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Interaction of water with the surface of a zeolite catalyst during catalytic cracking: a spectroscopy and kinetic study

A. Corma,* O. Marie, and F.J. Ortega [1]

Instituto de Tecnología Química, UPV-CSIC, Universidad Politécnica de Valencia, Avda. de los Naranjos s/n, 46022 Valencia, Spain

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Abstract

The potential effects of water on the conversion of Lewis into Brönsted acid sites and on the competitive adsorption with hydrocarbons for acid sites during hydrocarbon cracking with zeolites have been investigated by means of in situ infrared spectroscopy (IR) at reaction temperatures, as well as by studying the kinetics of *n*-hexadecane cracking. Both in situ IR and kinetic results show that under the cracking reaction conditions neither an increase of Brönsted acidity nor a competing adsorption effect of water occurs. On the contrary, the role of water is the same as that of nitrogen, i.e., to act as diluent, improving feed hydrocarbon dispersion and increasing the relative rate of unimolecular cracking versus bimolecular cracking and hydrogen transfer reactions. We also show that the mechanistic information achieved by spectroscopic and kinetic studies can be directly extrapolated to explain the effects observed when cracking industrial vacuum gas oil feed using water as dispersant.

Keywords: Catalytic cracking; Hydrocarbons adsorption; Water adsorption; Micro activity test; Hydrogen transfer; Olefins; Dilution

1. Introduction

Steam is introduced into industrial fluid catalytic cracking units (FCCU) in order to transport catalysts from regenerator to reactor, to vaporize and disperse the feed in the feed injectors for better catalyst–oil contact, to strip adsorbed hydrocarbons from spent catalyst avoiding valuable hydrogen-rich hydrocarbons entering into catalyst regenerator, to prevent coke building at the top of reactor, to fluidize catalyst in the stand pipe and catalyst hoppers allowing a smooth catalyst circulation, and to cool down regenerator cyclones when afterburning occurs [1–3].

From a chemical point of view, it has been suggested that the presence of steam in the riser may have a positive effect since it has been claimed that water can regenerate Brönsted active sites by partially rehydroxylating the surface [4]. Besides those positive effects, steam also has an important negative effect on fresh catalyst properties since under the conditions prevailing in the FCC regenerator, it promotes dealumination of the Y zeolite, resulting in a decrease of the surface area with a corresponding loss of activity [5]. Furthermore, water owing to its polar properties may be expected to compete with the feed for the catalyst sorption sites and to influence activity and selectivity. Zaho and Wojciechowski found that water has a promoting effect on methyl cyclopentane cracking when working at a low reaction temperature (673 K). They reported an increase in cracking and isomerization activity due to the presence of water [6]. However, no results have been reported working with industrial FCC feeds or with model hydrocarbons with higher boiling points under more realistic cracking reaction conditions.

In a previous paper [7], we have discussed the effect of feed dilution by nitrogen during cracking of gas oil and it was established that dilution has an important role-in hydrogen transfer reactions, leading to higher olefin yields. It was also shown that the presence of dilution gas improves feed vaporization and dispersion when mixed with the feed in the feed injector, resulting in higher conversions as it occurs in industrial practice where steam is used to disperse the feed. Thus, it was logical to study if the presence of steam can affect the chemistry of the cracking catalyst or simply acts as a diluent. To explore this, *n*-hexadecane as well as vacuum gas

* Corresponding author.
E-mail address: acorma@itq.upv.es (A. Corma).
[1] On leave from Instituto Mexicano del Petróleo, Eje Central Lázaro Cárdenas 152, 07730 México DF.

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oil have been cracked in a microactivity test reactor. A full kinetic study was performed in order to obtain the values of the adsorption constants as well as the heat of adsorption of the hydrocarbon and water. In parallel, an in situ infrared spectroscopy (IR) study was carried out at cracking reaction temperatures in the absence and in the presence of water at the same partial pressure as that in the cracking experiments. On the bases of the IR and kinetic results the chemical effect of water during catalytic cracking of hydrocarbons is presented.

2. Experimental

2.1. Materials

Cracking experiments were conducted using a vacuum gas oil (FCC feed) whose properties are given in Table 1, and with *n*-hexadecane from Sigma (> 99%).

A commercial low-rare-earth (1 wt%) USY catalyst from Engelhard was used to carry out the cracking experiments. It was equilibrated by steam treatment at 1089 K for 4 h with a mixture of 90 wt% steam and 10 wt% air. The resulting equilibrium unit cell size (UCS) was 2.428 nm. Additional properties are given in Table 2.

Owing to the very low IR signal of the zeolite bridging hydroxyl groups in the FCC equilibrium catalyst, in situ infrared experiments were performed with two ultrastable zeolites (USY), CBV720 and CBV760 from PQ Corporation, whose framework Si/Al ratios were 35 and 62, respectively. The corresponding UCS were 2.428 nm for CBV720 and 2.426 nm for CBV760. Additional properties are given in Table 2. Both samples were activated at 773 K under a flow of air in order to obtain the pure acidic form.

2.2. Infrared studies

Infrared experiments were carried out with a commercial AABSPEC 2000 stainless-steel transmission cell under flow conditions. The cell was equipped with thallium bromide iodide (KRS5) windows, since this material provides a good transmission range (20000–285 cm^{-1}) and is very resistant to water content in the gas flow. Spectra were recorded with a Bio-Rad FTS 40 A FTIR spectrometer associated with the 3.04 version of win-IR software. The number of scans per spectrum was varied from 10 to 64 with a 4 cm^{-1} optical resolution. The experiments were conducted at atmospheric pressure. Water in the gas phase was obtained by passing a carrier gas (nitrogen) through a saturator containing distilled liquid water. Water vapor pressure was determined by Antoine's equation and used to calculate the corresponding weight hourly space velocities (WHSV). All lines located after the saturator were heated at a temperature high enough to avoid water condensation.

The AABSPEC cell offers a very good thermal regulation but presents a large dead volume. Since we wanted to

Table 1
Feed physicochemical properties

Physical		Method	Chemical		Method
Specific gravity, 288/288 K	0.917	ASTM-D-287	Molecular weight	407	ASTM-D-2502
Refractive index, 340 K	1.4909	–	Sulfur (wt%)	1.65	ASTM-D-2622
Aniline point (K)	352	ASTM-D-611	Nitrogen (ppm)	1261	ASTM-D-4222
K (UOP)	11.82	UOP-375	Sodium (ppm)	0.18	IMP-QA-006
Distillation ASTM-D1160 (K)		ASTM-D-1160	Nickel (ppm)	0.2	IMP-QA-006
5% vol	592		Vanadium (ppm)	0.4	IMP-QA-006
10% vol	625		Composition (wt%)		ASTM-D-3238
30% vol	687		Aromatics	22.96	
50% vol	709		Naphthenes	15.16	
70% vol	732		Paraffins	61.88	
90% vol	785		Aromatic rings	1.17	
			Naphthenic rings	1.01	

Table 2
Catalyst physicochemical properties

	Method	Commercial fresh	Commercial equilibrated	CBV720	CBV760
Bulk density (g/ml)	UOP-254	0.9	0.905	0.85	0.85
Total specific area (m^2/g)	ASTM-D-3663	412	277	780	720
Zeolitic specific area (m^2/g)	ASTM-D-3663	272	170	780	720
Pore volume (ml/g)	ASTM-D-4222	0.198	0.218	0.232	0.179
Unit cell size (nm)	ASTM 3942/80	2.449	2.428	2.428	2.426
Framework silica/alumina	[a]	6	35	35	62
Average particle size (μm)	ASTM-D-4464	70	70	70	70
Rare earth oxides (wt%)	IMP-QA-803	1	1	0	0

[a] Fichtner et al., Crystal Res. Technol. 19 (1984) K1.

observe the interaction of water with the zeolite surface we made an experiment without zeolite inside the cell. By doing this we were able to obtain for each temperature the pure water gas-phase spectrum under flow conditions. When a zeolite wafer was introduced inside the cell, the obtained spectra could be corrected from the water gas phase in order to obtain the desired zeolite surface spectra.

2.3. Catalytic cracking experiments

The reaction was performed in an automated computer-controlled MAT unit, which may carry out up to 8 continuous experiments. Reactor and capillary tube inner diameters are 15.6 and 1.0 mm, respectively. Details of the apparatus and methodology have been described previously [8]. The reactor was adapted so that nitrogen and/or water could be injected through the upper part of the reaction tube or through the capillary feed injection tube, in both cases simultaneously with the hydrocarbon feed. Water and hydrocarbon feed were injected by two separated syringes driven by the same motor, and both liquids were mixed before entering into the reaction system. In a first series of experiments, gas oil or *n*-hexadecane was cracked without any diluent to obtain the base case. A second series was run under the same conditions as above but with nitrogen added as diluent at selected hydrocarbon/diluent ratios and, a third series was run using water instead of N_2 at the same hydrocarbon/diluent molar ratios. Experiments with gas oil were carried out at 773 K, whereas *n*-hexadecane experiments were conducted at 673 and 773 K. The experimental protocol was the same as described in a previous paper [7]: 3.00 g of equilibrated catalyst was located in the catalytic bed, and after each set of experiments, catalyst was discharged and characterized for specific surface area and zeolite unit cell size. A bed of 4 cm length of silicon carbide was placed above the catalyst bed as a preheater to ensure feed and water vaporization. Thermal cracking on the preheater zone was measured, resulting in less than 1% for gas oil at 773 K and 0.3 wt% for *n*-hexadecane.

Hydrocarbon stripping was done at reaction temperature while regeneration was carried out at 813 K.

2.4. Product analysis

Gaseous products were analyzed in a Varian 3600 CX chromatograph, equipped with a molecular sieve column with argon as carrier gas and a thermal conductivity detector to analyze H_2 and N_2, and a plot alumina column with helium as carrier gas and a flame ionization detector to analyze C_1–C_6 hydrocarbons.

Liquid products from gas oil cracking were analyzed by simulated distillation according to the ASTM-2887-D method using a Varian 3800 chromatograph. PIONA analysis was used for liquid products from *n*-hexadecane using a Varian 3900 equipped with a Petrocol-100 fused silica column and a FID detector.

Coke was determined by measuring the CO_2 from the regeneration flue gas using a Binos 100 infrared analyzer.

2.5. Kinetics

The kinetic equation used to fit the experimental conversion data and to calculate the adsorption and reaction rate constants was derived by combining the mass balance of an ideal plug flow reactor, the reaction rate law according to the Langmuir–Hinselwood adsorption model, and the time-on-stream theory of catalyst decay [9]. Volume expansion during reaction was also taken into account. The resulting equation is

$$\begin{aligned}\frac{\partial X}{\partial \tau} = {} & \left(\sum K_{\mathrm{r}_i} K_{\mathrm{A}} C_{\mathrm{A0}} \frac{(1-X)}{(1+\varepsilon X)}\right) \\ & \times \left(1 + K_{\mathrm{A}} C_{\mathrm{A0}} \frac{(1-X)}{(1+\varepsilon X)} \right. \\ & \quad + \sum K_{\mathrm{p}_i n_i} C_{\mathrm{A0}} X \frac{(1+\varepsilon)}{(1+\varepsilon X)} \\ & \quad \left. + K_j \frac{C_{jo}}{(1+\varepsilon X)}\right)^{-1} (1+Gt_{\mathrm{f}})^{-1}, \end{aligned} \tag{1}$$

where K_{r_i} is the global kinetic rate constant; K_{A}, K_{p_i}, and K_j are the adsorption constants for *n*-hexadecane, reaction products, and diluents (nitrogen or water), respectively; X is *n*-hexadecane conversion; τ is the space time; C_{A0} is *n*-hexadecane initial concentration; G is the catalyst decay parameter; t_{f} is the time on stream; and ε is the expansion coefficient.

This equation accounts for a global reaction mechanism of *n*-C16 cracking, includes the adsorption constants of reactant, products, and diluents, and describes the evolution of instantaneous conversion as a function of space time, time on stream, and dilution ratio. As the reaction test renders average conversions, calculated instantaneous conversion was averaged from time $t = 0$ to time $t_{\mathrm{f}} =$ time on stream by means of the following equation,

$$\overline{X} = \frac{1}{t_{\mathrm{f}}} \int_0^{t_{\mathrm{f}}} X \,\mathrm{d}t, \tag{2}$$

where $\overline{X}$ is the average conversion, and X and t_{f} are defined above.

Kinetic parameters were calculated by solving Eqs. (1) and (2) coupled with the Buzzi optimization algorithm [10].

3. Results and discussion

3.1. Spectroscopic study

Fig. 1 illustrates the results obtained for the zeolites tested after correction from the gas-phase infrared absorption and the spectra recorded with and without water in the gas phase.

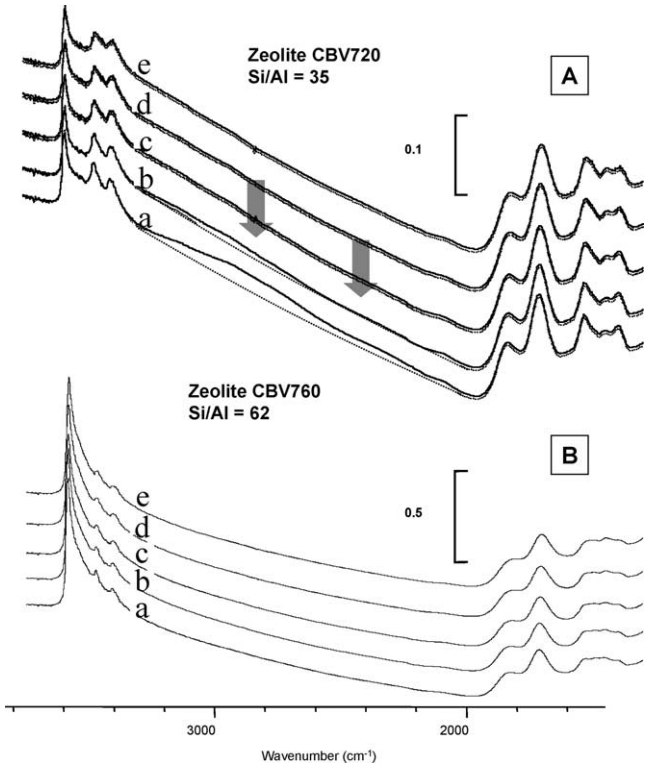

Fig. 1. Evolution of the infrared spectra of USY zeolites: (···) under pure N_2 gas flow (only showen for A as a reference) and (—) under N_2 + H_2O gas flow as a function of the temperature (a) 573, (b) 623, (c) 673, (d) 723, and (e) 773 K. All the spectra are corrected from the gas-phase IR absorption.

Experiments were done in the temperature range from 573 to 773 K and at the same water partial pressure. At 573 K on the zeolite sample with the lowest Si/Al ratio there is clear perturbation of the hydroxyl groups, which may be interpreted as an interaction of water with acidic hydroxyls forming hydrogen-bonded species. Indeed, according to Hadjiivanov et al. [11], perturbation of free hydroxyls to form hydrogen-bonded hydroxyls leads to the appearance of a typical Fermi resonance spectroscopic infrared system at 2850, 2400, and 1700 cm^{-1}. As indicated by arrows in Fig. 1, only the 2850 and 2400 cm^{-1} bands are observed with our samples since the band at 1700 cm^{-1} has low intensity and overlaps with the zeolite structural vibration bands. However, when the zeolite with the lowest framework aluminum content (CBV760) is considered, there is no appreciable interaction of water with hydroxyls even at 573 K. This result indicates that the water interaction with the zeolite surface is less intense when the framework Si/Al ratio of the zeolite is higher, or in other words when the zeolite is more hydrophobic.

Regarding the evolution of IR spectra with zeolite CBV720 with adsorption temperature (Fig. 1), it can be seen that water adsorption decreases whith increasing temperature and for values higher than 673 K the interaction of zeolitic hydroxyls with water is not visible anymore. These results suggest that at high reaction temperatures (> 673 K), the adsorption of water on the hydroxyl groups of the USY zeolite does not occur, at least in the time frame observable by infrared. If this is so, from a spectroscopic point of view we may conclude that water does not increase the population of bonding hydroxyl groups and also should not compete with the feed for the surface hydroxyl acid sites. This conclusion is somewhat surprising since water by being more polar than hydrocarbons should compete favorably for adsorption on the acid sites, especially in the case of alkanes. However, in order to properly discuss this, the adsorption equilibrium constants for water and hydrocarbon should be obtained under reaction conditions. In order to do this, we have carried out a kinetic study using the Langmuir–Hinselwood formalism and the adsorption constant and the heat of adsorption for water and *n*-hexadecane were also calculated.

Table 3
Kinetic parameters

	Temperature (K)	
	673	773
Adsorption constants (lt/mol)		
n-Hexadecane	2.31	0.096
Nitrogen	0.0019	0.00023
Water	0.0027	0.00032
Products	1.82	0.016
Reaction rate constants (s^{-1})		
n-Hexadecane	8.6	1147
n-Hexadecane + N_2 capillary tube	18	2050
n-Hexadecane + H_2O capillary tube	17	2000
Deactivation constants (s^{-1})		
n-Hexadecane	2.2	2.1
n-Hexadecane + N_2 capillary tube	2.0	2.0
n-Hexadecane + H_2O capillary tube	2.0	2.0

3.2. Kinetic results

In Fig. 2 the close correlation between calculated conversions (according to the kinetic model described above) and experimental conversions is shown. In all cases, conversion increases with increasing contact time and reaction temperature and decreases with time on stream due to catalyst deactivation, as could be expected. The correlation factor between experimental and calculated data was in all cases higher than 0.98. The kinetic parameters obtained are given in Table 3. It can be seen that the value of a true kinetic rate constant is the same regardless of whether nitrogen or water is introduced together with hydrocarbon feed, indicating that water does not interact with the catalyst, at least to the point of changing either the intrinsic rate constant or the concentration of active sites. This conclusion is in agreement with the very low value of the adsorption equilibrium constant for water (as it is for nitrogen) which in any case is much lower than the adsorption constant for *n*-hexadecane. Note, however, that the kinetic rate constant increased when water or nitrogen is introduced due to the reported effect of better dispersion and contact between the feed and the catalyst [7].

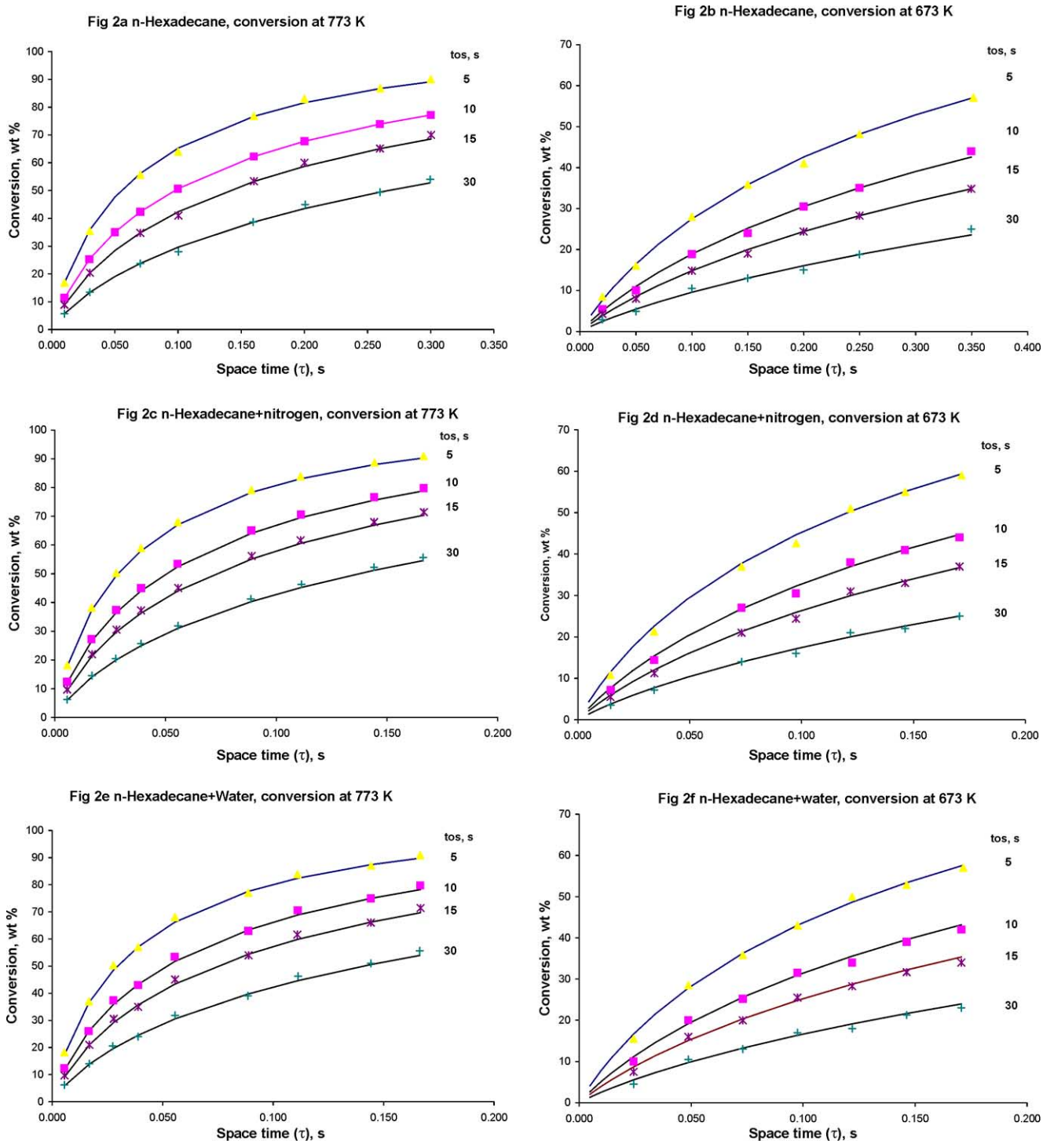

Fig. 2. Theoretical curves and experimental points for *n*-hexadecane conversion as function of space time (τ) and time on stream (tos).

When the heat of adsorption of *n*-hexadecane was calculated by means of Vant Hoff's equation, a value of 137 kJ/mol was obtained, which is in good agreement with the value of 130 kJ/mol that should be obtained from Kiselev's correlation for adsorption of *n*-paraffins on faujasite X zeolite as a function of the number of carbon atoms in the linear chain [12]. It is possible then to conclude that under our *n*-hexadecane cracking conditions and with the equilibrium catalyst used, water does not interact with the hydroxyl groups of the zeolite either by generating new acidic sites or by competing with the adsorption of *n*-hexadecane. On the contrary, the role of water is the same as that of nitrogen, i.e., to act as a diluent. If this is the case, we should expect from water the same effect that nitrogen has on product selectivity, i.e., a decrease in selectivity for bimolecular reactions such as those responsible

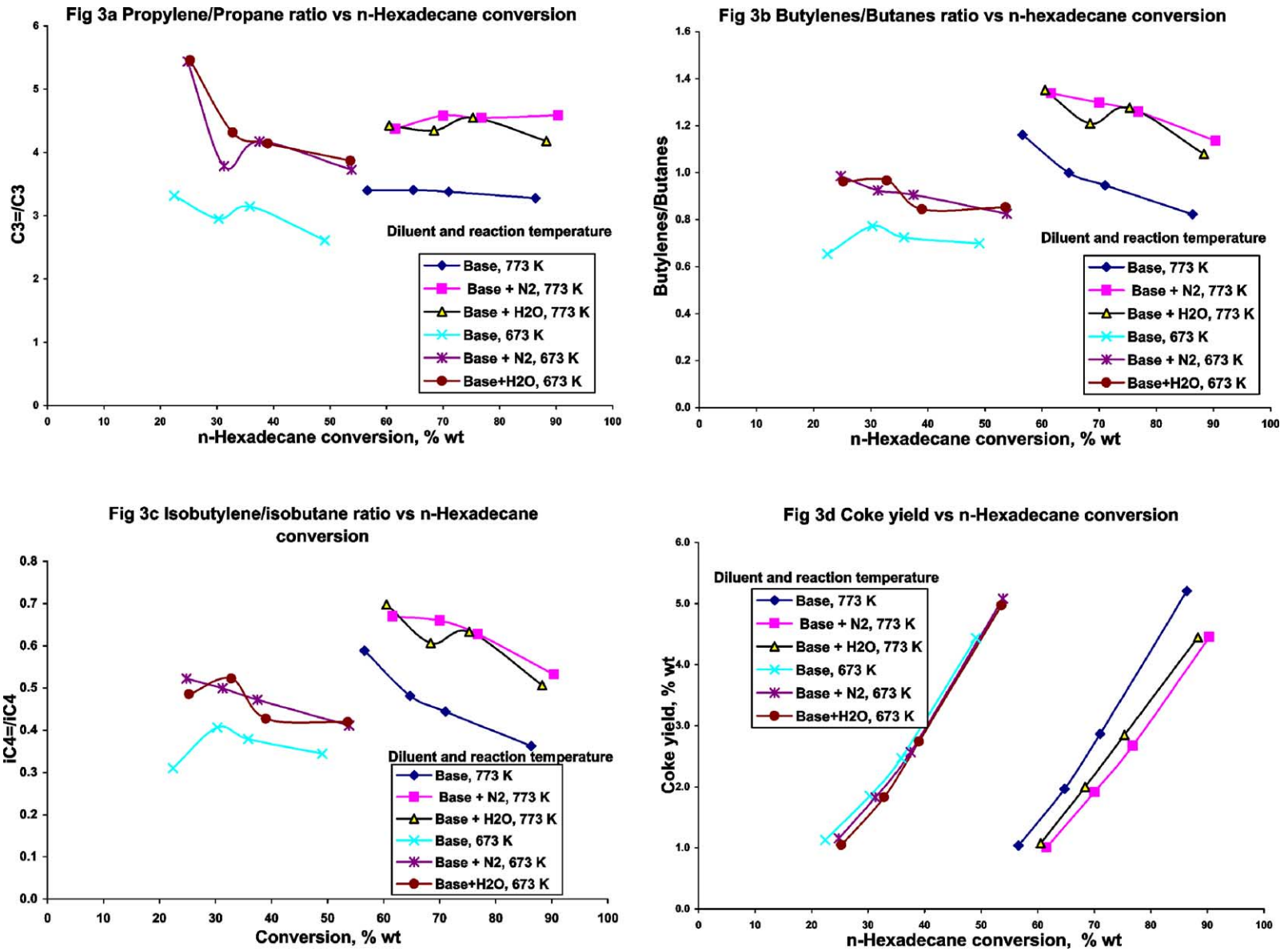

Fig. 3. Dilution effect on olefin to paraffin ratio as a function of conversion and reaction temperature. Diluent/n-hexadecane molar ratio = 1.63. n-Hexadecane feed rate = 3 g/min.

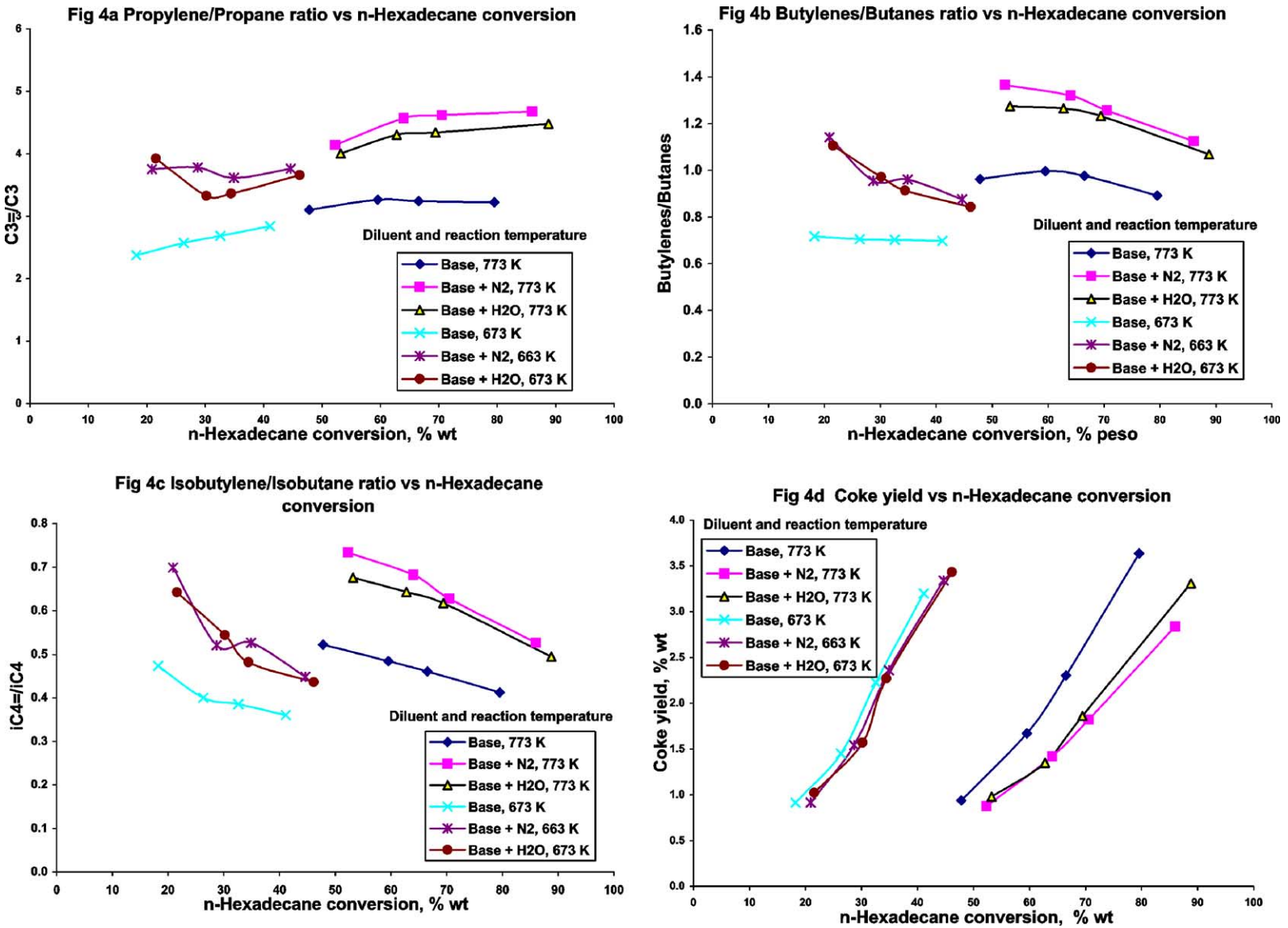

Fig. 4. Dilution effect on olefin to paraffin ratio as function of conversion and reaction temperature. Diluent/n-hexadecane molar ratio = 1.63. n-Hexadecane feed rate = 4 g/min.

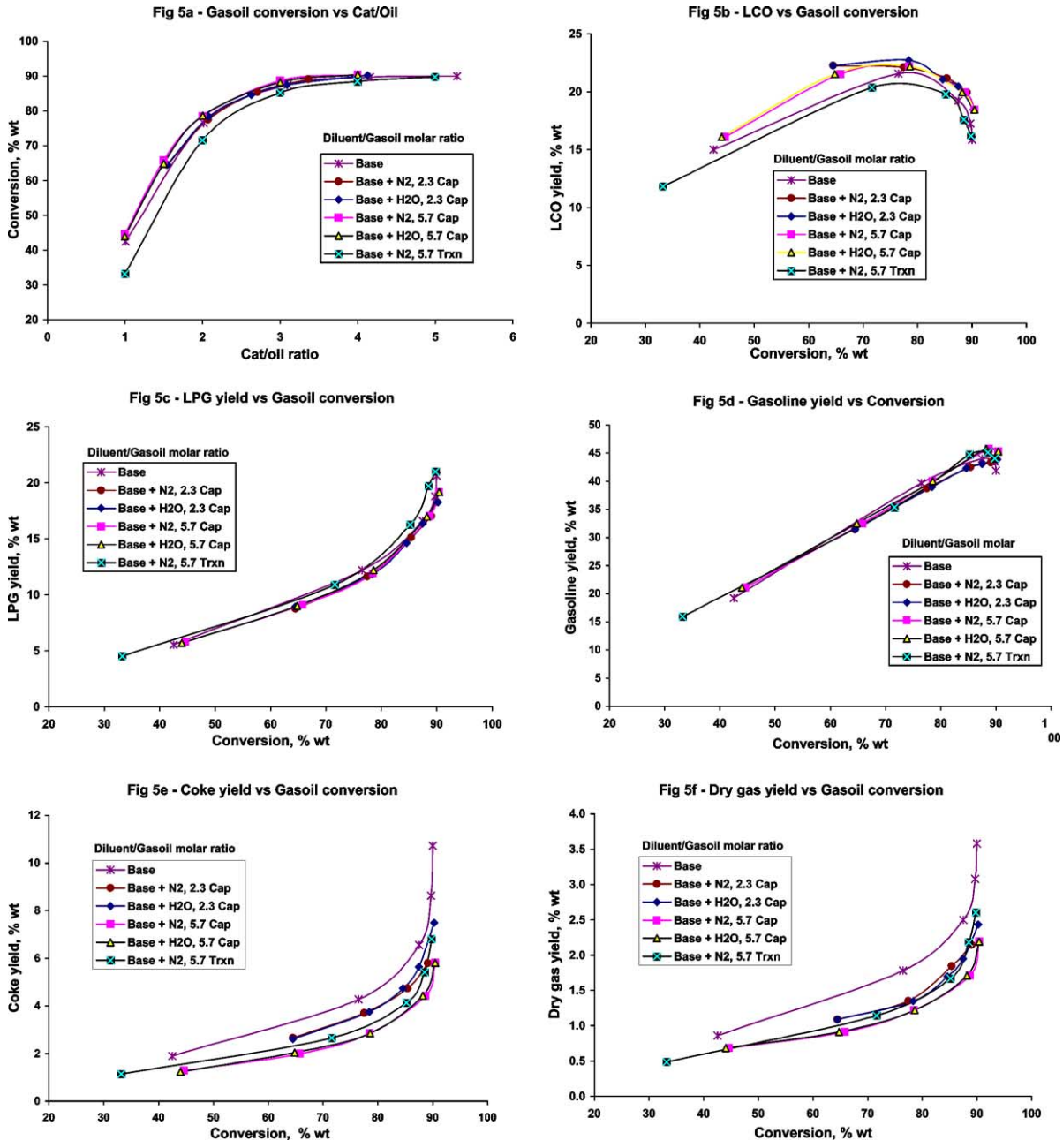

Fig. 5. Diluent effect on gas oil conversion and product yield at 773 K. Gas oil and diluent fed together through capillary feed injection tube, Cap. Diluent fed separated from gas oil through reaction tube, Trxn.

for hydrogen transfer and coke formation. Indeed, results from Figs. 3 and 4 clearly show that the introduction of either nitrogen or water produces an increase of the olefin to paraffin ratio and a decrease of coke yield. A lower selectivity to coke should result in a decrease of the catalyst decay constant. The results presented in Table 3 show the same decay constant for the reaction in the presence of nitrogen or water, which is almost the same as that when the reaction is carried out in the absence of diluents, indicating that a direct correlation between catalyst decay and coke yield is not necessarily found, in agreement with previous reports [13].

If the conclusions obtained from *n*-hexadecane cracking are extrapolated to the cracking of a vacuum gas oil industrial feed, it could be expected that water should not have any effect on activity except that derived from a better dispersion of the feed as observed when cofeeding nitrogen. However, the presence of water should have an important effect on selectivity and thus coke and dry gas should decrease and the olefin to paraffin ratio in LPG should increase. Indeed, Figs. 5 and 6 show that when the gas oil was cracked in the presence of water or nitrogen at the same partial pressure, and they were fed mixed with the hydrocarbon through the capillary feed injection tube, conversion curves were prac-

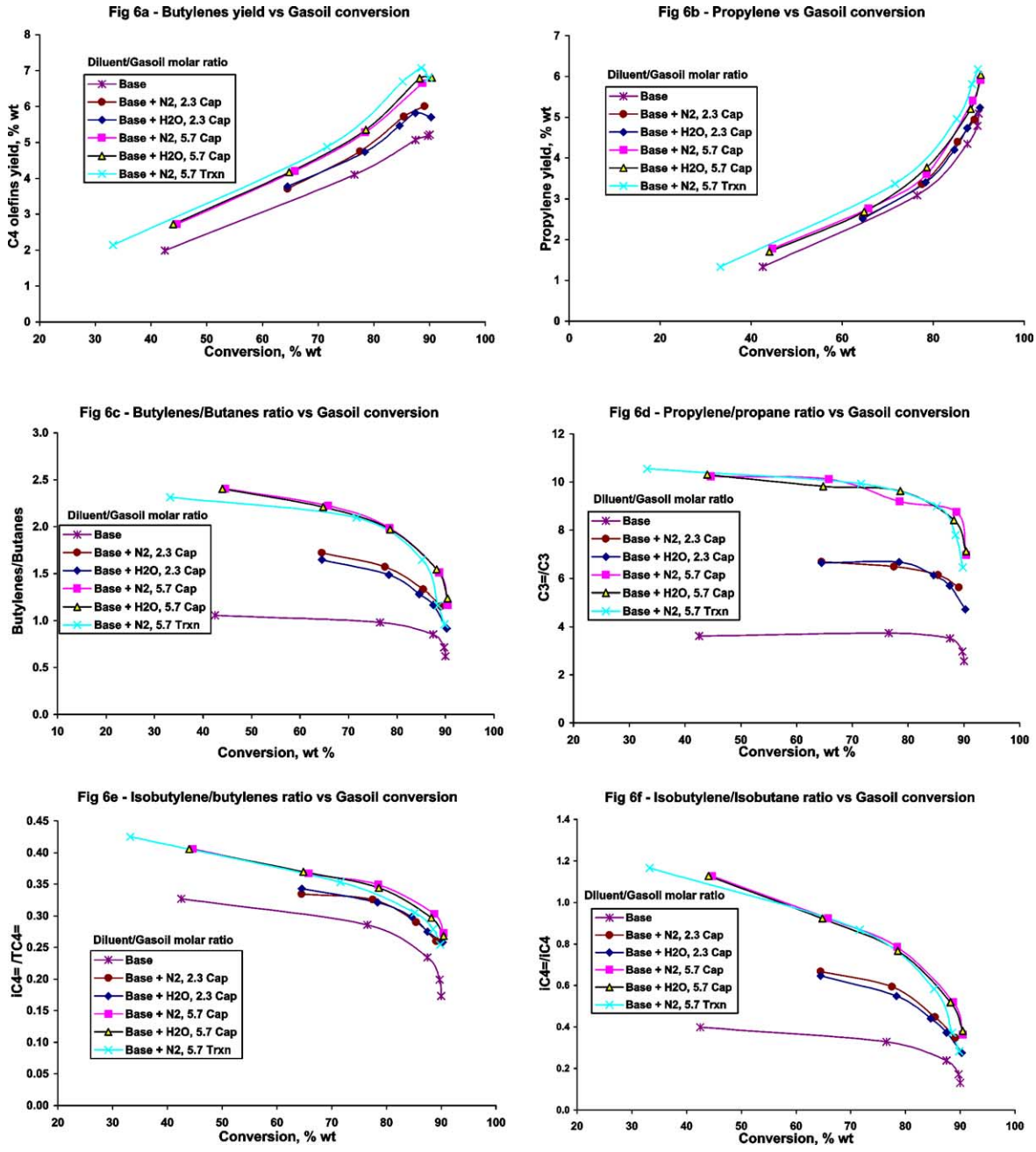

Fig. 6. Diluent effect on olefin yield and olefin to paraffin ratio at 773 K. Gas oil and diluent fed together through capillary feed injection tube, Cap. Diluent fed separated from gas oil through reaction tube, Trxn.

tically equivalent. Contrary to this, when nitrogen was fed simultaneously but separately from the hydrocarbon feed, conversion decreases when the partial pressure of nitrogen is descreased. These results indicate again that water plays the same role as nitrogen, i.e., acting as diluents as occurred when cracking *n*-hexadecane. The diluent effect of water is also shown when studying the yields to the different products. When adding either water or steam together with gas oil, selectivity to the different cracking products is practically the same and different than that obtained when cracking gas oil alone. Indeed, when adding the diluent, propylene and butene increase while propane and butane yields decrease. Meanwhile gasoline and LCO selectivity show little variation. Conversion and product yields clearly indicate that the presence of steam has a dilution effect in the same way as nitrogen, and decreasing the hydrocarbon partial pressure has a larger effect on bimolecular reactions, leading to hydrogen transfer and coke, than on unimolecular cracking reactions. Following this, it can be established that the higher the dilution the lower the relative rate of the hydrogen transfer reactions and consequently the higher the yield to olefins.

4. Conclusions

1. Infrared spectroscopy shows that at low temperatures (< 623 K), there is an interaction between the bridging hydroxyl groups of the USY zeolite and water. This interaction is less intense when the unit cell size of the zeolite is decreased.
2. Neither interaction of water with the acid OH groups nor formation of new hydroxyl groups is observed at more realistic cracking reaction temperatures (> 673 K) regardless of the unit cell size of the USY zeolite. Thus, as far as IR spectroscopy is concerned, formation of new acidic OH groups by interaction of Lewis acid sites with water is not observed under the conditions studied here. Moreover, water adsorption on zeolite Brönsted sites with the corresponding effect on the IR spectrum is neither observed at temperatures typical of catalytic cracking.
3. In agreement with spectroscopic results, the kinetic study shows that at typical cracking temperature, neither water nor nitrogen adsorbs significantly on the catalyst surface, which is evidenced by the low values of the corresponding adsorption constants. The presence of water in the reaction media during catalytic cracking has the same effect as nitrogen; i.e., they act as diluents.
4. Besides the dilution effect, water or nitrogen addition to the feed through the capillary injection tube improved feed dispersion, which resulted in a higher reaction constant rate. Addition of an inert diluent decreases the ratio of bimolecular to cracking reactions, producing an increase of olefins in the C_3 and C_4 fractions, while decreasing coke yield.

Acknowledgments

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