Normal Heptane Reforming of Promoted Platinum Composite Catalysts: Preparation, Characterization and Catalytic Performance

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Abstract

Pt/Zr(x)-HMS/HZSM-5 catalysts with different ratios of Silicium/Zirconium (denoted as x) were studied for normal heptane reforming at 350-450 $^\circ$C temperature range. For this purpose, the properties of the catalysts such as X-ray diffraction, X-ray fluorescence, Fourier-transform infrared spectroscopy, Ultraviolet–visible diffuse reflectance spectroscopy, NH_3-temperature programmed desorption, H_2 chemisorption, N_2 adsorption-desorption, and thermal gravimetric analysis were used. The results show that the produced Pt/Zr(x)-HMS/HZSM-5 catalysts have highly efficient performance for n-heptane reforming with a high isomers selectivity up to 69.4% (mono branched isomers = 31.8% and multi branched isomers = 37.6%) and a good selectivity to aromatic compounds (especially toluene = 6.9%), in spite of an appropriate selectivity to light products. It was revealed that the proper structure of these catalysts facilitates the reforming of n-heptane. According to these results, Pt/Zr(35)-HMS/HZSM-5 catalyst showed the favorable properties for this investigated catalytic process.

Keywords: Normal Heptane reforming; Pt/Zr(x)-HMS/HZSM-5; Isomers selectivity; Toluene.

Introduction

In order to achieve high-quality and clean fuels with appropriate octane number, various catalytic processes are used. One of them is reforming that controls reasonably the quality of naphtha and increases its octane number with increasing the production of aromatics and isomerized paraffins [1-3].

A great variety of compounds with various octane number can be produced through this reaction, which are affected by the type of catalyst [3]. Bifunctional catalysts (metal/acid) with platinum (as active phase) dispersed on acidic supports have shown the best performance [4-7]. Hence, many researchers focused on these types of catalysts.

Among them, mesoporous silica has favorable stability, pore size distribution, high specific surface area and functional capacity [7]. On this basis, this matter is widely applied as support to load active metals for the catalytic processes.

Pt-hexagonal mesoporous silica (HMS) catalyst modified by zirconium was developed by our group [7]

and it gave ~45% selectivity to isomerize products at ~85% conversion of n-heptane under reforming conditions. Moreover, this catalyst presented high catalytic activity, selectivity, and stability compared with pure catalysts as a result of better particle dispersion and acidic effects. According to the obtained results from this work, Pt/Zr(5)-HMS catalyst has good catalytic activity for n-heptane reforming, which can be due to its good acidic site density. Meanwhile the generation of lightweight (cracking and hydrogenolysis) products by this catalyst is very high, the production of desired aromatic products (as toluene) is very low and most importantly, its catalytic stability against the coke formation is very low, the need for preparing a new catalyst is still felt.

Since there are four most important groups' reactions in reforming, as isomerization to isoparaffins, cracking of paraffins to lower hydrocarbons, aromatization and hydrogenolysis [8], we focused on these reactions. The present study consists of two sections. The first section includes the preparation and characterization of Pt/Zr-HMS/HZSM-5 catalysts with different Si/Zr ratios. The physicochemical properties of platinated catalysts were analyzed by XRF, XRD, FTIR, BET, NH_3-TPD, UV-vis DRS and TGA techniques.

The second section addresses the catalytic performances of n-heptane (as a model for naphtha) reforming. The different tests were operated to evaluate catalyst activity, selectivity, research octane number measurements and stability against the coke deposition. The prepared catalysts were studied at different temperatures in each test. Finally, the obtained results with the aim of selecting the best catalyst for n-heptane reforming were judged.

Materials and Methods

The preparation of catalyst

The Pt/Zr(x)-HMS/HZSM-5 catalysts with 40 wt% of HZSM-5 and Si/Zr=5, 10, 20 and 35 were synthesized as our previous work [9]. However, in the present work, zirconyl (IV) nitrate hydrate as a zirconium source was used in the manufacture of catalyst instead of aluminum isopropoxide.

Characterization methods

The instructions and full description of the characteristics of the analytical devices used are presented in our previous work [9]. We did not provide this explanation here for non-repetition.

Catalytic performances and measurements
Activity measurement

Similar to the method used in the reactor test described in the previous work [9], the prepared catalysts were tested at 350 to 450 °C. n-Heptane conversion is defined as following equation;

$$conv. (\%) = \text{percentage of } n - C_7 \text{ transformed into products} \quad (1)$$

The selectivity equation is also as follow;

$$S_x(\%) = \frac{n-C_7 \text{ transformed into a certain product}}{\text{total amount of } n-C_7 \text{ converted}} \times 100 \quad (2)$$

In these equations *conv.* is a catalytic conversion to various products and S_x is the selectivity to each product that were denoted as x.

Stability test

The coke deposition over the catalyst surfaces and its deactivation are the main difficulty in the catalytic operations. So to get more information about the zirconium effect during the catalytic activities, the stability of prepared catalysts was also examined at the 400 °C for 72 h onstream. The products were also recognized by an on-line GC.

Results and Discussion

Catalyst characterization

To ensure from Si/Zr amounts in the structure of synthesized and calcined catalysts and their compatibility with desired values, these materials were analyzed by the XRF method (Table 1).

The Pt/Zr(x)-HZ XRD patterns were shown in Fig. 1. All catalysts have the intense [1 0 0] reflections at 2.3°. It shows the wormhole framework of HMS. Also, the ZSM-5 phases and the amorphous part of the HMS can be observed at 6°–11°, 22°–25° and 20°-30°, respectively [10].

A comparison of the peaks shows that the intensity and breadth of HMS peak increases and decreases with reducing zirconium amount, respectively. This indicates the insertion of zirconium is related to the lattice disorder of catalyst. The typical peaks of platinum do not seem, signifying that the Pt was spread regularly without the creation of agglomerated crystal.

The FTIR spectra under room environments present the peaks of physisorbed water at ~1600 and ~3400 cm^{-1} (Fig. 2). The asymmetric stretching and bending modes of Si–O–Si in HMS structure are appearing in 1200, 1100 and 440 cm^{-1}. The asymmetric and symmetric stretching vibration bands of Si–O–Si and the vibration

Table 1. Physicochemical properties for Pt/Zr(x)-HMS/HZSM-5 (Pt/Zr(x)-HZ)

Samples	Pt/Zr(5)-HZ	Pt/Zr(10)-HZ	Pt/Zr(20)-HZ	Pt/Zr(35)-HZ
	Surface characteristics			
S_{BET} (m^2/g)	710	727	749	784
V_p (cm^3/g)	0.39	0.41	0.44	0.47
S_{micro} (m^2/g)	130	135	139	145
$V_{micro-p}$ (cm^3/g)	0.14	0.15	0.16	0.17
d_p (nm)	2.25	2.31	2.41	2.45
	Acidic characteristics			
Weak [a]	0.45	0.44	0.44	0.43
Strong [a]	0.32	0.32	0.31	0.31
M_d (%)[b]	85	87	88	92
Si/Zr[c]	4.41	9.81	18.31	33.85

[a] Weak and strong acids (vs. mmol NH_3/g) were recorded in 230-250 °C and 460-570 °C, respectively; [b] By H_2-chemisorption technique; [c] By XRF analysis.
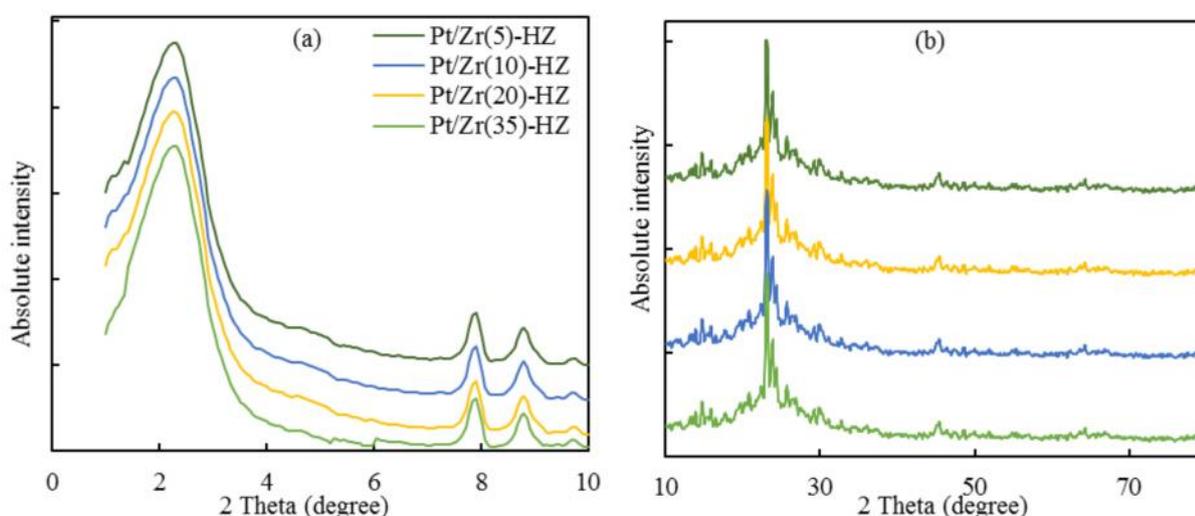
Figure 1. XRD patterns for Pt/Zr(x)-HMS/HZSM-5 catalysts, in (a) 1° to 10° (low angle) and (b) 10° to 80° (high angle) regions

of double-ring in HZSM-5 structure are appeared at ~1000, 790 and 540 cm^{-1} wavenumbers, respectively [10, 11].
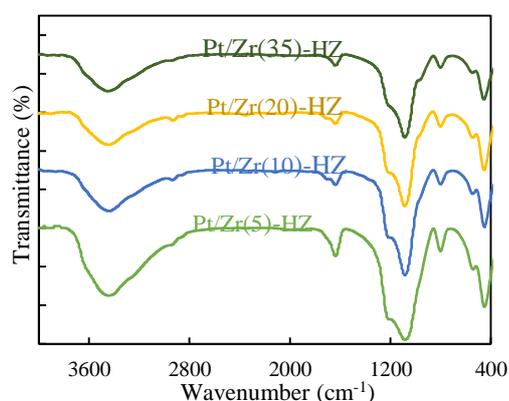

Figure 2. FTIR spectra for the powder Pt/Zr(x)-HZ catalysts

Figure 3 presents the UV–vis DRS of Pt/Zr(x)-HZ. This analysis was used to recognize and distinguish the chemical structure of platinum. The position of the absorption bands in these spectra presents the degree of coordination and aggregation of the metal oxides. The ~250 nm absorption band is related to a charge transfer transition (CT) of O^{2-}-Pt^{2+} in PtO structure. Also, the weak shoulder at above 300 nm can be assigned to the d-d transitions of Pt^{2+}. The observed shifts in the intensities of these peaks can because of the diversity in the interaction strength of particles and their population on the supports [10].

Structural virtues of Pt/Zr(x)-HZ materials were evaluated by nitrogen physisorption (Fig. 4). According to IUPAC classification, the type of isotherm for Pt/Zr(x)-HZ catalysts is a type IV. These isotherms have a H1 hysteresis loop that is characteristics of meso porous catalysts, with highly similar cylindrical pores. These isothers have two steps of capillary condensation.
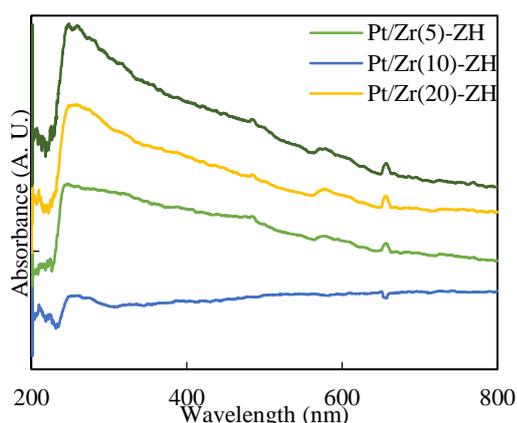
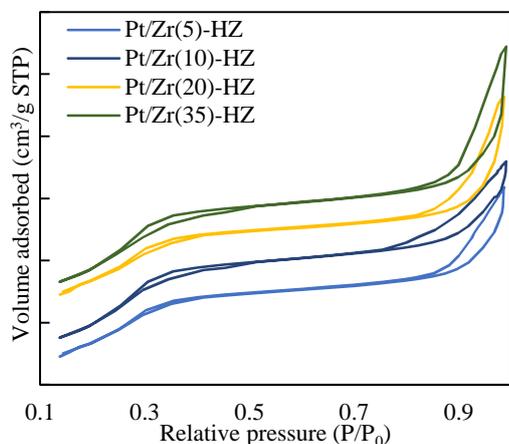**Figure 3.** UV-vis DRS of the Pt/Zr(x)-HZ catalysts

Figure 4. BET isotherms of platinated Zr(x)-HZ catalysts

One of them is at $P/P_0=0.3$ assigned intra particles meso porosity and at a higher partial pressure of 0.9, a small hysteresis loop ascribed to inter particle textural porosity and deviously demonstrates the particle size [12]. Table 1 summarizes the textural characterizations (S_{BET}, V_P and d_P). These results change as follows: Pt/Zr(35)-HZ > Pt/Zr(20)-HZ > Pt/Zr(10)-HZ > Pt/Zr(5)-HZ.

The results show that the incorporation of Zr species decreases the textural specifications. The decrease pore volume and surface area by introducing zirconium (or decreasing Si/Zr) displays that the zirconium alleviates the pore diameter and fully obstruction the majority of them.

The acidity of Pt/Zr(x)-HZ catalysts were summarized in Table 1 and shown in Fig. 5. All catalysts have two desorption peaks in the temperature region of 230-250 °C and 460-570 °C, interpreting as the weak and strong acids. The results are evolving as
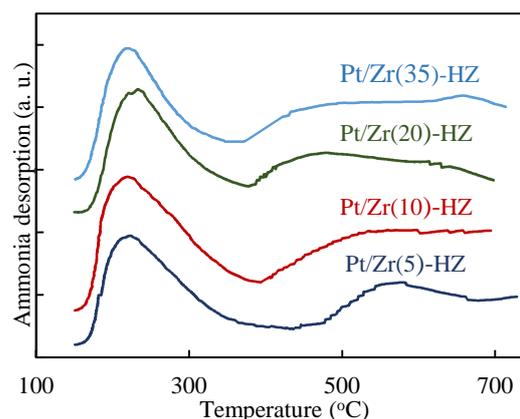

Figure 5. NH$_3$-TPD diagrams for platinated Zr(x)-HZ catalysts

follows: Pt/Zr(5)-HZ > Pt/Zr(10)-HZ > Pt/Zr(20)-HZ > Pt/Zr(35)-HZ. The results show that the increase in Zr amount promotes the acidity of prepared catalysts. According to the acidity distributions, zirconium improves the weak acid sites than the strong acid sites.

Catalytic performance

The prepared catalysts (Pt/Zr(x)-HZ) were used in n-heptane reforming and the results during the first hour on stream in the range of 350-450 °C are listed in 2. The main products are four classifications as n-heptane isomerization to isoparaffins (i-C$_7$), cracking of paraffins to lower hydrocarbons (crack.), aromatization (arom.) and hydrogenolysis (hydro.).

It can be seen from Table 2 that the increment of reaction temperature increases the n-C$_7$ conversion and selectivity to cracking, hydrogenolysis and aromatic products. This condition decreases the selectivity to isomerization products, both mono branched (MOB) and multi branched (MUB) isomers. High cost Si/Zr catalysts (Pt/Zr(35)-HZ and Pt/Zr(20)-HZ) show 100% n-C$_7$ conversion and >57% selectivity to i-C$_7$ in this temperature range.

For Pt/HZ catalyst, as the Zr is loaded, n-C$_7$ conversion increases from 79% to 100% and the selectivity to i-C$_7$ increases from 8.6% to 69.4%. The conversion of n-C$_7$ and the selectivity to i-C$_7$ show inconspicuous promote with the increment of the Si/Zr from 5 to 35 wt%, hence 35% Si/Zr ratio was adopted.

Notably, the n-C$_7$ conversion is greatly improved with temperature. The reason may be the production of cracking, hydrogenolysis and aromatic products at high temperature.

The selectivity to monobranched isomers (MOB) is more than multibranched isomers (MUB) over all

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prepared catalysts, it indicates that MUB isomers are prone to take place on larger pore size and channels due to ease of diffusion among pores and channels [7].

The results show that a group of parameters such as surface characteristics, structural regularity, metal function and its distribution, geometry, strength and type of acid sites are effective over the catalytic performance.

The gasoline octane number is reported as an antiknock index. To determine the quality of generated products, the research octane number (RON) according to the follow equation was calculated (Table 2):

$$RON = \sum_{i=1}^{k} y_i\, RON_i \qquad (3)$$

where RON_i is the RON of pure material (as i) and y_i is the volume fractions of component i [11].

The results of research octane number in Table 2 present Pt/Zr(35)-HZ at 450 ^{o}C has the best RON (RON=85.1), because of producing molecules with
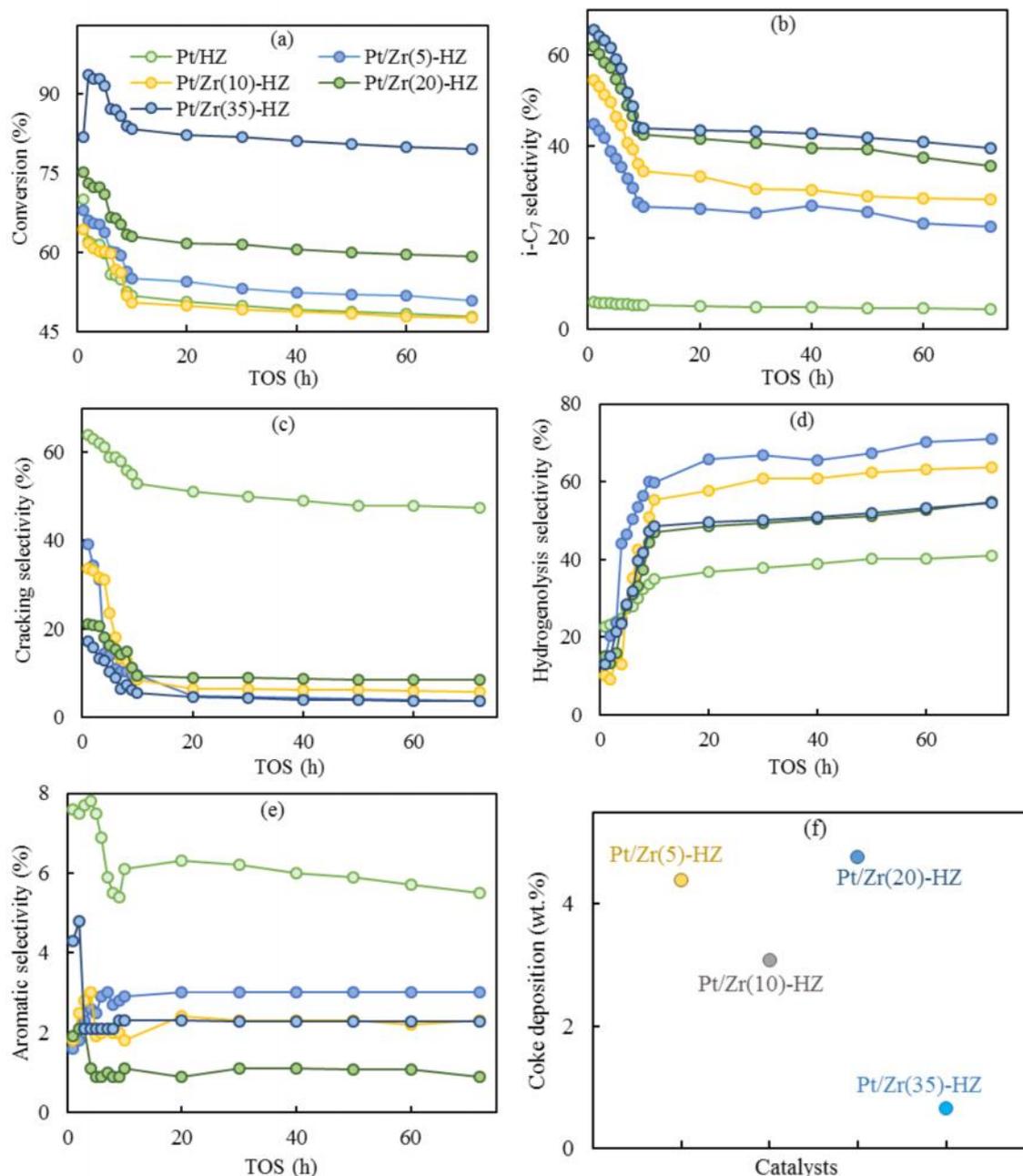

Figure 6. The stability of Pt/Zr(x)-HZ catalysts during 72 h on stream (TOS) at 400 ^{o}C for various reactions of reforming; (a) conversion and selectivity to (b) i-C$_7$ isomers, (c) cracking, (d) hydrogenolysis, (e) aromatic and (f) coke deposition.

better RON_i.

The effects of reaction time over the prepared catalysts were shown in Fig. 6 at 400 $^\circ$C. The n-C_7 will not be fully converted to the product until the reaction time is more than 5 hours. At above 5 hours time of reaction, the selectivity to i-C_7, cracking and aromatics decreases to 39.6, 47.5 and 5.5% and also the hydrogenolysis selectivity is up to 71%. In a word, Pt/Zr(35)-HZ gives the best catalytic stability under 72 h on stream and 400 $^\circ$C.

The amounts of coke formed are the reason why these results are observed. These amounts were measured using thermal gravimetric analysis (Fig. 7). The low amount of coke deposited indicates the good stability of these catalysts against deactivation during the long processes.

These results partially follow the acidic properties of the catalysts. However, Pt/Zr(20)-HZ does not follow from this trend.

Conclusions

Generally, a well-performing catalyst for reforming process is active, has a high specific surface area and appropriate acidity and also provides favorable conditions for the best selectivity to important products such as aromatics (except benzene due to its environmental and carcinogenic effects) and isomers (especially multi branched isomers). On the basis of the conversion, selectivity and stability tests done in this work, Pt/Zr(35)-HZ catalyst has the best catalytic behavior, with the highest n-C_7 conversion (100%), i-C_7 selectivity (69.4%), aromatic selectivity (6.9%) and RON (85.1) and the lowest hydrogenolysis selectivity (12.4%), cracking selectivity (16%) and coke formation (0.65 wt%). The catalytic activity is determined by catalysts chemical composition. This catalyst showed better results than our previous reported work (Pt/Zr(5)-HMS) [7]. Particularly, its high stability against the deactivation by the coke deposition is very impressive. Different identification tests were carried out on the prepared catalysts, and the best results were obtained for
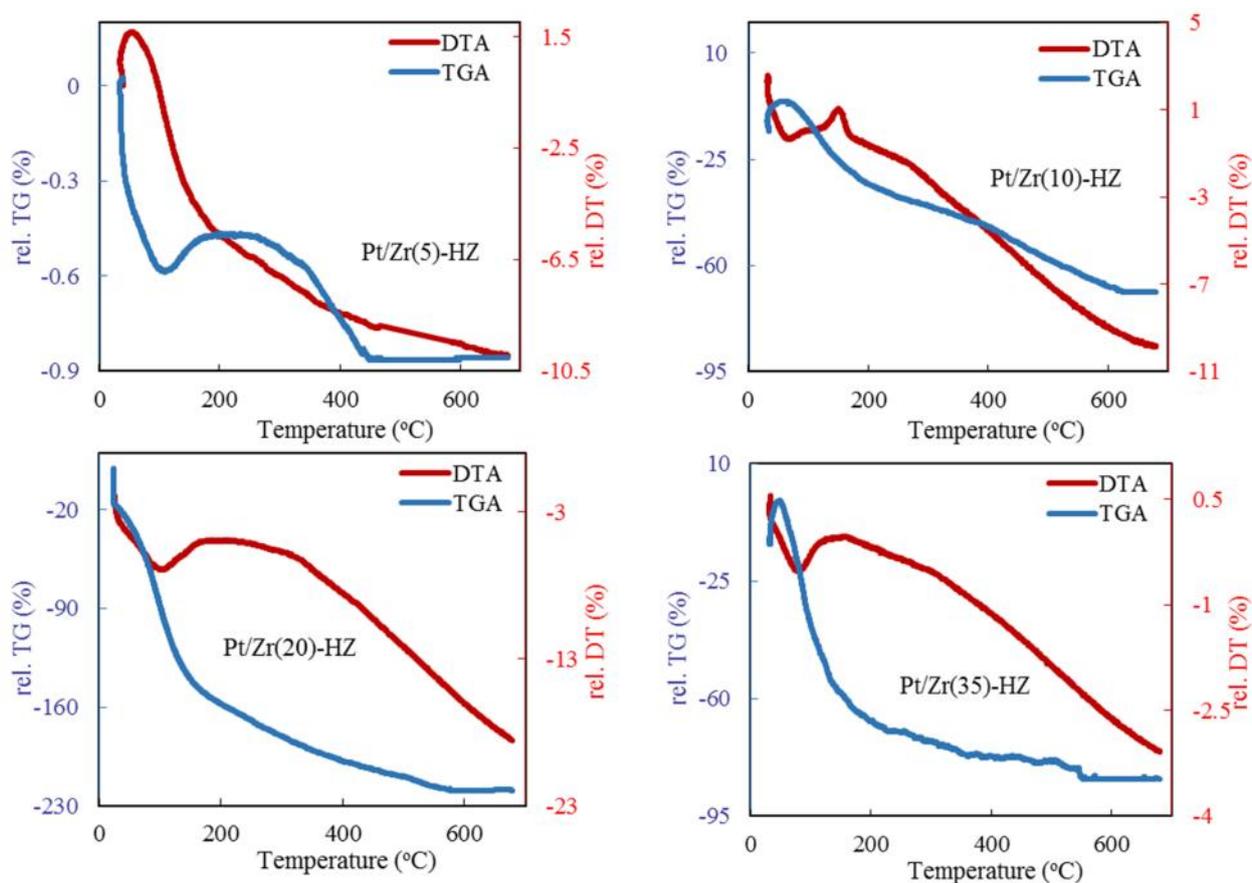

Figure 7. TG-DTA plots of the used catalysts after 72 h (time on stream)

Pt/Zr(35)-HZ as the amount and nature of catalytic acidity, specific surface area and metal dispersion.

Acknowledgments

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