” feeds were significantly higher than those obtained with “pure” petroleum naphtha feed. It is to be noted that with these mixed feeds, the product selectivity (for propylene and ethylene) surprisingly did not significantly change with the steam dilution (Fig. 2).

3.2.2 *Steam Dilution Effect on the Thermal Cracking*

The same behaviors (for conversion and product selectivity) were found for TC (Figs. 3, 4). It was obvious that the present conversion levels were much lower than those recorded for the OC (Fig. 1 vs. Fig. 3). Interestingly, the conversion of methanol in the TC reaction was more influenced by the steam dilution. In addition, the product selectivity for (ethylene + propylene) when pure methanol was used as feed, was almost nil (not reported in Fig. 4), methane being the main product.

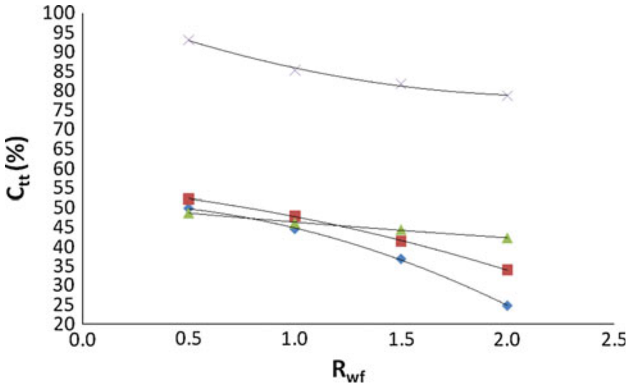

Fig. 1 Methanol in its mixtures with petroleum naphtha: effect of the steam dilution (R_{wf}) on the total feed conversion (C_{tt}) in the OC. *Symbol*: LN (*diamond*); 20 MeOH (*square*); 50 MeOH (*triangle*) and methanol (*cross*). *Note* T = 635 °C, WHSV = 4.5 h^{-1} for all except for methanol (WHSV = 10 h^{-1}) because of its high reactivity

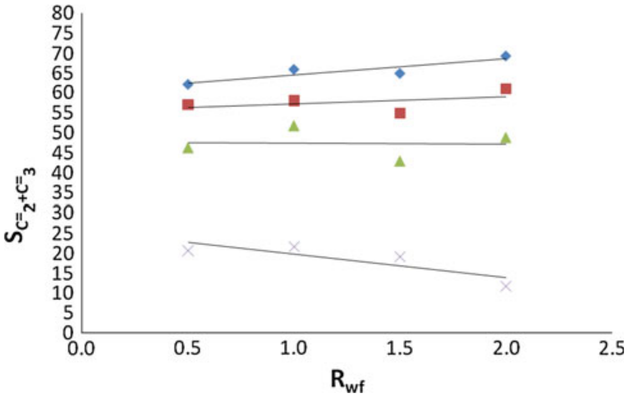

Fig. 2 Methanol in its mixtures with petroleum naphtha: effect of the steam dilution (R_{wf}) on the product “ethylene + propylene” selectivity ($S_{C2} = {}_{+C3} =$) in the OC. *Symbols*: same as in Fig. 1

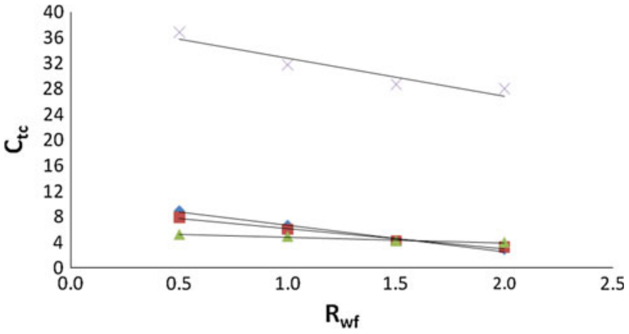

Fig. 3 Methanol in its mixtures with petroleum naphtha: effect of the steam dilution (R_{wf}) on the total feed conversion (C_{tc}) in the TC. *Symbol*: same as in Fig. 1

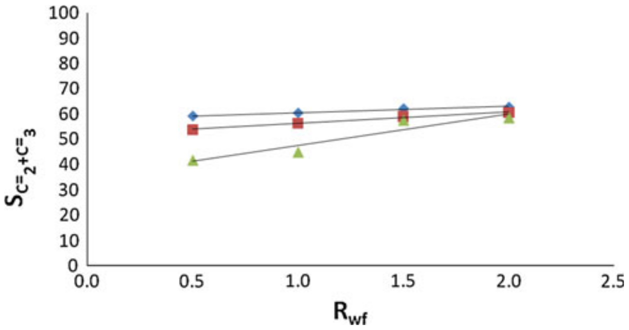

Fig. 4 Methanol in its mixtures with petroleum naphtha: effect of the steam dilution (R_{wf}) on the product “ethylene + propylene” selectivity ($S_{C2} = {}_{+C3} =$) in the TC. *Symbol*: same as in Fig. 1

3.2.3 *Effect of the Steam Dilution on the Coke Deposition onto the Catalyst Surface*

In our previous work [5], it was shown that the coke deposition onto the hybrid catalyst was less than one-third of that deposited on the reference catalyst (only ZSM-5 component): it was suggested that hydrogen species produced by the co-catalyst surface that were then transferred (spilt-over) onto the zeolite cracking sites, were effective to reduce the amount of coke formed, with as a result, significantly enhanced conversion and product selectivity.

In this work, the amount of coke laid down on the hybrid catalyst (w_c) was measured at various steam dilutions (0.5, and 2.0; Table 2). To assess the effect of fouling on the catalyst activity, the Z factor, defined as the ratio of w_c (g of coke per 100 g of catalyst) to the total conversion (C_{tt}: g of reaction products per 100 g of feed), was used herein.

It is well known that normally, the more important the presence of steam in the feed, the lower the conversion: this was primarily due to the reactants dilution by steam. In addition, steam is also known for its coke cleaning effect in most cracking reactions involving hydrocarbons.

Table 2 shows the following tendencies when the steam dilution (R_{wf}) increased from 0.5 to 2.0:

(a) A “normal” behavior for pure naphtha (LN) feed, i.e. lower conversion but also lower coke build-up at higher steam dilution. The Z factor moderately increased.

(b) A quite different behavior for pure methanol feed that gave a massive and a slightly increasing coke deposition while the total conversion did not significantly decrease. However, there was also a slight increase for the Z value. It is important to note that in the experimental conditions used, methanol feed led to very high total conversions.

(c) A very significant increase of Z value when mixed feeds were used. For feed with 20 wt% methanol, the coke production, being quite low at $R_{wf} = 0.5$, steadily increased with increasing steam presence. On the other hand, the behavior of the (50 MeOH) feed was approaching to that of pure methanol.

For now, it is difficult to interpret the results obtained with mixed feeds, except that methanol in these feeds appeared to express a stronger fouling effect than the hydrocarbon component of the feed (much larger w_c values). It should also be noted that, at higher steam dilution, these mixed feeds led to much higher coke formation, in line with pure methanol feed but in clear contrast with the pure naphtha (hydrocarbons) feed.

These interesting results about the effects of steam dilution induced us to carry out some kinetic investigations because the measurement of some key kinetic parameters might allow us to understand better the interactions of various species (reaction intermediates) in the two different reaction media (TC and OC).

3.3 Kinetic Study

3.3.1 *Initial Rates*

By using the procedure described in the Experimental section, initial rates of reaction were calculated from curves of total conversion versus time (residence time or contact time).

Figures 5 and 6 show the variation of the total conversion versus the residence time and the contact time, for TC and OC, respectively (at 635 °C, as examples only). These data were related to various feeds used in this work. In addition, these figures also show the curve fitting via polynomial functions (of degree 2) for TC and OC, respectively.

3.3.2 *Determination of the Apparent Activation Energy, E_a*

3.3.2.1 Thermal (Steam) Cracking Arrhenius plots related to TC alone are shown in Fig. 7. In Table 3 are reported the values of the apparent activation energy determined with various feeds used in this work.

The value of apparent activation energy E_a determined for the “pure” methanol feed was very low in the range of temperature investigated, suggesting a great methanol reactivity (radical-driven decomposition) in such relatively

Table 2 Effect of the steam dilution on the coke deposition onto the catalyst surface and the total conversion of the OC

	C_{tt}	w_c	Z	C_{tt}	w_c	Z
R_{wf}	0.5	0.5	0.5	0.2	0.2	0.2
LN	49.8	0.82	1.7	24.8	0.60	2.4
20 MeOH	52.2	1.21	2.3	34.0	2.08	6.1
50 MeOH	48.7	3.00	6.2	41.3	3.25	7.9
MeOH	95.5	4.05	4.2	91.0	4.38	4.8

Conversion C_{tt} in wt%, *coke deposition* w_c in g/100 g of catalyst, and $Z = w_c/C_{tt}$ ($\times 10^2$). *Reaction conditions* T = 635 °C, $W_{cat} = 1.0$ g and WHSV = 4.5 h^{-1}

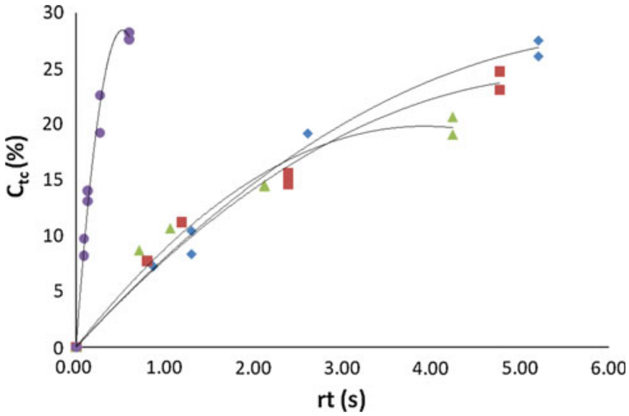

Fig. 5 TC: variations of total conversion (C_{tc}) versus residence time (rt) at 635 °C. R_{wf} = 0.5. *Symbols*: same as in Fig. 1

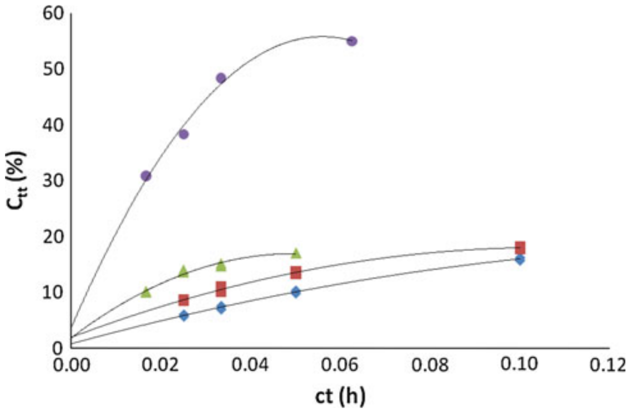

Fig. 6 OC: variations of total conversion (C_{tt}) versus contact time (ct) at 635 °C. R_{wf} = 2.0. *Symbols*: same as in Fig. 1

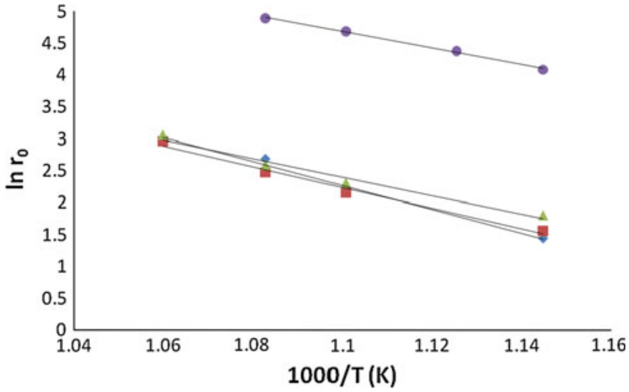

Fig. 7 Arrhenius plots of the TC within the range of temperature studied (T = 600, 635, 650 and 670 °C for mixtures and T = 600, 615, 635 and 650 °C for "pure" methanol). *Symbols*: same as in Fig. 1

high temperature conditions. Table 3 also reports the values of the apparent activation energy of "pure" naphtha (cracking = endothermic reaction) and "naphtha–methanol" mixtures. These mixed feeds showed E_a values that decreased with increasing concentration of methanol in the feed. However, the extent of such variations was not actually very large, meaning that there were almost no extensive interactions between the co-reactants (hydrocarbons and methanol) and their intermediates.

3.3.2.2 Overall Catalytic Cracking The corresponding Arrhenius plots are shown in Fig. 8. The values of the apparent activation energy for the OC with various feeds used in this work are reported in Table 4. In the presence of the hybrid catalyst, the total conversions and the reaction rates were so high that, for kinetic study purpose (i.e. for measurement of initial rates, very low total conversions at low contact times were necessary), a steam dilution ratio R_{wf} of 2.0 was used for all mixed feeds and a much higher steam dilution (R_{wf} = 10) was required for "pure" methanol.

Again, the presence of methanol in the feed contributed to the decrease of the apparent activation energy. However, by comparing the data of Table 3 with those of Table 2, the variations observed with the OC were much more important than with the TC.

3.3.3 Interpretation of the Kinetic Results

3.3.3.1 Thermal Cracking and Overall Catalytic Cracking Data of Tables 3 and 4 (and also, of Figs. 1, 2) lead to the following interpretation:

(1) The need for very high steam dilution ratio R_{wf} to keep the activity of OC at a reasonably low level (suitable for obtaining acceptable initial rate measurements) is due to the extremely high activity of methanol and relatively high activity of hydrocarbons of the petroleum naphtha over the zeolite acid sites.

(2) When the concentration of methanol increased, there was a decrease of the activation energy for both the TC and the OC.

    (a) The value of apparent activation energy in the case of TC moderately decreased with increasing methanol presence in the feed (Table 3): this was indicative of a simple averaging of apparent activation energies between the two components of the feed (i.e. hydrocarbons and methanol). Without using sophisticated kinetic modeling methods for this reaction with free-radical chain mechanism as in Ref. [20], we can simply state that there were practically no extensive interactions between these two components (and their intermediates) during their passage through the reaction zone.

    (b) In the case of the OC (Table 4), the much more important decrease of the value of the apparent

Table 3 Values found for E_a for TC

	r_0	T (K)	Ea (KJ/mol)
LN	19.946	943.5	155.8
	14.637	923.5	
	8.6983	908.5	
	4.23	873.5	
LN + 20 MeOH	19.291	943.5	134.9
	11.847	923.5	
	8.6304	908.5	
	4.7492	873.5	
LN + 50 MeOH	21.41	943.5	120.3
	13.391	923.5	
	10.102	908.5	
	6.0858	873.5	
MeOH	120.6	923.5	109.2
	91.899	908.5	
	70.98	888.5	
	61.776	873.5	

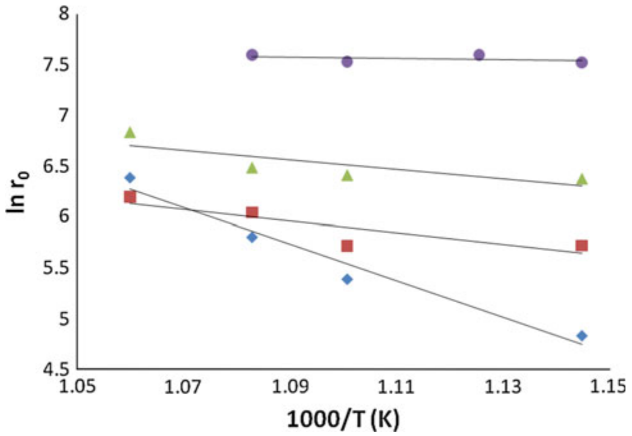

Fig. 8 Arrhenius plots of the OC within the range of temperature studied (T = 600, 615, 635, 650 and 670 °C for mixtures and T = 600, 615, 635 and 650 °C for "pure" methanol). *Symbols*: same as in Fig. 1

activation energy suggested an actually fierce competition for adsorption on the acid sites (located on the zeolite surface) between the methanol molecules on one side, and the hydrocarbon ones on the other side. Regarding the change in the apparent activation energy of paraffins (main components of the light naphtha) upon addition of methanol, we can recall the work of Kung and co-workers [21], showing that the differences in apparent activation energies could be entirely attributed to differences in heats of (*n*-hexane) adsorption, such that the intrinsic activation energies were identical. On the other hand, if the feed is light naphtha, the catalytic cracking of these hydrocarbons over ZSM-5 zeolite follows a monomolecular mechanism because all our tests were carried out at relatively high temperatures (in accordance with results of Ref. [22]). Finally, the value of the apparent activation energy with light naphtha feed as reported in Table 4, was quite close to that found by Kung and co-workers [21] for *n*-hexane cracking over H-ZSM-5 zeolite (E_{obs} = 149±8 kJ/mol).

3.3.3.2 Back to the "Hydrocarbon Pool" Mechanism Let us come back to the previous observation that the mixed feeds (light naphtha + methanol) at high steam dilution ratio showed total conversions higher than that obtained with the "pure" naphtha (Fig. 1) while the product selectivity of these cases was almost identical (Fig. 2). For the moment, we can explain these facts by:

(a) a preferential adsorption(-dehydration) of methanol molecules on the zeolite acid sites; then
(b) the "capture" by these adsorbed methoxy species, of hydrocarbon and/or methanol molecules from the gaseous phase, thus leading to the final cracking products.

This interpretation was in perfect agreement with those given by other authors who investigated the cracking of mixtures of hydrocarbons with methanol [10] or ethanol [13]: methanol or ethanol was adsorbed prior to *n*-hexane and immediately transformed into surface methoxy or ethoxy groups. According to the same authors, these species acted as the active sites for the conversion of *n*-hexane and consequently improved the initial activity of *n*-hexane [12, 13].

In our case, in addition to methanol and hydrocarbons, there were water molecules that might significantly affect the course of the catalytic cracking reaction. In order to enable the determination of the apparent activation energy of the OC (low total conversion), we had to use a steam dilution of 2.0. Referring to Fig. 1, at that value of R_{wf}, steam decreased the total conversion of naphtha by half whereas that of the "pure" methanol was not significantly affected. In an adsorption study by Baron and co-workers [23] using chromatographic methods, it was shown that as polarity of the adsorbent (ZSM-5 zeolite) decreased (increasing Si/Al ratio, i.e. increasing zeolite hydrophobicity), the affinity for apolar molecules increased. Thus, the value of the partition coefficient of *n*-hexane (measured at room temperature) moved from 2.20 to 13.8 whereas that of methanol went from 3.35 to 2.69 for two ZSM-5 zeolites having a Si/Al ratio of 13 and 137, respectively. This

Table 4 Values found for the kinetic parameters of the OC

	R_{wf}	r_0	T (K)	Ea (kJ/mol)
LN	2.0	595.17	943.5	149.5
		332.05	923.5	
		219.34	908.5	
		125.37	873.5	
LN + 20 MeOH	2.0	490.46	943.5	47.6
		420.8	923.5	
		304.57	908.5	
		305.21	873.5	
LN + 50 MeOH	2.0	928.28	943.5	39.3
		656.16	923.5	
		609.7	908.5	
		588.7	873.5	
MeOH	10.0	1989.3	923.5	5.6
		1861.3	908.5	
		1988.7	888.5	
		1846.1	873.5	

means that water did not directly affect the adsorption of *n*-hexane or methanol: however, it could affect significantly the zeolite sites that were strongly hydrophilic by formation of water clusters [19], as in the case of the ZSM-5 used in this work (Si/Al ratio = 50).

Regarding the meaning of the apparent activation energy E_a, Rozanska and Van Santen [24] reported that in a monomolecular reaction, the apparent activation energy could be simply expressed as:

$$E_a = E_{act} + (1 - \theta)E_{ads} \qquad (3)$$

where E_{act} is the intrinsic activation energy of the elementary reaction step, θ the coverage of the molecule on the catalytic site, and E_{ads} the adsorption energy of the molecule adsorbed to the active site. So, it would be possible to have the value of E_{act} knowing those of θ and E_{ads}. Several methods including the chromatographic ones [23] and adsorption/temperature programmed surface reaction could be used [25]. However, in practice, it is nearly impossible to do so because:

(a) It is very risky to extrapolate adsorption data from room temperature (or quite low temperatures) used for the adsorption study to a temperature of 635–650 °C (normal operating temperature for the TCSC process). Moreover, zeolite particles used in the industry are imperfect sub-micron sized crystallites, presenting large pore mouths, having particle size smaller than that of the crystals currently utilized in fundamental studies, and showing quite random distribution of the acid sites (zoning effect in ZSM-5 zeolites = higher acid sites density in particle zones close to the pore mouths and to the external surface), etc.

(b) Although in the Eq. 3 the entropy aspect could be taken into consideration, at high temperatures, however, the molecular diffusion regime through the zeolite micropores could change because of important variation of the kinetic diameters. In addition, during the long outward trip of the products, the latter could undergo further re-adsorption and subsequent reaction. Another point is that light naphtha was actually a mixture of several hydrocarbons with various molecular configurations. Theoretical studies such as mentioned in Ref. [26], would actually be very difficult tasks in real conditions of industrial use.

(c) It should be noted that the zeolite component is only a part of the hybrid nano-catalysts in which we have also the co-catalyst and some special binder. Thus, we must do a real effort to think about all the phenomena that could occur within the hybrid nano-catalyst: reactions occurring in the zeolite particles, those in the co-catalyst particles, interactions between the catalyst surfaces, pore continuum effect, etc. Researchers using in situ methods [27] would have quite hard time to elucidate the mechanism of each reaction step in such complex reaction medium.

Therefore, we have to stay with our macroscopic results (catalytic results). With light naphtha as feed, the hydrocarbon pool mechanism is our preferential mechanism in consideration of our past work [5, 14, 15], our present results, and also its quite large acceptance [28–31]. In fact, a solid experimental evidence from this work was provided by Fig. 2 that shows almost constant product selectivity (to propylene + ethylene) although steam dilution increased steadily, suggesting that the final products came from a "reaction pool" instead of some precise reaction steps. At a moderate concentration in the feed, methanol that is known to produce adsorbed methoxy group onto the zeolite acidic surface can incorporate itself, through these species, into such hydrocarbon pool, in accordance with Fig. 9.

4 Conclusion

Results of this work showed that, in the TCSC of mixtures of naphtha–methanol, the increasing presence of methanol in the feed significantly modified the catalytic cracking kinetics. The gradual and significant decrease of the apparent activation energy with increasing methanol concentration in the mixed feed was attributed to the effect of intensive interactions between the two types of molecules: hydrocarbons and methanol.

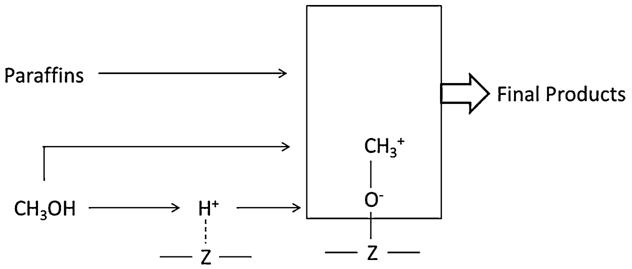

Fig. 9 Proposed mechanism for the overall reaction when mixed "light naphtha–methanol" feeds are used

The addition of methanol into petroleum naphtha feed, up to 25 wt%, did not significantly change the catalytic performance of the TCSC hybrid nano-catalyst, suggesting that this catalyst could create at such relatively low methanol concentrations, a certain compatibility between the feed components.

5 Ongoing and Future Research Work

Our future work will be focused on strengthening the in situ production of hydrogen species by the co-catalyst component. These hydrogen species being extremely active might contribute to decrease the consumption of (co-fed) molecular hydrogen in reactions that require dual functions "hydrogenation-acid cracking". Thus, hybrid catalysts with their unique configuration might be useful in hydrocracking, catalytic cracking or other similar reactions.

The concept of "pore continuum", discovered more than a decade ago [7] and that allows species produced on one catalytically active surface to migrate to another catalytically active surface and subsequently react with other species being adsorbed there, has recently found some similarity with that is called "tandem catalysis" [32].

This apparently simplified kinetic study is however useful because it helps industrial catalysis researchers understand the phenomena of feed compatibility and thus achieve further an important goal: to partially replace petroleum feedstocks currently used in the petrochemical industry, with long-lasting or renewable sources. The long-lasting sources include methanol that can be derived from natural gas or coal. The renewable sources include methanol, ethanol, butanol, furfural, levulinic acid, glycerol, etc. These sources will be produced in large volumes owing to the booming bio-refining industry. Our recent work [14, 15] has shown that methanol can be advantageously mixed with naphtha or gas oils up to 25 wt% in the TCSC process: in fact, with such methanol concentration in the feed, the operating conditions are not significantly modified while the catalyst performance remains, at least, the same. This feed compatibility although resulting in limited percentage of non-petroleum compounds that can be added, will have a considerable impact for all the industrial sector of fuels and chemicals. We are confident that in the near future, one will succeed to develop hybrid nano-catalysts that advantageously enable the (partial but significant) replacement of gas oils used as feeds in the gasoline producing technology (fluid catalytic cracking or FCC). Gas oil substitutes may be biomass-derived glycerol, furfural, or ultimately bio-oil that can be derived (by pyrolysis) from biomass or C-containing organic wastes (general formula: CH_xO_z, instead of CH_y for hydrocarbons). Such catalysts are capable of carrying out an "in situ" hydro-deoxygenation of the oxygenate component of the feed and immediately insert the resulting intermediates into the main hydrocarbon conversion stream.

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