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Propane Reactions over Faujasite Structure Zeolites Type-X and USY: Effect of Zeolite Silica over Alumina Ratio, Strength of Acidity and Kind of Exchanged Metal Ion

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Abstract In this work we prepared various zeolite-X and USY samples partially exchanged with copper, iron and platinum. These samples were characterized by XRD, Chemical Analysis, SEM-EDS, N_2-adsorption–desorption, ammonia-TPD, and tested as catalysts in high temperature (400 and 550 °C) propane transformation. The obtained results revealed the strong effect of Si/Al ratio in faujasite zeolite structure, the number and strength of acid sites and of the presence of different metal ions in countered ion sites, on the catalytic activity and selectivity of zeolite-X and USY. The highest propane dehydrogenation activity was achieved with the platinum-exchanged X zeolite (~11.2% propylene yield, ~31% selectivity). On the contrary USY zeolites showed high cracking capability and relatively low dehydrogenation activity excepting the platinum-exchanged sample which yielded notably high aromatization products.

Keywords Propane · Catalysis · Dehydrogenation · Cracking · Zeolites type-X and USY

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1 Introduction

The reaction of propane and other small alkane molecules with microporous acid catalysts such as zeolites yields cracking (e.g. methane, ethylene), dehydrogenation (e.g. propylene) and cyclo-oligomerization (e.g. aromatics) products, according to reaction conditions and catalyst type. The key-factors in these reactions are the type and amount of acid sites, as well as, the presence or absence of metals in the zeolitic framework [1–4].

Dehydrogenation of light paraffins is a very important process for the modern chemical industry. The increasing worlds demand for light olefins, may cause the already existing routes for their production [5, 6] to become insufficient, and the research for alternative ways for their production becomes imperative. One of these alternative ways is the direct catalytic dehydrogenation or oxidative dehydrogenation of light paraffins to the corresponding olefins. Another way is the increase of the production of olefins in the Fluid Catalytic Cracking (FCC) units (which utilize USY and ZSM-5 zeolites as catalysts).

In recent years oxidative or non-oxidative dehydrogenation of light paraffins, over zeolitic catalysts, was investigated by various researchers, as an alternative way for the selective production of light olefins, yielding promising results [7–23].

In addition dehydrogenation processes constitute the first and most significant step of the transformation of paraffins to aromatic hydrocarbons (Benzene, Toluene and Xylene, BTX chemicals). The main route for the production of aromatics is the catalytic reforming of naphthas. This process is incapable of converting light paraffins, like propane, to aromatics. This is the reason for the introduction of the M2 Forming process by Mobil [2], which converts light paraffins to aromatics over H-ZSM-5 zeolite catalysts. British Petroleum (BP) and Universal Oil Products (UOP) later developed the Cyclar process [1, 23], which converts Liquid Petroleum Gas (LPG) to BTX chemicals.

Following the pioneering work of Mobil and BP, various researchers suggested that the catalytic mechanism for the dehydro-cyclo-dimerization of propane to aromatics, over metal modified MFI-type zeolites, consisted by the combination and interaction of metallic species, inside or outside the zeolitic framework, with the acid sites of the ZSM-5 zeolite. Metals (such as Platinum [24, 25], Gallium [26–32], Zinc [33–36] and others [37]) induced the dehydrogenating properties of the material whereas acid sites were responsible for the oligomerization of the dehydrogenation products (bifunctional mechanism).

In addition it has been also previously shown that under experimental conditions that selectively restricted conversion of propane to primary products, the strongest Brønsted acid sites favored cracking whereas the milder Brønsted acid sites favored dehydrogenation of propane over H-Y and H-ZSM-5 zeolites, in accordance with the soft–soft and hard–hard acid–base interaction model [38].

The above facts suggest that paraffin reaction over zeolite catalysts can be used as a valuable tool for the characterization of the amount and type of acid sites in the zeolitic framework [39–41].

In this work we investigated how the differences in Si/Al ratio of faujasite type zeolitic structure, the number and strength of acid sites as well as the kind of metal ion in the countered ion sites, affect the propane transformation activity and product selectivity of zeolite-X and USY based catalysts, under conditions of high hourly space velocity.

2 Experimental Section

Zeolite samples Na-X (BDH) and USY (obtained by the Davison division of W.R. Grace) were ion-exchanged for 24 h at 80 °C with low concentration solutions (in order to achieve a maximum of 10% ion-exchange) of copper [$Cu(CH_3COO)_2$-Analar] [42], iron [$Fe(NO_3)_2$-Analar] [43] and platinum [$Pt(NH_3)_4Cl_2$-Merck]. Ion exchange solution of $Pt(NH_3)_4Cl_2$ was obtained after dissolution with NH_3 solution at pH = 10.8. The platinum samples were later degassed at 450 °C for 3 h, under He flow, in order to desorb the ammonia molecules present in the ion-exchanged complex ($[Pt(NH_3)_4]^{2+}$). The H-form of X-zeolite was prepared by ion-exchange of Na-X with NH_4Cl solution and then calcination at 500 °C under He flow. All the samples were stored in desiccators over controlled water vapor atmosphere (saturated $MgCl_2$ solution) to equilibrate with water vapor).

The exchanged zeolites along with their precursors and their H-forms were characterized by various techniques. Chemical analysis was carried out by means of Atomic Absorption Spectroscopy (Shimadtzu 6800 AAS) and Electron Dispersive Spectroscopy (Oxford ISIS 300 EDS). Powder X-ray Diffraction (XRD) was carried out on a Siemens D-500 diffractometer with Cu*K*a-radiation. Scanning Electron Microscopy (SEM) images were obtained with a JSM 840-A JEOL SEM. Specific Surface Area (SSA) was measured by nitrogen sorption isothermally at 77 K using a Sorptomatic 1900 instrument (multipoint BET). Temperature-Programmed Desorption (TPD) of ammonia tests were performed on a conventional apparatus which consisted of a cylindrical quartz microreactor, a vertical well-controlled high-temperature furnace and a gas chromatograph equipped with a thermal conductivity detector (TCD). The mass of the catalysts sample used was 0.2 g. Sorption of dry ammonia (Merck, H_2O-free) took place at 100 °C, in a static system for 90 min at 1.5 bar ammonia pressure. Stripping was done afterwards for 40 min at 100 °C under He flow. In this way, the weakly and physically adsorbed ammonia was minimized in the sample. Desorption of ammonia was done at a rate of 10 °C/min from 100 up to 800 °C under He flow (50 mL/min). The desorbed ammonia was detected on a Shimadzu GC-8A gas chromatograph (with TCD), and then it was trapped in an HCl aqueous standard solution (0.01 N). The total desorbed NH_3 was estimated by titrimetric determination of the excess standard 0.01 N HCl solution, using a standard 0.01 N NaOH solution.

The catalytic activity of the zeolite samples was investigated using a cylindrical fixed-bed continuous-flow glass reactor. The reaction was carried out between 400 and 550 °C. Temperature in the reactor was monitored by a thermocouple located at the center of the catalyst bed. The catalyst (mass 0.2 g) was placed into the glass reactor between two layers of glass-beads (Serva). Before reaction, the catalysts were outgassed at 500 °C for 3 h under He flow. The reactant mixture had a molar composition $He/C_3H_8 = 10/1$ and space velocity of 1,000–2,000 h^{-1}. Products were analyzed using a Shimadtzu GC-14 b gas chromatograph equipped with a Supelco SP-1700 column and a Thermal Conductivity Detector (TCD).

3 Results and Discussion

3.1 Compositional, Structural and Acidic Characteristics of the Tested Catalysts

The physicochemical characterization results of the zeolites used in this work are listed in Table 1. From Table 1 it

Table 1 Compositional and structural characteristics of the zeolite catalysts

Sample	Cu (wt.%)/(% i.e.)[f]	Fe (wt.%)/(% i.e.)[f]	Pt (wt.%)/(% i.e.)[f]	SSA[a] (m^2/g)	Relative crystallinity[b] (%)
Na-X[c, d]	–	–	–	832	100
H-X[c]	–	–	–	221	26
Cu-X	(0.90/4.5)	–	–	838	100
Fe-X	–	(0.73/6.1)	–	807	99
Pt-X	–	–	(0.33/0.5)	630	92
USY[c, e]	–	–	–	808	100
Cu-USY	(0.75/6.1)	–	–	816	94
Fe-USY	–	(0.67/9.1)	–	772	90
Pt-USY	–	–	(0.66/1.7)	814	100

[a] Specific surface area (multi-point BET)

[b] Relative crystallinity considering the Na-X and USY samples as 100% crystalline

[c] Na content in the samples Na-X, H-X and USY is: 14.18 wt.%, 10.37 wt.% and 3.26 wt.% correspondingly

[d] Molecular composition of Na-X sample is $Na_{83}H_3[Al_{86}Si_{106}O_{384}]$ $75H_2O$

[e] Molecular composition of USY sample is $Na_{16.5}H_{28.5}[Al_{46}Si_{146}O_{384}]$ $130H_2O$

[f] % Ion-exchange

is revealed that the metal concentrations achieved are between 0.3–0.9 wt.%; the very much lower weight percent platinum exchange in type-X zeolite compared to that in USY is an indication of the selective positioning of $[Pt(NH_3)_4]^{2+}$ in the mouths of the pores.

The XRD patterns of the zeolite samples and SSA measurements (Table 1), show that they were highly crystalline and retained their structural integrity to a high degree (relative crystallinity above 85% for all the samples except H-X) after the ion exchange procedure. The large structural breakdown observed in the H-X sample is a common phenomenon among the H-forms of zeolites with low Si/Al ratio, attributed to framework instability due to high concentration of acid sites [44]. SEM images of all the zeolites of this work (except again H-X) showed clear phases of zeolitic particles consisting of typical small-sized (<1 μm) X and USY crystals (Fig. 1). No amorphous particles or extra zeolitic metallic phases were detected. SEM images of H-X (Fig. 2) reveal that the sample consists of crystalline areas with typical 1 μm crystals, as well as, amorphous aluminasilicate phases.

The acidic characteristics of the zeolite samples of this work are given in Table 2. The splitting of total acid sites to sites of weak and higher acid strength was done after mathematical deconvolution of the experimental TPD curves and by assigning the individual peaks with maxima lower than 300 °C to weak sites and with maxima above 300 °C to strong acid sites.

The deconvoluted ammonia-TPD curves of H-X and metal exchanged X samples, are shown in Fig. 3, and the corresponding of USY and Pt-USY in Fig. 4. As it is clear from Table 2 the total acidity as well as the strong acidity of the X-type zeolites is considerably lower in comparison to the corresponding of USY. The latter is in agreement with the fact that Si/Al ratio is close to one in type-X zeolite, while in USY is round five. However, the partial

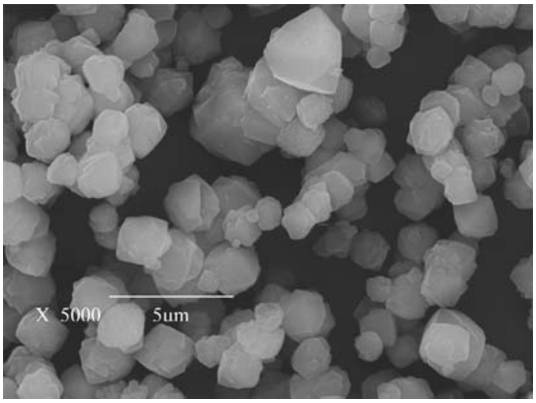

Fig. 1 SEM image of the Pt-X sample

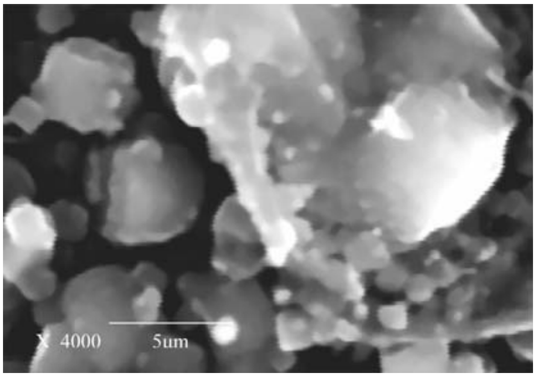

Fig. 2 SEM image of the H-X sample

Table 2 Acidic characteristics of the zeolite samples

Sample	Number of acid sites (desorbed ammonia) (mmoles NH_3/g sample) (±0.05)			Strong/weak (mole ratio)
	Total	Weak	Strong	
Na-X	0.05	0.04	0.01	0.25
H-X	1.20	0.59	0.61	1.03
Cu-X	0.70	0.57	0.13	0.22
Fe-X	0.31	0.31	~0	~0
Pt-X	1.04	0.42	0.62	1.48
USY	1.62	1.01	0.61	0.60
Cu-USY	1.88	1.19	0.69	0.58
Fe-USY	1.75	1.12	0.63	0.56
Pt-USY	2.22	1.20	1.02	0.85

breakdown of H-X zeolite can be attributed to the formation of a large number of acid sites.

The incorporation of copper and iron into both X and USY frameworks, leads to an increase of the weak acidity and a negligible increase of strong acidity. It is therefore evident that the inducted copper and iron cations function as weak acid sites.

In contrast the introduction of platinum cations in ion exchange positions results in a major increase of both weak and strong acidity. Although the amount of platinum introduced in the counter ion positions of both type-X and USY structure is substantially low, it is possible that platinum cations can form –OH groups with acidic properties in faujasitic structures. Furthermore, it is known that transition metal ion exchange in faujasite structure zeolite is associated with the formation of Brønsted acid sites

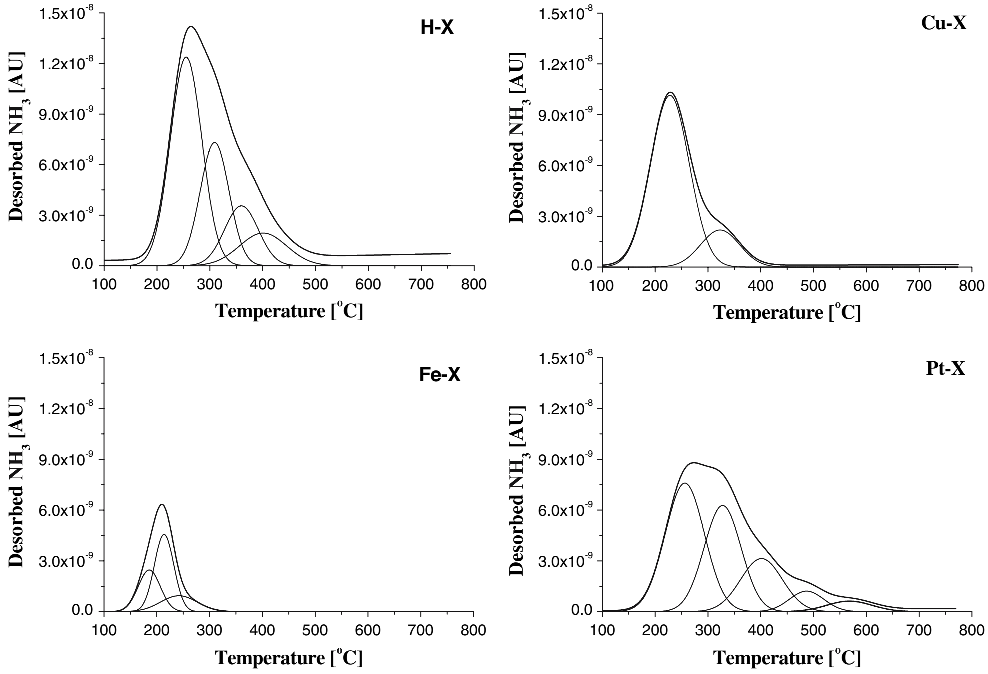

Fig. 3 Deconvoluted temperature-programmed desorption (TPD) curves of the zeolite-X catalysts

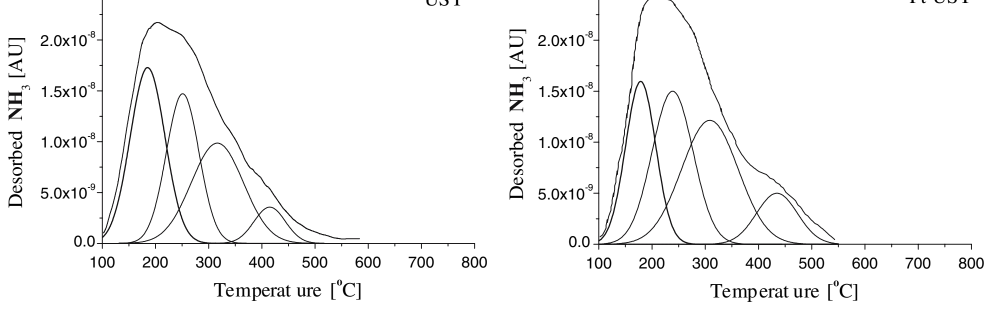

Fig. 4 Deconvoluted temperature-programmed desorption (TPD) curves of USY and Pt-X catalysts

[45, 46]. Another scenario for the major increase in the acidity of the platinum loaded samples is the possible presence of NH_4^+ cations in ion exchange positions, which created structural hydroxylic groups during the outgassing of ammonia from the sample, as mentioned in the Sect. 2.

3.2 Catalytic Activity of the Tested Catalysts

The reaction of propane over zeolitic catalysts yields, as mentioned previously, cracking (e.g. methane, ethane, ethylene, coke), dehydrogenation (e.g. propylene) and cyclo-oligomerization (e.g. aromatics) products, according to reaction conditions and catalyst type [10, 14]. The maximum total conversion of propane over the tested samples as well as their maximum dehydrogenation activity and selectivity, are shown in Table 3. The selectivities of the tested catalysts towards non-dehydrogenation products are given in Table 4.

The dependence, of the total conversion of propane and the product selectivities to propylene and aromatics, on the reaction temperature for the platinum loaded catalysts, is shown in Fig. 5.

From Table 3 it is revealed that over X-zeolites (except from the sample exchanged with platinum) the total conversion of propane is relatively low due to structural and acidity limitations. As a result, the selectivity to propylene of the zeolite-X catalysts is high whereas the propylene yield is low attributed mainly to the lack of acid sites which could lead to higher conversion rates. In addition the deactivation, due to coking, of all the tested X-catalysts with 2 h time-on-stream is negligible (no deactivation of the samples after five catalytic cycles).

The small amounts of copper and iron do not upgrade the dehydrogenation capability of the catalysts. In fact iron seems to function as an inhibitory agent of propylene production. The enhanced acidity of H-X results to improved propylene yield but the total conversion remains low, due to the lack of dehydrogenation agents, such as transition metals, and the decrease of the crystallinity and surface area in this sample.

Table 3 Maximum total conversion of propane over the tested samples and their dehydrogenation activity and selectivity (at 550 °C)

Sample	Propane conversion[a] (%)	Selectivity to propylene (%)	Propylene yield (%)
H-X	19.3	27.4	5.29
Na-X	9.6	26.1	2.51
Cu-X	21.1	18.1	3.81
Fe-X	12.2	9.3	1.13
Pt-X	36.9	30.4	11.22
USY	48.0	6.3	3.02
Cu-USY	38.5	9.8	3.77
Fe-USY	33.6	11.7	3.92
Pt-USY	31.2	7.3	2.28
Pt-USY[b]	46.7	2.0	0.92

[a] Reactant mixture $He/C_3H_8 = 10$, space velocity 1,200 h^{-1}

[b] Dehydrogenation activity at 525 °C

Table 4 Selectivities of the tested catalysts to non-dehydrogenation products (at 550 °C)

Sample	Cracking products[a] (methane and ethylene) (%)	Ethane (%)	Aromatics (%)
H-X	49.4	11.4	3.1
Na-X	51.5	18.2	–
Cu-X	58.7	15.3	<1
Fe-X	68.9	17.6	<1
Pt-X	42.1	16.6	3.5
USY	77.5	7.4	–
Cu-USY	72.1	9.9	<1
Fe-USY	73.6	9.3	<1
Pt-USY	43.2	6.6	37.4
Pt-USY[b]	16.1	8.5	67.2

[a] Reactant mixture $He/C_3H_8 = 10$, space velocity 1,200 h^{-1}

[b] Dehydrogenation activity at 525 °C

On the other hand the total conversion of propane, over all USY samples, is higher with the main products of the reaction being methane and ethylene (cracking products). This can be explained by the action of the large amount of accessible to the reactants strong acid sites, present in these catalysts, which in addition possess the suitable pore structure and size for cracking, isomerization and oligomerization reactions of small hydrocarbon molecules. The introduction of copper and iron into the USY framework results in a minor increase of the selectivity to propylene, due to the small decrease of strong/weak acid site ratio (strong acidity favors cracking reactions). Total conversion over these catalysts is also lower, possibly explained by both, the above mentioned decrease in their acid site ratio, as well as by their minor loss of crystallinity after the ion exchange procedure. The deactivation with time-on-stream of the USY catalysts (except Pt-X, mentioned later) is also very low, in spite of the presence of a large amount of strong acid sites, perhaps due to the high space velocity that restricts diffusion of the reactant inside the pore structure.

Both platinum-exchanged samples show some unique catalytic characteristics (see Fig. 5). The zeolite-X sample presents high dehydrogenative activity and selectivity, comparable to the activity and selectivity under the same reaction conditions, of a platinum loaded (5 wt.% platinum) commercial alumina catalyst (propylene yield 10.8%, selectivity 15.3%). The enhanced acidity of Pt-X combined with the well known and excessive dehydrogenation

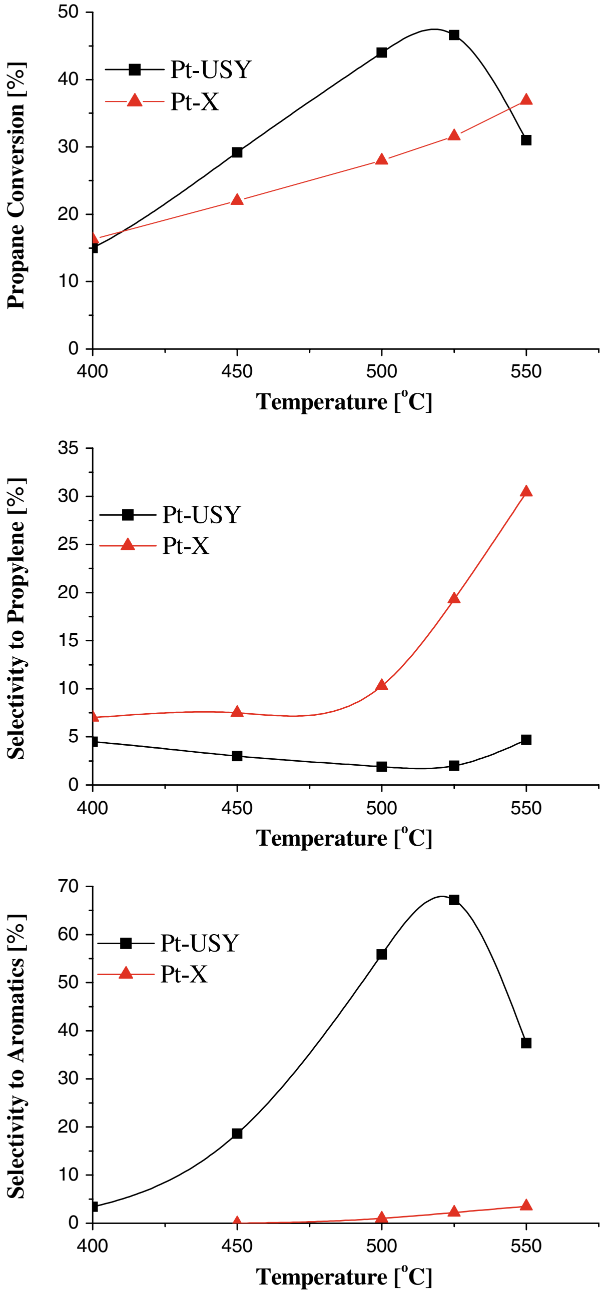

Fig. 5 Propane conversion, propylene selectivity and aromatics selectivity versus reaction temperature, for the platinum loaded catalysts

capacity of platinum [24, 25] and the decreased Si/Al ratio of the type-X structure, result to especially high propylene yield and selectivity. The low platinum exchanged capacity with the high aluminum content of the type-X structure, suggest that platinum species are located in the pore mouths area [47]; that may explain this behavior of the observed dehydrogenation reaction properties of Pt-X sample.

On the other hand the Pt-USY sample presents particularly high aromatization activity (aromatics yield 31.3%, selectivity 67% at 525 °C). Propylene molecules formed by the reaction of propane with the platinum species located inside the zeolitic supercages of the pore channels, react with the large number of strong acid sites producing aromatics, via oligomerization reactions.

As it is evident from Tables 3 and 4 and Fig. 5 the high aromatization rate of propylene over the Pt-USY catalyst decreases above the temperature of 525 °C. This results to a minor increase of the propylene yield (a smaller amount of propylene molecules oligomerize and consequently a higher amount of propylene is detected in the final products) and a major decrease of the total propane conversion. The above phenomenon is attributed to severe fouling of the catalyst due to the formation of coke molecules (coking) which block the oligomerization sites in supercage of the catalyst, preventing propane molecules to reach and react with them. This suggestion is supported by the facts that the decrease of the reaction rate begins only at temperatures above 525 °C (no deactivation is detected with time-on-stream at 525 °C or lower), and it is irreversible, unless the catalyst is reactivated by oxygen flow at high temperatures.

4 Conclusions

The above results reveal the strong effect of Si/Al ratio of faujasitic zeolite structure, of the number and strength of acid sites and of the different metal on the dehydrogenation activity and selectivity of zeolite-X and USY samples. X frameworks are more suitable for dehydrogenation whereas USY induce cracking and oligomerization reactions. Copper and iron do not substantially enhance the catalytic capability of the zeolitic hosts due to low dehydrogenation ability, insufficient acidity. Platinum loaded zeolites show some unique catalytic properties in spite of the very small amount of the exchanged metal ions. This can be explained by the high dehydrogenative activity of platinum, which in the zeolite-X sample is leading to high propylene yield due to cooperative action of weak acid sites with Pt-species localized in pore mouths, whereas in the USY sample the Pt-species act synergistically with the strong acid sites to produce aromatics due to its localization in the pores channels. It is, also, interesting to test the catalytic activity of X and USY zeolites loaded with larger amounts of platinum, or of Cu or of Fe elements, since the transition metal ions at higher loads may form clusters within zeolitic structures with unexpected catalytic results.

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