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Isomerization of *n*-butane to isobutane over Pt-modified Beta and ZSM-5 zeolite catalysts: Catalyst deactivation and regeneration

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Abstract

This work addresses the deactivation behavior of H-Beta, H-ZSM-5, Pt-Beta and Pt-ZSM-5 catalysts in the isomerization of *n*-butane to isobutane. Furthermore, the type of coke formed inside these catalysts was characterized. The regeneration of Pt-Beta and Pt-ZSM-5 with synthetic air was also investigated.

Most of the coke was formed during the first 70 min of TOS. Linear long-chain olefins formed the soluble coke, which was mainly determined by the reactant molecule and formed by consecutive oligomerization of *n*-butane molecules. On the other hand, the amount of insoluble coke is influenced by the reaction conditions, carrier gas and, most of all, zeolite structure. Pt and hydrogen inhibit successive reactions, i.e. alkylation, cyclization, that soluble coke undergoes before becoming insoluble. The beneficial effect of coke on the shape selectivity was observed, which increased the isomerization efficiency, defined as $\mathrm{IE} = i\mathrm{C}_4/(i\mathrm{C}_4 + \mathrm{C}_3 + \mathrm{C}_5)$. The activity on Pt-Beta was completely restored by oxidative regeneration, showing a higher IE than the fresh one.

Keywords: *n*-Butane; Isomerization; Beta; ZSM-5; Pt; Deactivation; Coke; Characterization

1. Introduction

The catalytic isomerization of *n*-butane to isobutane is an industrially important reaction due to the increasing demand of isobutane in the production of synthetic rubber and in the alkylation of isoparaffins, which are considered as an alternative for octane boosters instead of oxygenate and aromatic compounds that are subjected to strict environmental restrictions. At present, Pt on chlorinated-alumina catalysts are mainly used in the industry but due to environmental concerns, there is a great incentive to develop new environmentally friendly catalysts for this reaction where zeolites, e.g. ZSM-5, Beta and Mordenite, are potential catalysts for this and other reactions since they exhibit very attractive properties, i.e. acidity, shape selectivity and different kind of structures. For example, ZSM-5 is a ten membered ring (MR) zeolite system with a sinusoidal and circular channel system interconnected in its framework with pore opening sizes between 0.51 and 0.56 nm and channel intersection sizes of 0.9 nm [1]. On the other hand, Beta zeolite contains three-dimensional interconnected 12 MR channel systems where the three ordered framework and the disordered beta structure are all characterized by three mutually intersecting 12-ring channel systems. Two topologically identical linear channel systems have pore opening sizes of 0.75 nm × 0.57 nm and the third channel system (tortuous) with 0.65 nm × 0.56 nm [2]. Nonetheless, zeolite catalysts undergo rapid deactivation mainly because of coke formation. In this sense, the actual formation of coke and its action upon the zeolite catalyst depends not only on the characteristics of the zeolite and the nature of the reactant involved but also on the reaction conditions.

The deactivation of zeolite catalysts by coke is either caused by poisoning of the acid sites or pore blockage [3–5]. In the former case, a molecule of coke blocks the accessibility of the reactant to one active site, which affects the activity of the catalyst but mainly the reaction selectivity while the deactivating effect produced by the latter case is much more severe because a carbonaceous molecule is able to block the access to more than one active site or even worse to the entire channel as it has been observed on mordenite catalysts [6]. Nonetheless, numerous studies have been published on the beneficial effects of carbonaceous deposits on the catalytic transformation of hydrocarbons [4,6,7], such as higher selectivity to desired products. This occurs when side reactions, i.e. cracking, are inhibited due

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to the higher constrain created by coke deposit inside the catalyst pores.

Fortunately, the activity of the used catalysts can be regenerated by the combustion of coke at elevated temperatures. Moreover, regeneration of a catalyst is cheaper than replacement. Such oxidative treatment, which is normally done under high flow of air or diluted oxygen, depends on the characteristics of the coke and the thermal stability of the zeolite catalyst. Jong et al. [8] demonstrated that reactivating gases used during regeneration, i.e. diluted oxygen or hydrogen, play a decisive role on whether the coke removed is located at the pore mouth or inside the pore. In any case, the activity of the zeolite catalyst is not fully recovered due to several secondary effects under the severe conditions of coke removal: water presence, high temperature, sintering, segregation of metal particles, etc.

The aim of this work was to investigate the effect of deactivation of H-ZSM-5, H-Beta, Pt-ZSM-5 and Pt-Beta catalysts on the isomerization of *n*-butane to isobutane. The deactivation of Beta catalysts was studied quantitatively by TGA. Furthermore, the type of coke formed inside these catalysts was characterized. Finally, the Pt-modified zeolites were regenerated and their catalytic behavior was compared to that of the fresh materials.

2. Experimental

2.1. Catalyst syntheses

The synthesis of parent forms of the Na-Beta and Na-ZSM-5 zeolites was carried out in laboratory in 300 ml autoclaves as mentioned in References [9,10] with some modifications. The parent ZSM-5 and Beta zeolites were modified by ion-exchange method using an aqueous solution of ammonium chloride. After ion-exchange, ammonium forms were washed with distilled water, dried and calcined in a muffle oven and the protonic forms obtained were denoted H-Beta and H-ZSM-5 catalysts. Pt-Beta and Pt-ZSM-5 catalysts were prepared by impregnation, using a 2 wt% aqueous solution of H_2PtCl_6 in a rotavapor and evaporating after 24 h. The metal-modified catalysts were dried at 383 K, followed by calcination in a muffle oven at 723 K. If a used catalyst had to be regenerated, the suffix -REG would be added, e.g. Pt-Beta-REG. The catalysts were characterized by nitrogen adsorption, X-ray powder diffraction, Fourier-transform infrared spectroscopy and CO chemisorption.

2.2. Catalyst characterization

The specific surface area of fresh and used H-Beta and H-ZSM-5 and their Pt-modified counterparts was measured by nitrogen adsorption method (Sorptometer 1900, Carlo Erba Instruments). The catalysts were out-gassed at 473 K prior to the measurements and the Dubinin equation was used to calculate the specific surface area.

The X-ray powder diffraction measurements were performed on a Philips PW1820-based diffractometer using a Cu X-ray tube for the fresh catalysts and especially for the used Pt-Beta-REG and Pt-ZSM-5-REG. All samples were measured through an angular range 0.5–90° (θ) using 0.02° steps and measuring time for each step equal to 1 s. The diffractograms were analyzed using X'Pert HighScore software (Philips, 2001) and the Powder Diffraction File (PDF) database. The PDF database was used to identify the structure and phase purity of the sample.

The acidity of investigated samples was measured by infrared spectroscopy (ATI Mattson FTIR) using pyridine ($\geq$99.5%, a.r.) as a probe molecule for qualitative and quantitative determination of both Brønsted (BAS) and Lewis acid sites (LAS). The samples were pressed into self-supported pellets (15–19 mg/cm^2). Pyridine was first adsorbed for 30 min at 373 K and then desorbed in vacuo at different temperatures (523, 623 and 723 K) to obtain a distribution of acid sites strengths. All spectra were recorded at 373 K with a spectral resolution of 4 cm^{-1}. Spectral bands at 1545 and 1450 cm^{-1}, were, respectively, used to identify Brønsted and Lewis acid sites. The amount of BAS and LAS was calculated from the intensities of corresponding spectral bands using the molar extinction coefficients reported by Emeis [11].

The dispersion measurements were performed with Micromeritics Autochem 2910 gas-adsorption equipment using the CO pulse method. The sample was heated up with a rate of 10 K/min until 393 K and the temperature was held for 30 min under helium atmosphere. Then, the catalyst was reduced by hydrogen, while the temperature was increased to 623 K in two steps: first, it was heated until 493 K and then till 623 K with a rate of 10 K/min, the temperatures were hold for 30 and 120 min, respectively. After the reduction, the sample was kept under He for 90 min at 623 K. The temperature was quickly decreased to room temperature. Immediately, CO adsorption began using pulses of 0.07 ml (10% of CO in He) every 5 min while keeping the temperature constant at 303 K with the help of a water bath. The outlet gas, which passed through the sample, was led into a TC detector and the concentration of CO was recorded until this value was constant.

2.3. Coke characterization

The coked catalysts were treated with 2 ml of HF for every 0.25 g of used catalyst to destroy the zeolite structure. Once the silica was removed from the structure, 14 ml of dichloromethane for every 0.25 g of used catalyst were added in order to recover the soluble coke compounds. The samples were left overnight, then filtered and the insoluble coke obtained was weighted after drying the filtration paper. The soluble coke and the aqueous phase were then separated. Finally, the analysis of the coke molecules soluble in CH_2Cl_2 was made by GC–MS (Agilent 6890N-5973N) equipped with a capillary HP-5MS column (30 m × 0.25 mm × 0.25 μm).

2.4. TGA analyses

The experiments were performed at 623 K and atmospheric pressure in TGA equipment (Cahn 200). The catalyst was placed in a cup, hanging in the middle of the quartz reactor tube. The carrier gas, i.e. nitrogen or hydrogen, and *n*-butane were introduced into the bottom of the reactor, flowing upward and exiting the reactor 20 cm above the cup. Regular catalytic tests over H-

Beta and Pt-Beta were simulated in this system by keeping the same conditions for the pretreatment, reduction and reaction as described in the next section.

2.5. Catalytic testing and product analyses

The performance of the catalysts in the transformation of *n*-butane to isobutane was tested in a fixed-bed minireactor at atmospheric pressure. The screened catalysts were pelletized, crushed and sieved into the adequate particle size, i.e. 150–250 μm, to suppress internal diffusion. The catalyst was packed in the reactor and the reactant was fed through the catalyst bed using hydrogen as a carrier gas, obtaining a partial pressure of the reactant of 0.5 atm. The product analysis was carried out using a gas chromatograph (Varian 3700) equipped with a 50 m × 32 mm capillary column and a FI-detector (i.d. fused silica PLOT N_2O_3–KCl). The catalyst samples were heated to 773 K with a rate of 1 K/min (723 K if the sample contained Pt) under N_2 flow in order to desorb water. Regeneration of coked catalysts was carried out at 723 K with synthetic air for 2 h before the reduction with hydrogen for 2 h at the same temperature was performed. Finally, the temperature was decreased to the reaction conditions. Typical reaction conditions were: 623 K with WHSV 1.6 and 3.5 h^{-1}. Conversion measurements performed with different flows and amounts of catalysts at constant residence times confirmed that no external diffusion limitations took place.

3. Results and discussion

3.1. Catalyst characterization results

The X-ray powder diffraction was performed for the fresh H-Beta and H-ZSM-5 and the patterns obtained can be identified as pure Beta and ZSM-5. The diffractograms of Pt-Beta and Pt-ZSM-5 showed that their bulk structures are maintained after the metal-modification. Fig. 1a and b show correspondingly the XRD patterns of used Pt-Beta-REG and Pt-ZSM-5-REG. The bulk structure, for both Pt-modified Beta (-REG) and ZSM-5 (-REG), has not been significantly altered by the regeneration under air flow nor by the reduction and further reaction. However, both XRD patterns differ somehow from their references due to the presence of other phases. Two different phases were found: a Pt phase, i.e. peaks visible starting from approximately 39.9°, which is a consequence of the platinum modification and a quartz phase, which is a leftover from the catalytic experiments, e.g. mostly sharp peaks visible at 26.6°, 36.5° and 45.8°. The specific surface area of fresh and used H- and Pt-forms of Beta and ZSM-5 is summarized in Table 1. All the fresh catalysts presented fairly high specific surface areas (>445 m^2/g) but H-Beta showed the highest one. A decrease of the specific surface area of the zeolites after Pt impregnation was expected mainly due to the deposition of metallic particles on the pore mouth that were able to block the access of nitrogen. Such decrease is in accordance with CO chemisorption, which showed that the average Pt particle size was greater than 2.5 nm. After 300 min of TOS, H-Beta exhibited the highest decrease of the specific surface area (72%) while for H-ZSM-5, it was barely 8%, which could be attributed to the higher acidity possessed by Beta (Table 2)

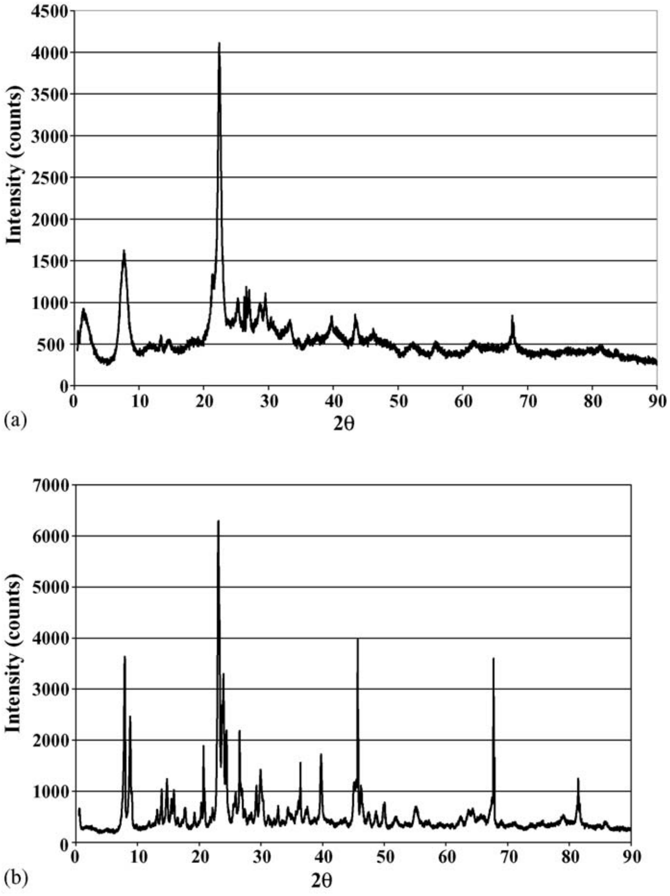

Fig. 1. XRD pattern of used (a) Pt-Beta-REG and (b) Pt-ZSM-5-REG.

Table 1
Physical properties of fresh and used H-Beta, H-ZSM-5, Pt-Beta and Pt-ZSM-5

Catalysts	Si/Al (mol/mol)	Specific surface area (m^2/g)			Pt content (wt%)	Pt dispersion (%)	Pt mean particle size[a] (nm)
		Fresh	Used	Decrease (%)			
H-Beta	11	730	203	72	N/A	N/A	N/A
H-ZSM-5	35	477	447	8	N/A	N/A	N/A
Pt-Beta	11	672	488	28	2	46	2.5
Pt-ZSM-5	35	445	415	7	2	19	5.9

Conditions: 623 K, WHSV 1.6 h−1 and H2/*n*-butane ratio of 50:50

[a] Assuming spherical particles.

Table 2
Brønsted and Lewis acidity of fresh catalysts

Catalysts	Brønsted acid sites (μmol/g)			Lewis acid sites (μmol/g)		
	523 K	623 K	723 K	523 K	623 K	723 K
H-Beta	269	207	120	162	128	113
H-ZSM-5	159	149	52	7	0	0
Pt-Beta	300	170	0	65	0	0
Pt-ZSM-5	170	128	0	5	0	0

that makes it more active towards *n*-butane isomerization and thus more vulnerable to coking. On the other hand, the positive effect that Pt-impregnation and hydrogen bring together to the catalysts is very obvious since the specific surface area of Pt-Beta decreased only by 28% after TOS 300 min.

Pyridine adsorption (FTIR) was utilized to obtain the Brønsted and Lewis acidities of the fresh zeolite catalysts, both proton and Pt-forms (Table 2). The difference between the acidity distributions of the proton-forms and Pt-modified zeolites is very significant. The total amount of Brønsted acid sites, i.e. acid sites that desorb pyridine at 523 K, is practically the same for H-Beta and H-ZSM-5 and their corresponding Pt-counterparts; even for medium-strength BAS, i.e. those which retain Py at 623 K, the same behavior is observed. Nonetheless, the strong BAS, i.e. those which desorb Py at 723 K, disappeared completely when the H-form zeolites were modified with Pt. Furthermore, a similar behavior was observed with the Lewis acid sites over Beta zeolite. Pt-impregnation reduced considerably the total amount of LAS, i.e. those which hold Py at 523 K, and suppressed completely the relative stronger LAS, i.e. those desorbing Py at 623 and 723 K. Lewis acidity on H-ZSM was already very low before the modification with Pt, but still the total amount of LAS was maintained. This very peculiar effect on the redistribution of acid sites on zeolites after Pt-impregnation has been observed on Pt-modified zeolite catalyst [6,12,13] and it has been attributed to interactions between acid sites and Pt particles, which confirms that part of them are located inside the pores. Moreover, it has been also demonstrated by XPS that the support and, more specifically, the acid sites also influence the Pt electronic properties and morphology. Stakheev and Kustov [14] have reviewed the latest findings and observations on the dual influence between the support and the metal over different zeolites.

3.2. Deactivation behavior of H-Beta, H-ZSM-5, Pt-Beta and Pt-ZSM-5 in the isomerization of n-butane

The isomerization of *n*-butane was carried out over H-Beta, H-ZSM-5, Pt-Beta and Pt-ZSM-5 at 623 K with WHSV 1.6 h^{-1} under hydrogen with the objective of studying the deactivation behavior of such catalysts. Figs. 2 and 3 show the results over H- and Pt-Beta and H- and Pt-ZSM-5, correspondingly. The positive effect that Pt brings to the zeolites is clear and has been thoroughly discussed for Pt-H-Mordenite and is attributed to the bifunctional nature of metal-supported zeolites. In essence, Pt promotes dehydrogenation of alkanes to alkenes, which skeletal isomerization is more feasible than that of alkanes [5,15]. Pt-Beta is much more active in the *n*-butane isomerization in comparison to the proton form. However, along the first 70 min of TOS, the conversion of *n*-butane over Pt-Beta dropped approximately 20% while the activity loss on H-Beta barely reached 5% in 200 min of TOS. Such activity loss is due to the blockage of the zeolite pores by highly polyaromatic molecules, i.e. insoluble coke, and completely concurs with the results obtained over these catalysts presented in Table 3. However, the isomerization efficiency (IE), i.e. defined as $iC_4/(iC_4+C_3+C_5)$, increases along TOS while the conversion of *n*-butane decreases, implying that selectivity to isobutane increases. In fact, it means that the bimolecular mechanism for the formation of isobutane and its

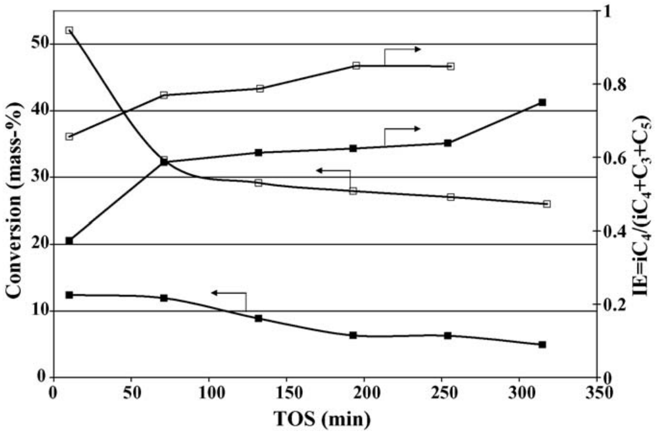

Fig. 2. Conversion of *n*-butane and IE over H-Beta (■) and Pt-Beta (□) at 623 K with WHSV 1.6 h^{-1}.

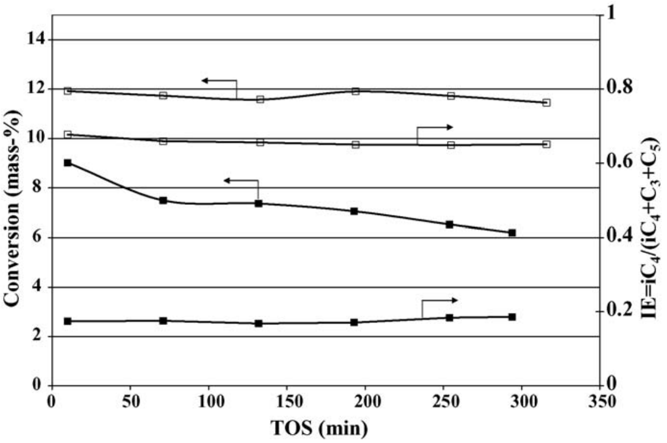

Fig. 3. Conversion of *n*-butane and IE over H-ZSM-5 (■) and Pt-ZSM-5 (□) at 623 K with WHSV 1.6 h^{-1}.

Table 3
Composition of coke soluble in dichloromethane present in used H-Beta, H-ZSM-5, Pt-Beta and Pt-ZSM-5

	H-Beta		H-ZSM-5	Pt-Beta		Pt-ZSM-5	
Insoluble coke (%)	7	32[a]	3	20	13[b]	7	14[b]
n_C	14–26	14–26	14–26	16–28	18–26	14–28	16–24
Main families Z = (C_nH_{2n+z})	0	−6, 0	−6, 0	0	0	0	0
Main components	C_nH_{2n}	C_nH_{2n-6}, C_nH_{2n}	C_nH_{2n-6}, C_nH_{2n}	C_nH_{2n}	C_nH_{2n}	C_nH_{2n}	C_nH_{2n}

Conditions: 623 K, WHSV 1.6 h−1

[a] Carrier gas: N_2.

[b] Used (-REG).

side-reaction, i.e. cracking to propane and pentane, is inhibited by the increasing steric constraints (accumulation of coke) that affect the formation of the bulky intermediates in the bimolecular mechanism. Furthermore, Cequeira et al. [4] demonstrated that coke molecules are preferentially adsorbed on BAS, which mainly has an effect on the bimolecular mechanism requiring two acid sites contrary to the monomolecular mechanism that needs only one. Moreover, it has been observed in the skeletal isomerization of 1-butene over Ferrierite that (insoluble) coke molecules may act as active sites for the monomolecular mechanism [4,7]. ZSM-5 zeolite was not very active towards *n*-butane isomerization due to its low acidity. Nonetheless, H-ZSM-5 showed some deactivation along TOS due to coke formation and a slight increase of the IE which was not possible to observe over Pt-ZSM-5 because of its stable catalytic behavior (Fig. 3).

3.3. Nature of coke deposited in Beta and ZSM-5

H-Beta, H-ZSM-5 and their Pt counterparts were used for, at least, 300 min on the *n*-butane isomerization with WHSV 1.6 h^{-1} at 623 K, while for the regeneration experiments on the Pt-modified zeolites, WHSV was increased to 3.5 h^{-1}. Moreover, a test reaction was carried out over H-Beta using nitrogen instead of hydrogen in order to study the influence of the carrier gas on the nature of the carbonaceous compounds. Coke was successfully removed from the silica structure and analyzed as described in Section 2.3 and the results were summarized in Table 3. The majority of coke deposited in the used zeolites was soluble in dichloromethane after the destruction of the silica structure, although the percentage of it strongly depended on the reaction conditions, carrier gas and, most of all, on the zeolite structure. It is possible to observe that there was more insoluble coke in H- and Pt-Beta than in their ZSM-5 equivalents under the same reaction condition. This is attributed to the different structure of the zeolites and to the higher Brønsted acidity that Beta zeolite shows over ZSM-5, which enables soluble coke to repeatedly undergo alkylation and cyclization until forming highly polyaromatic molecules, e.g. coronene ($C_{24}H_{12}$), as it has been observed by others in 1-butene isomerization [7,16]. Such polyaromatic molecules are most likely located at the pore mouth of the zeolite because the zeolite pores are too narrow, which makes them responsible for the loss of specific surface area. Hydrogen appears to inhibit, to some extent, the consecutive alkylation/cyclization that soluble coke undergoes before becoming insoluble since only by changing carrier gas, i.e. from H_2 to N_2, the amount of insoluble coke on H-Beta increased by approximately 25%, which also agrees with the different carbonaceous molecules obtained for used H-Beta under different carrier gases. Overall, the nature of soluble coke seemed to be very much independent of the reaction conditions and zeolite structure given that it was mainly constituted by linear long-chain alkenes (C_nH_{2n}), i.e. tetradecene, hexadecene, octadecene, eicosene, docosene, tetracosene, hexacosene and octacosene, for the zeolite catalysts tested. Nonetheless, it was the reactant molecule that determined the composition of soluble coke since the majority of the coke molecules varied from linear tetramers to heptamers of *n*-butane formed by consecutive oligomerization of *n*-butene along the zeolite channels. The long-chain olefins with a number of carbon number (n_C) not multiple of 4, i.e. 14, 18, 22, 26 proved that H transfer, cracking and alkylation of different molecules also took place inside the pores. Interestingly, a fraction of the soluble coke removed from H-Beta and H-ZSM-5 was identified as alkylaromatic, i.e. di-*tert*-butyl benzene ($C_{14}H_{22}$). This molecule may be considered as an insoluble-coke precursor that was formed by the aromatization of soluble-coke molecules. It is believed that this molecule will continue alkylizing with short-chain olefins and aromatizing until a highly stable and polyaromatic molecule is built up.

3.4. Regeneration of coked Pt-Beta and Pt-ZSM-5

Pt-Beta and Pt-ZSM-5 were used at 623 K with WHSV 3.5 h^{-1} for approximately 250 min of TOS. Then, the materials were regenerated under a flow of synthetic air for 2 h at 723 K prior to H_2 reduction and their catalytic performance was again tested under the same conditions. The most effective regeneration occurs during the first hour but it is closely related to the duration of the regeneration [8]. Fig. 4 shows that the oxidative regeneration was almost complete for Pt-Beta although there was a small difference between conversion of *n*-butane over the fresh and used Pt-Beta-REG and Pt-ZSM-5-REG, which could mean that the coke was not entirely removed from the zeolite. This residual coke reduces the effective pore diameter of the zeolite, increasing shape selectivity to the monomolecular mechanism of *n*-butane isomerization. IE thus is higher on the regenerated Pt-modified zeolites (Fig. 5). Unfortunately, regeneration of Pt-ZSM-5 was not successful at all and its activity was not recovered. Possibly, the regeneration conditions were not efficient enough to remove the coke trapped inside the pores and at the pore mouth. This explains the unusual high amount of insoluble coke found after the reaction over Pt-ZSM-5. Moreover, the lower content of insoluble coke found in Pt-Beta is

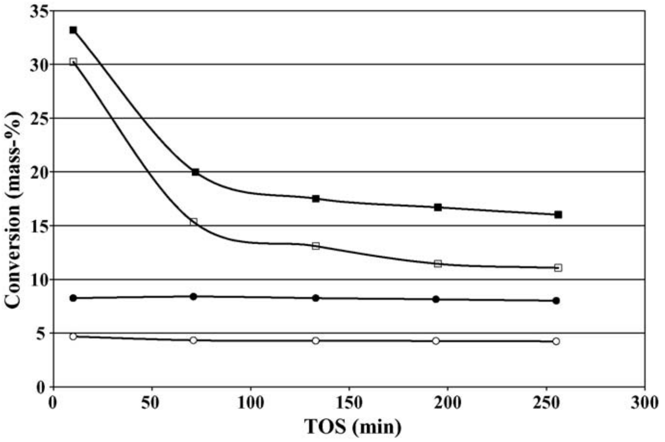

Fig. 4. Conversion of *n*-butane over Pt-Beta (■), Pt-Beta-REG (□), Pt-ZSM-5 (●) and Pt-ZSM-5-REG (○) at 623 K with WHSV 3.5 h^{-1}.

another proof that the monomolecular mechanism is favored over regenerated Pt-Beta since the bimolecular one is considered to promote the formation of coke. Otherwise, similar IE behavior as for Pt-Beta was observed.

3.5. Coke deposition

TGA analysis was used to study the weight gain by coking along TOS. Beta was chosen over ZSM-5 because it was more acidic, active and vulnerable to coking. The weight gain due to the formation of coke was very severe on both the H- and Pt-form of Beta (>18%) as it can be seen in Fig. 6. Coking proceeds very fast and the majority of coke is deposited in the first 70 min of TOS after that the deposition of coke slows down, which concurs with the loss of catalytic activity. In fact, coke deposition on H-Beta and Pt-Beta under the different carrier gases seemed to level out but not at the same weight gain. Each of them had a different maximum weight that could gain under the same reaction conditions. H-Beta gained more weight than the Pt-form as expected. Interestingly, more coke was deposited in H-Beta using hydrogen as a carrier gas. A possible explanation is that hydrogen at high concentrations not only enhances the isomerization of *n*-butane but also the side-reactions, i.e cracking and oligomerization, which are responsible for the formation of coke. Nonetheless, the beneficial effect that Pt and H$_2$ bring together to the stability of the zeolite is visible when coke deposition decreased approximately by 30% in comparison to H-Beta under hydrogen.

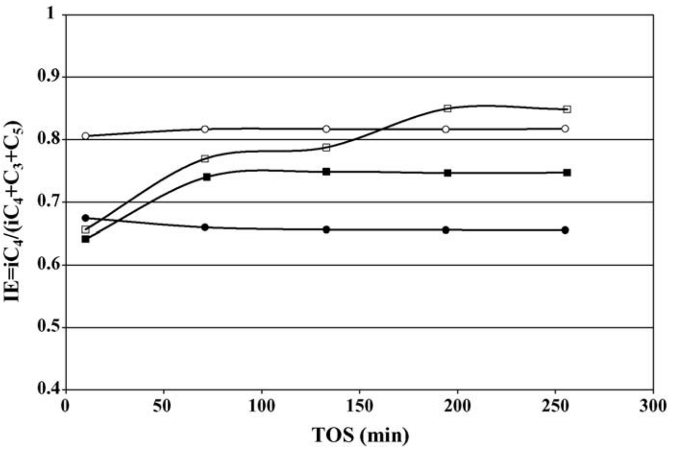

Fig. 5. IE of Pt-Beta (■), Pt-Beta-REG (□), Pt-ZSM-5 (●) and Pt-ZSM-5-REG (○) at 623 K with WHSV 3.5 h^{-1}.

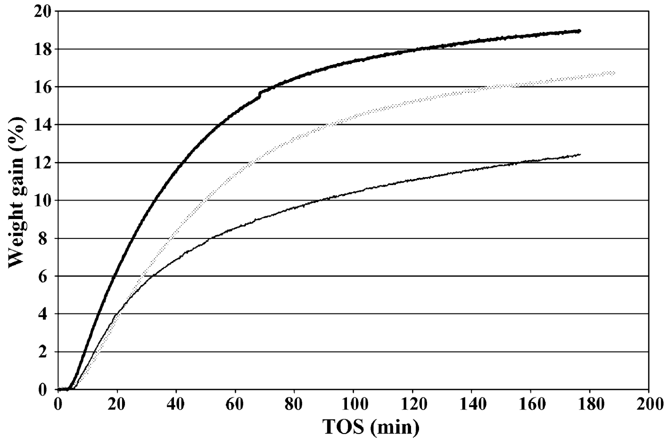

Fig. 6. Weight gain due to coking on H-Beta (▬) under N$_2$, H-Beta (⋯) and Pt-Beta (- - -) at 623 K with WHSV 1.6 h^{-1}.

4. Conclusions

The deactivation behavior of H-Beta and H-ZSM-5 and their Pt-modified counterparts was studied for the isomerization of *n*-butane. Moreover, the regeneration of Pt-Beta and Pt-ZSM-5 and their further catalytic performance were also investigated.

The majority of coke was soluble in dichloromethane although the percentage strongly depended on the reaction conditions, carrier gas and zeolite structure. More insoluble coke was found over H- and Pt-Beta than on the ZSM-5 due to the higher acidity that Beta shows, enabling soluble coke to repeatedly undergo alkylation and cyclization until forming highly polyaromatic molecules. These molecules are located on the pore mouths of the zeolite and are responsible for the loss of specific surface area. Platinum and hydrogen seem to inhibit these recurrent reactions since the amount of insoluble coke increased dramatically when nitrogen was replaced by hydrogen as carrier gas. However, the only factor determining the nature of soluble coke was the reactant molecule. Soluble coke was mainly constituted of linear long-chain alkenes, ranging from *n*-butane tetramers to heptamers, formed by consecutive oligomerization of *n*-butane. Similar molecules were also identified containing n_C not multiple of 4, which means that H transfer, cracking and alkylation of different molecules also took place. The main coke molecules identified were tetradecene, hexadecene, octadecene, eicosene, docosene, tetracosene, hexacosene and octacosene. Most of the coke is deposited during the first 70 min of TOS. The conversion of *n*-butane decreased along TOS due to coke formation. However, the coke inside the pores increased shape selectivity, inhibiting the formation of byproducts, which enhanced the isomerization efficiency along TOS. The regeneration of Pt-Beta with synthetic air was complete and the activity was restored by the burn-off of deposited carbonaceous compounds. Isomerization efficiency of regenerated Pt-Beta was improved due to residual coke inside the pores.

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