

# **Catalytic activity of Pt loaded zeolites for hydroisomerization of n-hexane using supercritical CO<sub>2</sub>**

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## Abstract

The present study investigates the synthesis of novel strontium (Sr) and barium (Ba) modified crystalline zeolites including Zeolite Socony Mobil-5 (ZSM-5) and Mordenite (MOR) by a batch-wise ion-exchange method with an appropriate chloride solution of 3 N at pH 7.2 and 50 °C and coated that modified zeolites (Ba-ZSM-5 and Ba-MOR, Sr-ZSM-5 and Sr-MOR) with an inert metal (Pt) by a novel supercritical CO<sub>2</sub> method by using the PtMe<sub>2</sub>COD as a precursor for n-hexane hydroisomerization in a micro-reactor unit at different temperatures (250-325 °C), H<sub>2</sub>/HC ratios of 3, 6, and 9 and pressure of 5 bar. The acidic and physical features of the Pt loaded zeolites were systematically characterized using FT-IR, XRD, BET surface area measurements, TGA, and TEM techniques. It is found that the metal loading in scCO<sub>2</sub> results in more uniform and very small metal nanoparticle (1.37 nm) dispersion with high stability after reduction and revealed that high loading pressure in scCO<sub>2</sub> (280–300 bar) results in higher catalytic activity and surface area. The maximum conversion and selectivity of about 80 and 90% for the n-hexane isomerization were achieved at 275 °C and H<sub>2</sub>/HC ratio of 6 for Pt/Sr-ZSM-5 catalyst. Results reported that Pt loaded over all the zeolites (H-MOR, Sr-MOR, Ba-MOR, H-ZSM-5, Ba-ZSM-5, and Sr-ZSM-5) by scCO<sub>2</sub> method showed the minimum production of cracking products (C<sub>1</sub>-C<sub>5</sub>) and maximum isomeric products including *iso*-C<sub>6</sub> isomers (2,2-DMB, 2,3-DMB, 2-MP, and 3-MP). Furthermore, the overall results of the rate of reaction revealed that Pt/Sr-ZSM-5 and Pt/Ba-ZSM-5 catalysts showed a better rate of isomerization (46.44%) and conversion (47%) for n-hexane at 300 °C, and H<sub>2</sub>/HC ratio of 9 with a minimum rate of cracking. However, it is concluded that the small, pored size Pt loaded ZSM-5 zeolite showed the highest catalytical activity contrast to large pored MOR zeolite and considered as of great interest for diesel and gasoline formation in the oil refining industry.

**Keywords:** Isomerization; n-hexane; Platinum; Zeolite; Catalytical cracking; Supercritical carbon dioxide; 3-methylpentane.

## 1. Introduction

With increasing the world population and new technologies, the demand for fuels like gasoline, diesel, and kerosene is increasing day by day to fulfill the challenge of quality fuel.<sup>1</sup> During the past few decades, the isomerization of n-C<sub>5</sub>-C<sub>6</sub>-C<sub>7</sub> alkanes got considerable attention toward the petroleum industry due to their high-octane number and branched isomers products.<sup>2</sup> Mostly, different bifunctional catalysts are applied for the hydroisomerization of n-C<sub>6</sub> alkanes (n-hexane) that consist of two active sites. One is a noble metal site for dehydrogenation and hydrogenation reactions and other acid sites on the surface of the support (like activated alumina and zeolite) for isomerization, cracking, and cyclization reactions.<sup>3</sup> It is noted that the isomerization of n-C<sub>6</sub> alkanes is critical for the production of environmentally friendly and sulfur-free fuel with a high octane number.<sup>4</sup>

Previously many types of bifunctional catalysts including Pt/Cl/alumina, Pt/HPW/MCM-41, Pt or Ni/MOR, Pt/ZSM-5, and Pd/MCM-22 have been used for n-hexane isomerization in the petroleum industry.<sup>5-7</sup> Recently, the isomerization of n-C<sub>5</sub>-C<sub>6</sub>-C<sub>7</sub> alkanes have been improved in different ways including; 1) the usage of composite zeolites (zeolite A, Mordenite, ZSM-5) loaded by noble metals (Pt, Pd, and Zn) to facilitate the formation of isomer products; 2) the isomerization is performed at fewer temperature to facilitate the formation of isomerized products over zeolite; 3) the hydride transfer agents are used to significantly decrease the cracking products and increased the branched products.<sup>8</sup> The zeolites are assumed as significant catalysts for the conversion of hydrocarbon especially n-C<sub>6</sub> alkanes at an industrial scale.<sup>9</sup> The activity of zeolites is mainly dependent on the presence of Bronsted acidic bridges such as Si-OH-Al that bears the tetrahedrally aluminum and silicon atoms in the structure.

However, the alkanes bind to the charged zeolite frameworks just like induced dipole for the isomerization, cracking, and aromatization reactions.<sup>10</sup> Mordenite (MOR) and Zeolite Socony Mobil-5 (ZSM-5) zeolites are considered as highly important catalysts for n-C<sub>5</sub>-C<sub>6</sub>-C<sub>7</sub> alkanes isomerization because of high hydrolytic stability, thermal stability, good acidic properties, and selectivity. Furthermore, the ZSM-5 and MOR zeolites possess great activity in contrast to former zeolites in the conversion of n-C<sub>5</sub>-C<sub>6</sub>-C<sub>7</sub> alkanes to diesel fractions and gasoline.<sup>11-13</sup> Pastvova et al.,<sup>14</sup> reported that H-MOR zeolite showed the 58% conversion of n-hexane at 275 °C that start to decrease at higher temperatures (>300 °C) due to non-selective cracking reactions. Yeh et al.,<sup>15</sup> stated that H-ZSM-5 catalyst showed only 4.0% conversion of n-hexane at 137 bar and 633 K temperature, and 3.6% conversion at 137 bar and 823 K. However, due to the few limitations including the low conversion rate, deactivation, and loss of activity during the isomerization of n-C<sub>5</sub>-C<sub>6</sub>-C<sub>7</sub> alkanes there was a need to develop an updated version of ZSM-5 and MOR catalysts<sup>16</sup>.

Therefore, several metal species including Pd, Ga, Ni, Ir, Zn, Fe, Mo, Co, Cu, Ru, Zr, and Pt were loaded on the zeolites framework for better stability, selectivity, and activity by different methods including the impregnated and supercritical CO<sub>2</sub>.<sup>1, 17, 18</sup> Among all, platinum (Pt) is known as an extremely effective metal for dehydrogenation and hydrogenation reactions. The Pt loading over the zeolites increased the bifunctionality of catalysts by modifying the acidic active sites and formation of redox sites that are considered as highly effective and stable for n-C<sub>5</sub>-C<sub>6</sub>-C<sub>7</sub> alkanes hydroisomerization.<sup>19-21</sup> Yeh et al.,<sup>22</sup> demonstrated that loading of Pt over ZSM-5 (Pt/ZSM-5) by impregnated method showed the 9.8 and 9.2% n-hexane conversion at 633 and 723 K temperature respectively with 137 bar constant pressure. They also revealed that Pt/ZSM-5 reported the maximum yield of about 12.5 and 8.9% for *iso*-C<sub>6</sub> isomers with an average 9.2% production of the cracked product at the same temperature and pressure. Sousa

et al.<sup>23</sup> reported that Pt/H-MOR (1.10 wt%) showed that the highest conversion and selectivity of about 38 and 96% respectively for the isomerization of n-hexane at 1 atm pressure and 250 °C.

Monteiro and coworkers<sup>24</sup> investigated the loading of Pt over the H-MOR zeolite (Pt/H-MOR) by an impregnated method and observed 100% conversion for n-hexane with 2.4 mol/h g activity. They also reported 46.1, 28.6, 4.5, 11.3, and 4.9% yield for 2,3-dimethylbutane (2,3-DMB), 2,2-dimethylbutane (2,2-DMB), 3-methylpentane (3-MP) and 2-methylpentane (2-MP), and cracked products (C<sub>1</sub>-C<sub>5</sub>) respectively at 250 °C and contact time of 1/WHHSV. Similarly, Travkina et al.,<sup>25</sup> observed that Pt/H-MOR (0.5) revealed the yield of about 1.0% of *iso*-C<sub>6</sub> isomer after n-hexane isomerization at 250 °C that increased to 5.3% at 400 °C along with average 3.1% production of cracked products at 250 °C and 16.95% at 400 °C at 3.0 MPa pressure and 1.5 1/h space velocity. The above-cited literature showed that Pt loaded Mordenite (MOR) and Zeolite Socony Mobil-5 (ZSM-5) (Pt/MOR and Pt/ZSM-5) are the most selective and active catalysts towards the isomerization of n-hexane but the rate of formation of cracking gases are equally high in the previously reported studies because of density and strength of sites of Bronsted acid alongside with space restrictions in the zeolites.<sup>26</sup> In addition, the control of dealumination or desilication by increasing the mesoporosity showed good selectivity but equally decreased the activity of the catalyst by reducing the acidity.<sup>27</sup>

However, to the best of our knowledge, for the first time, the proton in zeolites (H-MOR and H-ZSM-5) was exchanged by Sr and Ba (Sr-ZSM-5 and Sr-MOR, Ba-ZSM-5 and Ba-MOR) ions for better activities and reduce the cracking products in n-hexane hydroisomerization. Also, for the first time, the Pt was loaded by a supercritical fluid CO<sub>2</sub> (scCO<sub>2</sub>) method along with an impregnated method to expand the catalysts surface area, better isomerization, and

comparison of results obtained by two methods. Furthermore, the present study investigated the effect of different parameters including temperature (250-325 °C), pressure (1-5 bar), and H<sub>2</sub>/HC ratio (3, 6, and 9) on isomerization of n-hexane. Also, the low Pt content (0.3 wt%) is loaded over both zeolites to reduce the cost and achieve the desirable acid/metal sites ratio for n-hexane hydroisomerization. The present study also discussed the kinetic analysis and activation energy of the zeolite catalysts for a better understanding.

## **2. Materials and methods**

### **2.1. Chemicals**

Two types of zeolites including H-ZSM-5 (H<sub>n</sub>Al<sub>n</sub>Si<sub>96-n</sub>O<sub>192</sub>·16H<sub>2</sub>O) with Si/Al ratio of 90 and H-Mordenite (H<sub>8</sub>Al<sub>8</sub>Si<sub>40</sub>O<sub>96</sub>·nH<sub>2</sub>O) with Si/Al ratio of 40 were purchased from Sued-Chemie company, Germany in a palletized form (1.5 mm d\*2-3 mm L). n-Hexane (purity of 99.8% and density 0.659 g/cm<sup>3</sup>) was supplied from the Fisher Scientific International company. Strontium chloride (99% pure), barium chloride (99% pure), and sodium hydroxide (99.2% pure) were purchased from Fluka. Dimethyl (1,5- cyclooctadiene) Platinum II, chloroplatinic acid hexahydrate (99% pure with 38-40% Pt), platinum acetylacetonate (99% pure) were obtained from Strem Chemical. Methanol, hydrogen, nitrogen was supplied from the ITMC Lab line. Carbon dioxide and argon were procured from BASF.

### **2.2. Catalyst preparation**

The hydrogen form of zeolite types including H-MOR and H-ZSM-5 was used as support for the preparation of all catalysts. The hydrogen ions were exchanged by barium and strontium cations. The Pt-catalysts preparation was carried out by performing two simple steps including proton exchange and metal loading.<sup>28</sup>

### 2.2.1. Proton exchange

The hot batch-wise treatment was used as an operating procedure for ion-exchange experiments. A 50 g of each zeolite (H-MOR and H-ZSM-5) was slurred in an aqueous solution of barium chloride (3 N). The 183.21 g of BaCl<sub>2</sub>·2H<sub>2</sub>O (barium chloride) was added in 500 mL distilled water with constant stirring of 50 rpm for 2 h at 50 °C while in the case of strontium chloride, 199.96 g of SrCl<sub>2</sub>·6H<sub>2</sub>O was inserted in 500 mL distilled water for each batch. The pH of the solution was held constant at about 7.2 for all samples. The exchanged zeolites (Ba-ZSM-5, Ba-MOR, Sr-MOR, and Sr-ZSM-5) had been filtered off and cleansed by deionized water many times to eradicate chlorine ions and dry out at 110 °C for overnight and then calcinated in a furnace at 450 °C for 4 h for catalysts preparation.<sup>29</sup>

### 2.2.2. Metal loading

The metal loading experiment was performed by using two different types of methods including the impregnation method and supercritical CO<sub>2</sub> (scCO<sub>2</sub>) method concerning the percent of loading and surface area.<sup>30</sup>

#### 2.2.2.1. Supercritical CO<sub>2</sub> method

In the case of supercritical CO<sub>2</sub> (scCO<sub>2</sub>) loading method, autoclave (RWTH Aachen) was designed with stainless steel and equipped with two sapphire windows (Left-site PN 400) that contain 100 mL volume, maximum pressure, and temperature of 400 bar and 350 °C. The dimethyl (1, 5-cyclooctadiene) Platinum (II) (PtMe<sub>2</sub>COD) was operated as a precursor for Pt-based catalyst formulation due to its high solubility in supercritical carbon dioxide. A precise amount (41 mg) of PtMe<sub>2</sub>COD and an 8 g of substrate were put inside the container for loading of Pt on each zeolite and put in the autoclave under argon gas. The vessels were sealed and filled with a certain amount of CO<sub>2</sub> gas to a pressure of 80 bar and start to heat the autoclave by a heater shell (JEKA 100 w) and controlled with a very sensitive controller (Clavex) (error ± 0.5 °C).

After reaching a temperature of about 80 °C inside the autoclave, the autoclave was pressurized with CO<sub>2</sub> at 280 bar using a high syringe pump (HPLC NBA, PW-101) for overnight. After the time was done, autoclave was depressurized gradually and carefully through a restrictor at 5 bar/min, until reach atmospheric pressure. The substrate/precursor composites were eliminated after the cooling of vessel. The adsorbed quantity of precursor was calculated by an analytical balance (Sartorius CP 324 S) accurate to  $\pm 0.1$  mg and with an ICP-MS device to observe the error between measurements by measuring the substrate weight change. The substrate was dried under vacuum up to 15 min at  $27 \pm 3$  °C and then placed in a reactor tube. The different contents of Pt loading across all types of zeolites by scCO<sub>2</sub> are presented in **Fig. 1**. The percentage of Pt content on all these types of zeolites was between 0.210 to 0.268% by weight which is in the range that Pt required for isomerization reactions of n-hexane.<sup>31</sup>

#### 2.2.2.2. *Impregnation method*

Two types of zeolites namely H-MOR and H-ZSM-5 were used as support to produce Pt catalysts by impregnation. For an impregnation, 125 mg of H<sub>2</sub>PtCl<sub>6</sub> and 8 g of each zeolite were put in a conical flask with 20 mL distilled water. The hexachloro platinic acid could easily be dissolved in water and produced a yellow to an orange solution. The closed flask content (pH = <6.00) was then mixed for 6 h by a mechanical stirrer (RW28 Digital Overhead; Thomas Scientific, USA) to prevent cracking of zeolite pallets. It was observed that after about 5 h of mixing, the color of the solution was disappeared, indicating that the maximum quantity of platinum complex was impregnated. The loaded zeolite samples were filtered off and washed carefully with distilled water and then dried in an oven for 24 h at 110 °C. The calculations of the catalyst samples were carried out in the reactor at 260 °C for 3 h under a dry airflow of 100 mL/min.<sup>32</sup>



### 2.3. Characterizations

Characterization of the Pt-catalysts was studied by Thermogravimetric Analysis (TGA), Fourier Transform Infrared Spectroscopy (FTIR), Transmission Electron Microscopy (TEM), X-ray diffraction (XRD), and BET surface area measurement. The FTIR spectra (Shematzo) was used to observe the Lewis and Bronsted acid of original and prepared catalysts through the scan rate of 400-4000  $\text{cm}^{-1}$ . The background spectra of samples were recorded at 100 °C. At a retention time of about 1.62 min, the acidity of the catalysts was estimated from the peak of spectra<sup>12</sup>. The TEM (JEOL JEM-1400 Plus) was applied to determine the porosity and size of materials by using electron diffraction and imaging properties.<sup>33</sup> The ultra-sonic grinding, sawing, and punching mechanical treatments were used to prepare the TEM samples. The ImageJ program of TEM was operated to determine the inter-cluster distances and size of Pt particles.<sup>28</sup>

XRD patterns are applied to find the catalyst crystallinity and its purity. A moving phase-sensitive detector (Siemens D5000) was applied to determine XRD spectra of samples with Cu-K $\alpha$  radiation (44 kV, 35 mA) upon a  $2\theta$  range of 5-55° at a residence time of 5 s at each point to confirm crystallinity of catalysts.<sup>34</sup> The adsorption data of liquid nitrogen were used to determine the surface area and pore size of catalysts at -196 °C by Micromeritics ASAP 2000 instrument. Brunauer Emmett Teller (BET) method was applied to find the specific total surface areas at the sorption of N<sub>2</sub> at -196 °C.<sup>32, 35</sup> TGA of the catalysts was carried out by a Shimazu TGA-50 apparatus.

### 2.4. The catalytic hydro-isomerization of n-hexane

The n-hexane hydroisomerization studies of the catalysts were performed in a micro-catalytic reactor unit (ITMC, RWTH). A stainless-steel reactor was designed in a mechanical workshop

in RWTH, Germany, with a length of 15 cm and an inner and outer diameter of 20 and 50 mm, respectively (see **Fig. 2**). The Pt loading over cations H, Ba, and Sr for the zeolite samples (ZSM-5 and MOR) by supercritical CO<sub>2</sub> were analyzed for n-hexane isomerization and compared with Pt loaded by the impregnation method. 8 g of each catalyst, originally extruded (1.5 d\*2-3 L mm) loaded into the reactor and remained under the flow of oxygen for 4 h at 350 °C and then cleaned with pure N<sub>2</sub> at 450 °C for 15 min and cooled at 250 °C.

The n-hexane feed (1%) was mixed with 80% hydrogen + 20% nitrogen at 250 °C for 1 h using a glass saturator. The total flow of gas was set at 100 mL/min. The temperature inside the reactor was controlled by a PI controller using two K-thermocouples (120–250 °C), one inserted into the center of the zeolite and the other was placed in the oven. The one-way valve was used to pass the feed under pressure to microstructure evaporator for n-hexane heating up to 150 °C. The product was cooled with a heat exchanger using cooled water (inlet temperature 5 °C) then passed through a digital back pressure regulator (Burkert 8624-2). The product gas entered the separator that was filled with iso-propanol dry ice (T = -98 °C).

The uncondensed gas product connected online to GC (Siemens) furnished with the FID detector and capillary column (PLOT-FS-AL 203/KCL 2004), while condensed liquid samples were collected and analyzed with another GC. A pretest period of about 0.5 h was used before each run to adjust the feed rate and temperature to the desired values<sup>36</sup>. Selectivity, conversion, and yield of n-hexane were calculated after each run using defined equations in the literature. The percentage selectivity, conversion, and yield of n-hexane to products (iso-hexane) were calculated by **Eqs. (1)-(3)** respectively.<sup>35</sup>

$$Conversion (\%) = \left( 1 - \frac{N_A}{N_{A_0}} \right) * 100 \quad (1)$$

$$Selectivity (\%) = \frac{N_i}{N_{A0} - N_A} * 100 \quad (2)$$

$$Yield (\%) = \frac{N_i}{N_{A0}} * 100 \quad (3)$$

where  $N_A$  is the moles of component A at time t,  $N_{A0}$  is an initial mole of reactant A, and  $N_i$  represents the total moles of the product.

#### 2.4.1. Kinetic analysis

The rate of reaction was calculated using the design equation of the tubular reactor as in **Eq. (4)**<sup>37</sup>.

$$w = F_{A0} \cdot \int_0^x \frac{dx}{-r_A} \quad (4)$$

where w is the weight of catalyst filled in the reactor,  $F_{A0}$  is the flow rate of inlet n-hexane to the reactor,  $-r_A$  is the rate of reaction. For the calculation of reaction rate in a unit mole/g h, **Eq. (5)** was used. The integration of reaction rate was taken as on-increment because they calculated in a small range of time.

$$-r_A = \frac{F_{A0} \cdot X}{w} \quad (5)$$

The Arrhenius method gives the reaction rate k as a function of temperature as presented in **Eq. (6)**<sup>38</sup>.

$$k = A \cdot \exp\left(\frac{-E_a}{R \cdot T}\right) \quad (6)$$

where R is gas constant, A is the pre-exponential factor, k= is the rate constant of reaction at temperature T, T is the temperature of the reaction, and  $E_a$  is the activation energy. The rate of reaction is directly related to surface coverage  $\theta_n$ . The **Eq. (7)** was used for calculation of activation energy by plotting  $\ln(-r_A)$  vs.  $1/T$ , the slop indicates  $E/R$ , and Intercept gives  $\ln(A)$ .

$$\ln(-r_A) = \ln(A) - \left(\frac{E}{R.T}\right) \quad (7)$$

### 3. Results and discussion

#### 3.1. Characterization

##### 3.1.1. Spectroscopy study

The infrared spectroscopy lattice vibration spectra in the range of 400-4000  $\text{cm}^{-1}$  for original (H-MOR and H-ZSM-5) and activated zeolite (Ba-MOR, Sr-MOR, Ba-ZSM-5, and Sr-ZSM-5) are presented in **Fig. 3 (a, b)**. **Fig. 3 (a, b)** showed the original spectra of 3444.2  $\text{cm}^{-1}$  for H-ZSM-5 and 3448.6  $\text{cm}^{-1}$  for H-MOR zeolite samples which are the characteristic of Bronsted acid protons. Izan et al.,<sup>12</sup> also confirms the presence of 3610 and 3740  $\text{cm}^{-1}$  bands in HBEA and activated HSi@BEA spectrums due to the addition of silicate material. The band at 800  $\text{cm}^{-1}$  is because of symmetric stretching modes of Si-O-H, whereas a band at 585.8  $\text{cm}^{-1}$  is due to Si-O-Si rocking. The bands at 1075  $\text{cm}^{-1}$  attributed to the ratio of  $\text{SiO}_2/\text{Al}_2\text{O}_3$ .<sup>1</sup>

Similarly, the bands between 1500-2200  $\text{cm}^{-1}$  attributed to the stretching frequency of catalysts.<sup>39</sup> The O-H stretching was illustrated in the region of 3000-3700  $\text{cm}^{-1}$ . **Fig. 3 (a, b)** also showed the IR spectra for the exchanged barium and strontium cations. Thus, spectra of all Ba-MOR, Ba-ZSM-5, Sr-ZSM-5, and Sr-MOR reported the same features to the original H-form of corresponding zeolite structure. Therefore, the infrared spectroscopy results in the conclusion, that the H-MOR, H-ZSM-5, Ba-ZSM-5, Ba-MOR, Sr-ZSM-5, and Sr-MOR zeolite have similar surface characteristics and structure before and after the ion exchange operation, but the ion-exchange of protons by  $\text{Ba}^{2+}/\text{Sr}^{2+}$  cations significantly changes the acidic properties of the zeolites and has a significant effect on catalytic performance. However, all the higher intensity peaks indicate the agitation of Si-O-Si mode because of the development of lamellar

network outside the catalyst core, which area corresponds to the appearance of vibrational lattice frequency at  $1856\text{ cm}^{-1}$ .<sup>12</sup>

### 3.1.2. Crystallinity and structural properties

The powder X-Ray diffraction (XRD) analysis was employed to study the outcomes of the modification processes on the crystallinity and framework structure of zeolites. **Fig. 4 (a, b, c)** illustrates the XRD patterns of selected zeolite types including H-ZSM-5, H-MOR, barium, and strontium forms with different metal loaded catalysts. The findings of **Fig. 4 (a)** showed the appearance of sharp diffraction peaks at  $7-9.5^\circ$ ,  $22-26^\circ$  and  $46^\circ$  in a  $2\theta$  range in the H-ZSM-5 zeolite, while in H-MOR, Ba-MOR, and Sr-MOR the sharp peaks have appeared at  $6^\circ$ ,  $9^\circ$ ,  $10^\circ$ ,  $14^\circ$ ,  $20^\circ$ ,  $22^\circ$ ,  $24-27^\circ$  and  $31^\circ$  in  $2\theta$  range (see **Fig. 4 (b)**). Interestingly, the results indicated that the crystalline nature of both zeolites did not alter even after ion exchange with Sr and Ba.<sup>1, 40, 41</sup> Furthermore, no extra peak in the Pt catalyst loaded zeolites were reported corresponds to the original zeolites during the XRD structural analysis, which could be due to several reasons including high dispersion and low metal loading in the zeolites, and different percent of loading because the loading with supercritical  $\text{CO}_2$  ( $\text{scCO}_2$ ) gave small Pt particles size that should be appeared at  $45^\circ$  in  $2\theta$  range (see **Fig. 4 (c)**)<sup>41, 42</sup>.

### 3.1.3. BET surface area measurements of catalyst

The BET surface area strongly dependent on the noble metal content of zeolite produced by the impregnation method, while the metal loading by supercritical  $\text{CO}_2$  ( $\text{scCO}_2$ ) presented a different sense. **Table 1** showed the BET surface area, pore-volume, pore size, and pore area of unmodified (H-MOR and H-ZSM-5), modified (Ba-MOR, Ba-ZSM-5, Sr-ZSM-5, and Sr-MOR), and Pt loaded zeolite by  $\text{scCO}_2$ . The maximum pore volume of about  $0.53\text{ cm}^3/\text{g}$  and area of pores of about  $206.41\text{ m}^2/\text{g}$  were identified for Pt loaded H-ZSM-5. Similarly, the maximum pore size of  $105\text{ \AA}$  was recorded for H-ZSM-5 zeolite. The findings showed that original zeolites including H-MOR and H-ZSM-5 showed the surface area of  $539.21$  and

403.74 m<sup>2</sup>/g respectively that reduced to 385.19 and 338.35 m<sup>2</sup>/g for both zeolites after Pt loading for 24 h at 80 °C and 280 bar. The increase in the time duration resulting also increased the surface area that may be because of mesoporous creation and acid leaching in crystallites of zeolites.<sup>43</sup> It is worthy to note that the BET surface area depends on the size and quantity of platinum loaded.

#### **3.1.4. Weight loss measurements**

TGA of pure PtMe<sub>2</sub>COD and for Pt loaded to H-MOR and H-ZSM-5 were carried out over the range of 30-580 °C and are presented in **Fig. 5**. The decomposition of Pt loaded to H-ZSM-5 and H-MOR showed that weight losses started at around 80 °C and stopped at 400 and 480 °C for Pt/H-MOR and Pt/H-ZSM-5 respectively. The decomposition at 80 °C indicated the exclusion of moisture from samples. The total weight losses were observed as 7.41 and 5.58% for Pt/H-ZSM-5 and Pt/H-MOR respectively. Our results are correlated with the previously reported studies, Tamizhdurai et al.,<sup>3</sup> stated that a maximum of 7.92, 9.67, and 6.96% of weight loss were observed for ZSM-5 (10), ZSM-5 (50), and ZSM-5 (5.4) zeolites at 320-530 °C. The weight loss was happened into two steps which parallel to the removal of water and breakdown of organic material.<sup>44</sup>

#### **3.1.5. Morphological properties**

The morphology features of the supported metal nanocomposites were characterized by High-Resolution Transmission Electron Microscopy (HR-TEM). **Fig. 6 (a, b, c, d)** showed the TEM micrograph taken by High-Resolution TEM (HR-TEM). They give a comparison between the Pt-loading by impregnation method and the supercritical CO<sub>2</sub> (scCO<sub>2</sub>) method. The mean nanoparticles size of Pt particles was confirmed as 8.85 and 6.89 nm for Pt/H-ZSM-5 and Pt/H-MOR respectively by impregnation loading method. Previously the TEM microgram showed the Pt nanoparticles size between 30–70 nm by impregnation loading method that could be significantly decreased (10-40 nm) by increasing the Pt content to 0.6–0.9%.<sup>45</sup> The distribution

of particles is the approximately equal size and equal distance that can be obtained by loading with scCO<sub>2</sub>. However, the average Pt nanoparticles size was confirmed as 1.84 and 1.38 nm for Pt/H-MOR and Pt/H-ZSM-5 respectively by the scCO<sub>2</sub> method. The smaller size of Pt loaded zeolites in the present study could be because of carbon present as a template in the zeolite that significantly facilitates the greater nucleation rate contrast to crystal construction rate and resulted in the production of beneficial small-sized zeolite particles.<sup>46</sup>

### **3.2. Ion-exchange study of zeolites**

Extrudes of the zeolites including H-MOR and H-ZSM-5 were exchanged with two different cations including strontium and barium (Sr and Ba). The Sr and Ba were selected for the ion-exchange due to their very fewer effects toward decrease the crystallinity of zeolites after a longer treatment time as compared to acids like HCl.<sup>47</sup> **Fig. 7** demonstrated the impact of treatment time on the cation content and calcination in the zeolites. As expected, the percent of ion exchange for Sr and Ba was increased with treatment time. This increase was not linear and differs according to the cation solutions and the type of zeolites. The highest percentage of ion-exchange of about 25.21 mg/g was achieved with Sr for the large-pored Mordenite zeolite after 2.5 h treatment. However, the replacement of hydrogen ion by barium was noticeable less as compared to strontium ion for both zeolite types. The pH of the solutions was decreased directly when the cationic solutions were added to the zeolite samples due to the formation of a mild concentration of HCl by ion exchange. Therefore 0.1 N solution of NaOH was added to maintain the pH of solution around 7.0.<sup>48</sup>

### **3.3. Catalytic activity for n-hexane isomerization**

#### **3.3.1. Hydroisomerization of n-hexane by unmodified catalysts**

The temperature and H<sub>2</sub>/HC ratios' effects on the selectivity and conversion for unmodified Pt/H-MOR and Pt/H-ZSM-5 catalysts by an impregnated method are presented in **Fig. 8**, while

for supercritical CO<sub>2</sub> are summarized in **Fig. 9** at 5 bar pressure. The temperature impact was studied at different temperatures range as 250–325 °C and the H<sub>2</sub>/HC ratio was quantified as 3, 6, and 9. The maximum 92.09% conversion of n-hexane was achieved for Pt/H-MOR at 325 °C and H<sub>2</sub>/HC ratio of 6 by the impregnation method. Similarly, the maximum selectivity of about 99% was observed at a lower temperature of 250 °C and all H<sub>2</sub>/HC ratios for both catalysts (Pt/H-MOR and Pt/H-ZSM-5) loaded by scCO<sub>2</sub>. Tamizhdurai et al.<sup>43</sup> stated that the maximum of 91.4% of n-hexane conversion activity was achieved for MOR at 250 °C that reduced to 82.5% at a higher temperature, and suggested that 250 °C is the optimum temperature for the conversion of n-hexane with MOR (40) catalyst. Similarly, Luo et al.<sup>44</sup> observed that H-MOR, USY, H-BEA, and H-ZSM-5 catalysts showed the maximum n-hexane conversion of about 6.8, 12.1, 15.4, and 11.7% respectively at 633 K and 137 bar.

It is reported that the temperature rise precedes a gradual increase in conversion rate, while the selectivity decreases with temperature increase. It could be concluded that 290 °C is the optimum temperature and 6 is the optimum H<sub>2</sub>/HC ratio to achieve selectivity more than 90% and conversion about 65-76% for both zeolites including Pt/H-MOR and Pt/H-ZSM-5. Furthermore, the results showed that the Pt/H-ZSM-5 catalyst is more effective and selective than Pt/H-MOR catalyst for n-hexane isomerization based on temperature and H<sub>2</sub>/HC ratio effects. Moreover, hydrogen to hydrocarbon ratio seems to be having little effect on n-hexane isomerization and hydrocracking. All findings showed that the percentage of n-hexane conversion is slightly higher on catalysts prepared by impregnation method than supercritical carbon dioxide (scCO<sub>2</sub>) technique, while the selectivity towards C<sub>6</sub>-isomers is significantly higher on catalysts prepared in scCO<sub>2</sub> than impregnation for all temperatures and H<sub>2</sub>/HC ratios studied. Our findings are also in agreement with previously reported studies, Sazama and coworkers stated that Pt loaded ZSM-5 zeolite showed the better n-hexane conversion rate and



turnover frequency for 2-MP and 3-MP than the BEA zeolites.<sup>36</sup> Huang et al.<sup>49</sup> reported that conversion of n-hexane over H-Y and H-ZSM-5 catalysts was about 3.5% (673 °C) and 2.8% (588 °C) respectively with a turnover frequency of about 0.24 and 0.08% at 6 MPa pressure.

### **3.3.1.1. Yield percentage**

The n-hexane isomerization reaction results in four major different types of *iso*-C<sub>6</sub> isomers including 3-Methylpentane (3-MP), 2, 2-Dimethylbutane (2, 2-DMB), 2-Methylpentane (2-MP), and 2, 3-Dimethylbutane (2, 3-DMB). 2-MP and 3-MP are the most required compounds for the upgrading of motor gasoline due to their sufficient volatility and high-octane number.<sup>50</sup> Therefore, it was worthy to examine the effectiveness of the Pt loaded H-ZSM-5 and H-MOR catalysts towards the yield of these compounds. **Fig. 10** and **Fig. 11** reported the yield of four isomers (2,2-DMB, 2-MP, 3-MP, and 2,3-DMB), and C<sub>1</sub>-C<sub>5</sub> on Pt/H-MOR and Pt/H-ZSM-5 at distinct temperatures including 250, 275, 300, and 325 °C and H<sub>2</sub>/HC ratios of 3, 6, and 9 for both Pt loading methods. The maximum yield of 28.04 and 36.72% was determined for 3-MP and 2-MP respectively at 275 °C and H<sub>2</sub>/HC ratio of 6 for Pt/H-ZSM-5 catalyst loaded by the impregnation Pt loading method.

Similarly, greater of 39.29 and 31.44% yield of 2-MP and 3-MP were achieved for scCO<sub>2</sub> loaded Pt/H-ZSM-5 at 275 °C and H<sub>2</sub>/HC ratio of 9. Findings also revealed that the temperature impact on the production of C<sub>1</sub>-C<sub>5</sub> hydrocarbons produced interesting results. At 5 bar and H<sub>2</sub>/HC ratio of 9, the yield of cracked products (C<sub>1</sub>-C<sub>5</sub>) was about an average of 21.25% for the Pt/H-MOR catalysts loaded by impregnation at all temperatures. However, the catalysts loaded by scCO<sub>2</sub>, showed nearly an average 8.62% yield of cracked products at H<sub>2</sub>/HC ratio of 9 and all temperatures for Pt/H-ZSM-5. The outcomes revealed that the catalysts of scCO<sub>2</sub> showed a significant reduction in the formation of cracked products as compared to impregnated catalysts. Our findings are also correlated with the previously reported studies, Pastvova et al.

<sup>51</sup> stated that hydroisomerization of n-hexane by Pt/H-MOR/5.8 catalyst results in a lower yield of *iso*-C<sub>6</sub> isomers (2,2-DMB, 2-MP, 3-MP, and 2,3-DMB) at a lower temperature (150 °C) that increased up to 44% at 275 °C, but surprisingly decreased to 23% at a higher temperature (325 °C). They also suggested that the 275 °C is an optimum temperature for a better yield of *iso*-C<sub>6</sub>.

Similarly, Modhera et al., <sup>52</sup> described that n-hexane hydro-isomerization by ZSM-5 zeolite catalyst results in a yield of about 32.67 and 23.85% of 2-MP and 3-MP respectively with a smaller yield of cracked products (0.30%) at 623 K temperature and 10 atm pressure. According to the findings, the yields of 2-MP and 3-MP for catalysts loaded by scCO<sub>2</sub> are higher than those prepared by the impregnation method, because the former method gives uniform metal distribution on the support and resulted in more selective catalyst behavior. Furthermore, Pt/H-ZSM-5 showed more selectivity towards 2-MP and 3-MP than Pt/H-MOR generally for both loading methods. Generally, the findings revealed that the maximum yields for 2-MP and 3-MP were achieved at 275 °C within the temperature range of 250–325 °C. The decline of yields by increasing the temperature is probably due to hydrocracking of these *iso*-C<sub>6</sub> isomers (2-MP and 3-MP) to low hydrocarbons mainly by using impregnated loading catalysts. The findings also indicated that the decrease in yield by increasing temperature is more noticeable for impregnated catalysts than scCO<sub>2</sub>. Huang and his research group revealed that the molar selectivity of n-hexane was 16 and 70% for *iso*-C<sub>6</sub> isomers and about 4 and 15% for cracked products (C<sub>1</sub>-C<sub>5</sub>) over H-Y and H-ZSM-5 catalyst respectively at 6 MPa.<sup>49</sup> The results discussed in this section indicate that the loading of Pt in supercritical carbon dioxide possesses higher selectivity for n-hexane isomerization, particularly between 275 and 300 °C and H<sub>2</sub>/HC ratio of 6 and 9 for Pt/H-ZSM-5 catalyst.

### 3.3.2. n-Hexane hydroisomerization by ion modified catalysts

The catalytic behavior of Pt loaded catalysts on cationic forms including strontium and barium (Sr and Ba) on MOR and ZSM-5 zeolites were analyzed for hydro-conversion of n-hexane. The Pt was loaded by only the supercritical carbon dioxide (scCO<sub>2</sub>) method in ion modified catalysts. **Fig. 12** indicated the conversion and selectivity percentage of different temperatures and H<sub>2</sub>/HC ratios at 5 bar. Pt loading on ZSM-5 and MOR zeolites by scCO<sub>2</sub> resulted in a stable and effective catalyst. The temperature impact on the percentage of n-hexane selectivity and conversion was almost similar to the above studied unmodified catalysts. The maximum n-hexane conversion of about 79.57 and 84.73% was achieved for Pt/Ba-ZSM-5 and Pt/Ba-MOR respectively at 325 °C and H<sub>2</sub>/HC ratio of 6. **Fig. 12** showed the same trend as unmodified zeolites, the increase in temperature also rises in a conversion rate of n-hexane but decreases the selectivity.

The average 99 and 96% selectivity reported for both Sr modified catalysts (Pt/Sr-ZSM-5 and Pt/Sr-MOR) that gradually decreased to average 86 and 74% respectively by enhancing the temperature range from 250 to 325 °C. The results demonstrated that the Sr modified catalyst (Pt/Sr-ZSM-5) is more selective and gave better selectivity at a lower temperature, while the Pt/Sr-MOR is more active showed a better conversion rate of n-hexane at a higher temperature (325 °C) and H<sub>2</sub>/HC ratio of 6. The previously published researches also revealed that modified MOR zeolite is much active and selective among all studied zeolites due to its strong acidic bridge of Si-OH-Al for the hydroisomerization of n-hexane.<sup>53,54</sup> Sazama et al.,<sup>55</sup> observed that Si/Al-rich Pt/H-BEA catalyst significantly increase n-hexane to iso-hexane conversion rate from 5.9 to 35.5% at high density and 175 °C without the formation of any by-product gases.

Similarly, Nasser et al.,<sup>56</sup> revealed that the dealuminated of MOR zeolite with 1M nitric acid for 20 min treatment only give 20% catalytic conversion of n-hexane that is reduced to 17.3% after 240 min treatment mainly due to pore blockage by reduction of mesopore channels or coke. Martins and his research group demonstrated that the 40Ni60Pt/H-MOR catalyst showed the maximum n-hexane conversion of about 24%, while the 60Ni40Pt/H-MOR revealed the 99% selectivity at 250 °C.<sup>57</sup> It is concluded that a temperature of 300 °C is an optimum temperature to get about 90-94% isomerization selectivity with about 77% conversion of n-hexane by all Ba and Sr modified Pt-zeolites. However, the variation of the H<sub>2</sub>/HC ratio in the range of 3-9 had little effect on these catalyst types.

### ***3.3.2.1. Yield percentage***

The yields of desired isomers including 3-MP, 2,3-DMB, 2-MP, and 2,2-DMB and undesired crack gases including C<sub>1</sub>-C<sub>5</sub> were investigated in the existence of Sr and Ba modified MOR and ZSM-5 Pt-catalysts. **Fig. 13** showed the yields of n-hexane at different temperatures and H<sub>2</sub>/HC ratios on Sr and **Fig. 14** for Ba cations modified Pt/MOR and Pt/ZSM-5 catalysts. The results indicated that the yields of cracked gases (C<sub>1</sub>-C<sub>5</sub>) decreased rapidly from an average of 9 to 0.1% for Pt/Sr-ZSM-5, and 18.85 to 0.97% for Pt/Sr-MOR catalyst by decreasing the temperature from 325 to 250 °C. The findings revealed that a maximum average yield of about 38% was noted for 2-MP at 300 °C for Pt/Ba-ZSM-5 catalyst, while the average yield of 35% was calculated for 3-MP at the same temperature in Pt/Sr-ZSM-5 catalyst.

The overall percentage yields of 2-MP and 3-MP isomers were increased as temperature increase from 250 to 300 °C and then decreased at 325 °C on all catalyst types. Therefore, a temperature of 300 °C could be considered as an optimum for a higher yield of 2-MP and 3-MP. The findings suggested that the ZSM-5 catalysts were much energetic for these isomers than MOR catalysts. The findings also showed the yield of more volatile isomers including

Dimethylbutanes (DMB) reported that the MOR zeolite catalysts were highly selective to DMB production rather than ZSM-5 catalysts could be because of channel structure, the influence of acidity, metallic centers distribution, pore size, and dispersion.<sup>51</sup> The yields of these isomers (2,3-DMB and 2,2-DMB) for Pt loaded ZSM-5 zeolite (both Sr and Ba forms) were between 0.27-5.08% at 325°C, while at the same temperature the DMBs yield value increases to 1.30-14.26% for Pt/MOR (both Sr and Ba forms).

For comparison, Pastvova and coworkers reported that dealuminated Pt/MOR/6.6 showed the 55% yield of *iso*-C<sub>6</sub> isomers with 4 to 12% production of cracked gasses (C<sub>1</sub>-C<sub>5</sub>) at 250 °C.<sup>51</sup> Modhera and coworkers reported that dedicated ZSM-5 catalyst yield in 11.89, 17.92, 7.07, and 24.14% of 2,2-DMB, 2,3-DMB, 2-MP, and 3-MP respectively with the production of cracked gases of about 2-3% at 623 K temperature and 10 atm pressure with H<sub>2</sub>/HC ratio of 10.<sup>52</sup> Luo et al.<sup>44</sup> showed the yield of hydroisomerization of n-hexane of about 56.6, 55.8, 14.6, 79.8% for *iso*-C<sub>6</sub> isomers over H-MOR, H-BEA, H-ZSM-5, and USY, and catalysts at 633 K and 137 bar.

### 3.3.3. Activation energy and rate of reaction

The rate of reaction for overall conversion, isomerization, and cracking reactions were calculated from Eq. 4 and 5 and presented in **Table 2**. The cyclization reactions were neglected because there was no or low products for cyclic compounds. The results presented that the maximum conversion of about 51.25% was observed for Pt/Sr-MOR at 325 °C and maximum isomerization of 45.83% was achieved at 300 °C for the same zeolite catalyst. The average results showed that Pt loaded ZSM-5 (in both Ba and Sr forms) zeolites showed the better n-hexane conversion and isomerization at 300 °C, 5 bar, and H<sub>2</sub>/HC ratio of 9 along with the minimum rate of cracking (0.01 at 250 °C and 4.05 at 325 °C). The pre-exponential factor and activation energy (E<sub>a</sub>) were calculated by Eq. (7). The activation energy values were taken from

the slopes of plotting  $\ln(-r_A)$  vs.  $1/T(K)$ , while the pre-exponential factor (turnover frequency; TOF) were taken from the intercepts of the line with the y-axis.

The values of activation energy and TOF are listed in **Fig. 15**. The results revealed that the maximum  $E_a$  of 45.31 kJ/mol was obtained for Pt/Ba-MOR catalysts due to their high stability at the temperature range applied, while the maximum TOF of about  $5.81 \times 10^{11}$  1/s achieved for Pt/Sr-MOR catalyst. Lyu et al.,<sup>58</sup> presented the maximum TOF of 98 1/h and  $E_a$  114 kJ/mol over Ni-SP/ $\beta$  zeolite catalyst for *iso*-C<sub>6</sub> isomer conversion from n-hexane. Yeh et al.,<sup>15</sup> stated that H-ZSM-5, Li-ZSM-5, and Zn-ZSM-5 catalysts showed the 7.9, 6.9, and 45.2 kJ/mol activation energy of n-hexane at 137 bar, 633 K temperature, and n-hexane flow rate of 0.3 mL/min. Under the current scenario of environmental pollution,<sup>59</sup> there is a need to develop sustainable materials, fuels,<sup>60, 61</sup> and renewable technologies<sup>62, 63</sup> to reduce CO<sub>2</sub> emissions and control global warming.<sup>64, 65</sup> Hence, platinum loaded zeolites are excellent materials that could be used in various applications including fuels to reduce carbon dioxide.

## 4. Conclusions

The present study aims were to synthesize the barium (Ba) and strontium (Sr) forms of ZSM-5 and MOR zeolites and coated that zeolites with Pt using two methods including the impregnated method and a novel supercritical CO<sub>2</sub> method for n-hexane hydroisomerization. The results revealed that the noble metal (Pt) loading by supercritical carbon dioxide (scCO<sub>2</sub>) technique was very efficient. The efficiency of loading was increased by increasing the pressure. The metal particles loaded by scCO<sub>2</sub> had good distribution and gave very small nanoparticles rather than that made by the impregnation Pt loading method. The BET surface area increased despite the zeolite sample has higher platinum content. The maximum average yield of about 38 and 35% was observed for 2-MP and 3-MP at 300 °C by Pt/Ba-ZSM-5 and Pt/Sr-ZSM-5 catalysts respectively. The overall percentage yields of 2-MP and 3-MP isomers

were increased as temperature increase from 250 to 300 °C and then decreased at 325 °C on all catalyst types. Therefore, a temperature of 300 °C could be considered as an optimum temperature for a higher yield of 2-MP and 3-MP. Furthermore, the overall results disclosed that Pt loaded ZSM-5 (in both Ba and Sr forms) zeolites showed the better rate of conversion (47%) and isomerization (46.44%) for n-hexane at 300 °C, 5 bar, and H<sub>2</sub>/HC ratio of 9 along with the minimum rate of cracking (0.01 at 250 °C and 4.05 at 325 °C). The findings stated that ZSM-5 catalysts are generally much selective and effective than MOR catalysts for n-hexane isomerization. However, it is proposed that the process of isomerization should be examined at a longer time to check the activity and stability of prepared noble-metal zeolite catalysts. Furthermore, the experimental work could be extended to examine the dealumination effect of zeolite support to improve the selectivity and activity of the catalytic isomerization process.

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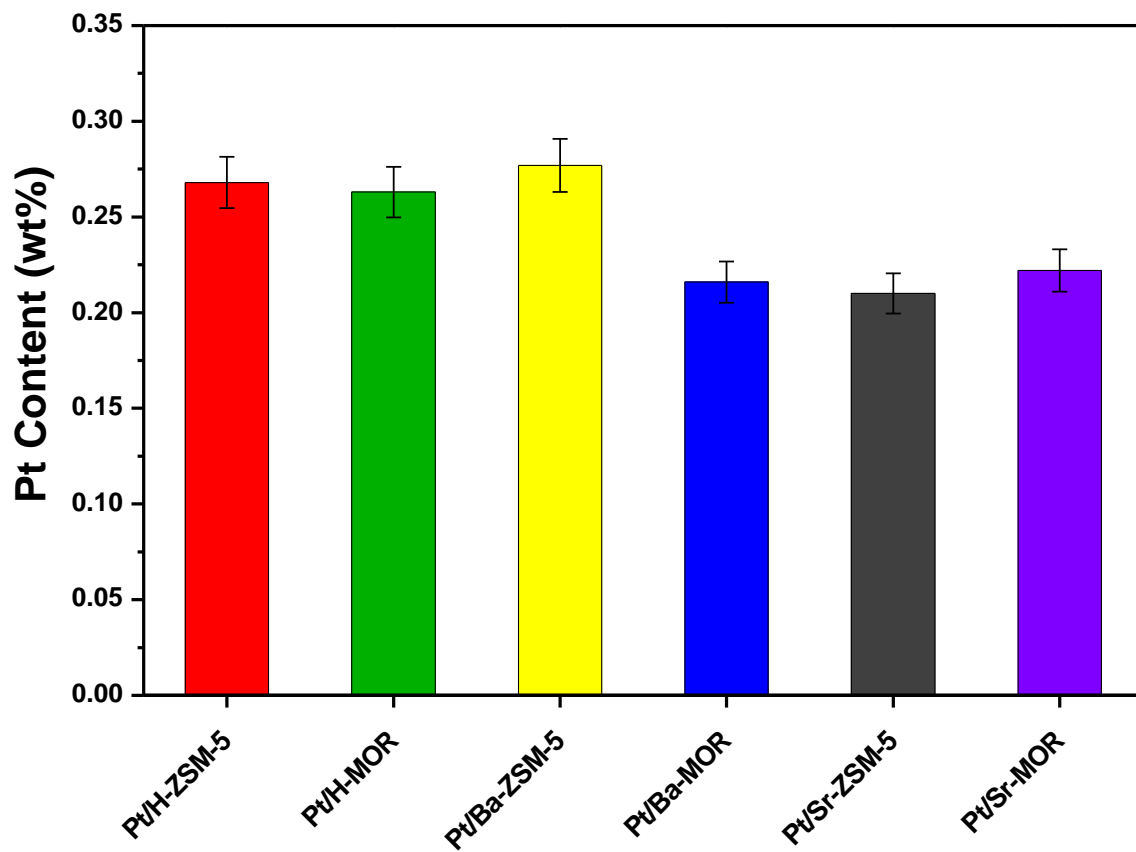
**Table 1.** BET surface area, pore volumes, and pore size for different zeolite catalysts loaded with Pt by scCO<sub>2</sub> at 80 °C and 280 bars.

Sample	BET surface area (m <sup>2</sup> /g)	Pore area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)	Pore size (Å)
<b>MOR</b>				
H-MOR	539.21	117.56	0.26	90.72
Ba-MOR	337.14	-	-	-
Sr-MOR	360.90	-	-	-
Pt/H-MOR	385.19	105.89	0.24	92.92
<b>ZSM-5</b>				
H-ZSM-5	403.74	195.30	0.51	105.05
Ba-ZSM-5	355.32	-	-	-
Sr-ZSM-5	309.92	-	-	-
Pt/H-ZSM-5	338.35	206.41	0.52	101.90

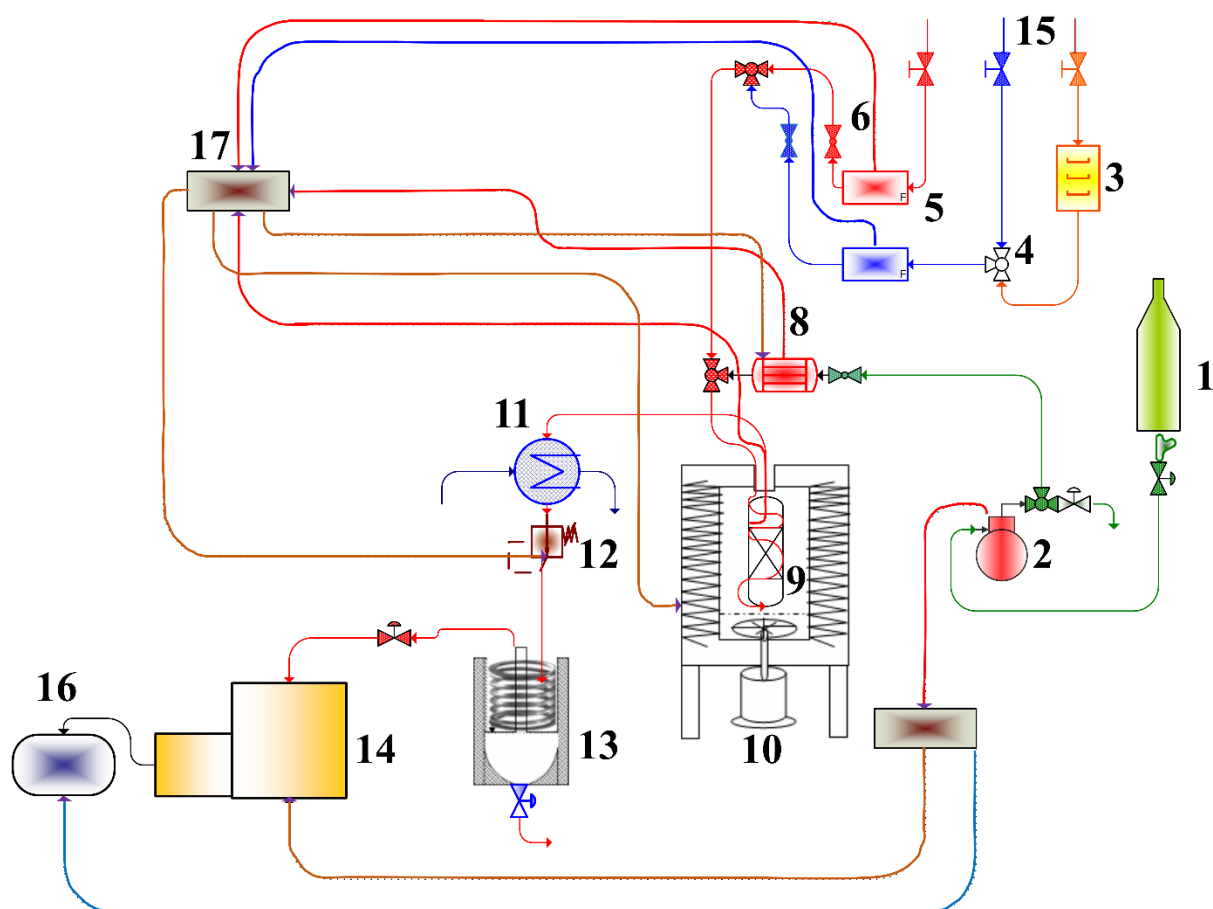
**Table 2.** The overall rate of conversion, isomerization, and cracking for n-hexane at different temperatures, H<sub>2</sub>/HC ratio of 9 and 5 bar.

Temperature (°C)	Conversion rate (%)	Isomerization rate (%)	Cracking rate (%)
<b>Pt/Ba-MOR</b>			
250	12.65	11.83	0.82
275	41.24	38.18	3.05
300	46.76	42.54	4.21
325	50.36	37.35	13.00
<b>Pt/Sr-MOR</b>			
250	19.01	18.45	0.55
275	37.97	36.50	1.47
300	49.31	45.83	3.48
325	51.25	40.56	10.69
<b>Pt/Sr-ZSM-5</b>			
250	25.35	25.33	0.01
275	42.20	41.74	0.46
300	46.89	45.44	1.44
325	47.32	42.68	4.63
<b>Pt/Ba-ZSM-5</b>			
250	12.71	12.69	0.02
275	42.33	41.94	0.38
300	46.70	45.44	1.26
325	47.76	43.70	4.05

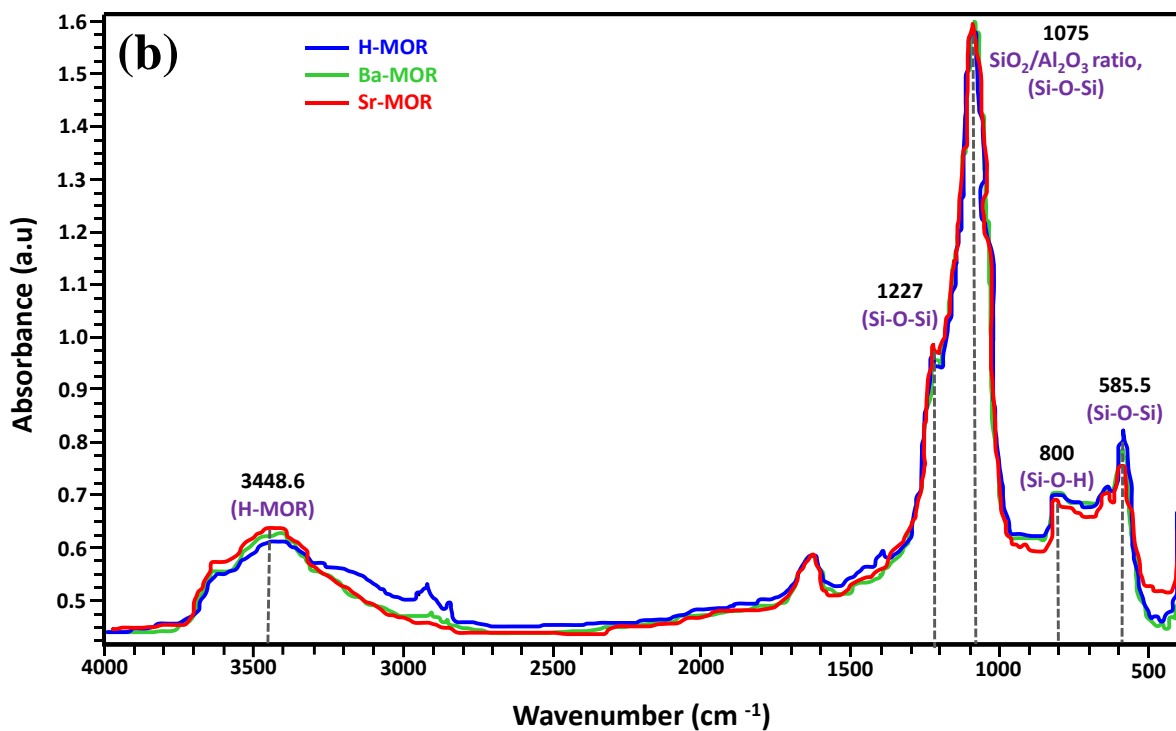
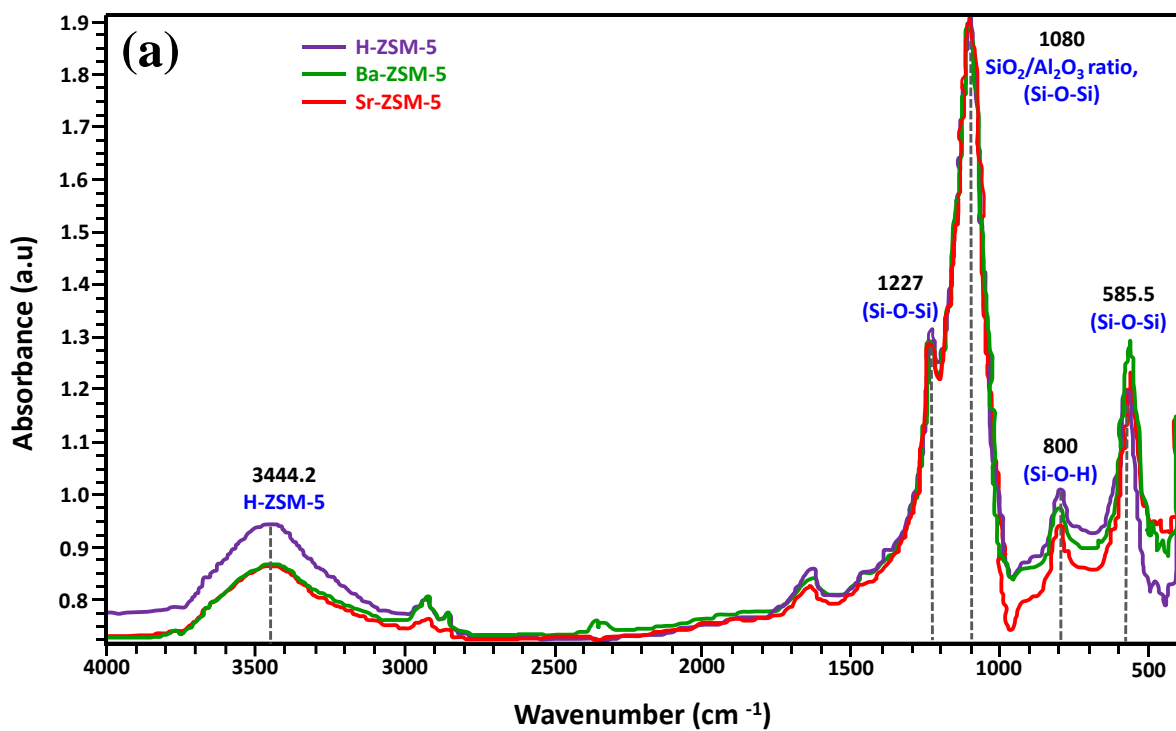
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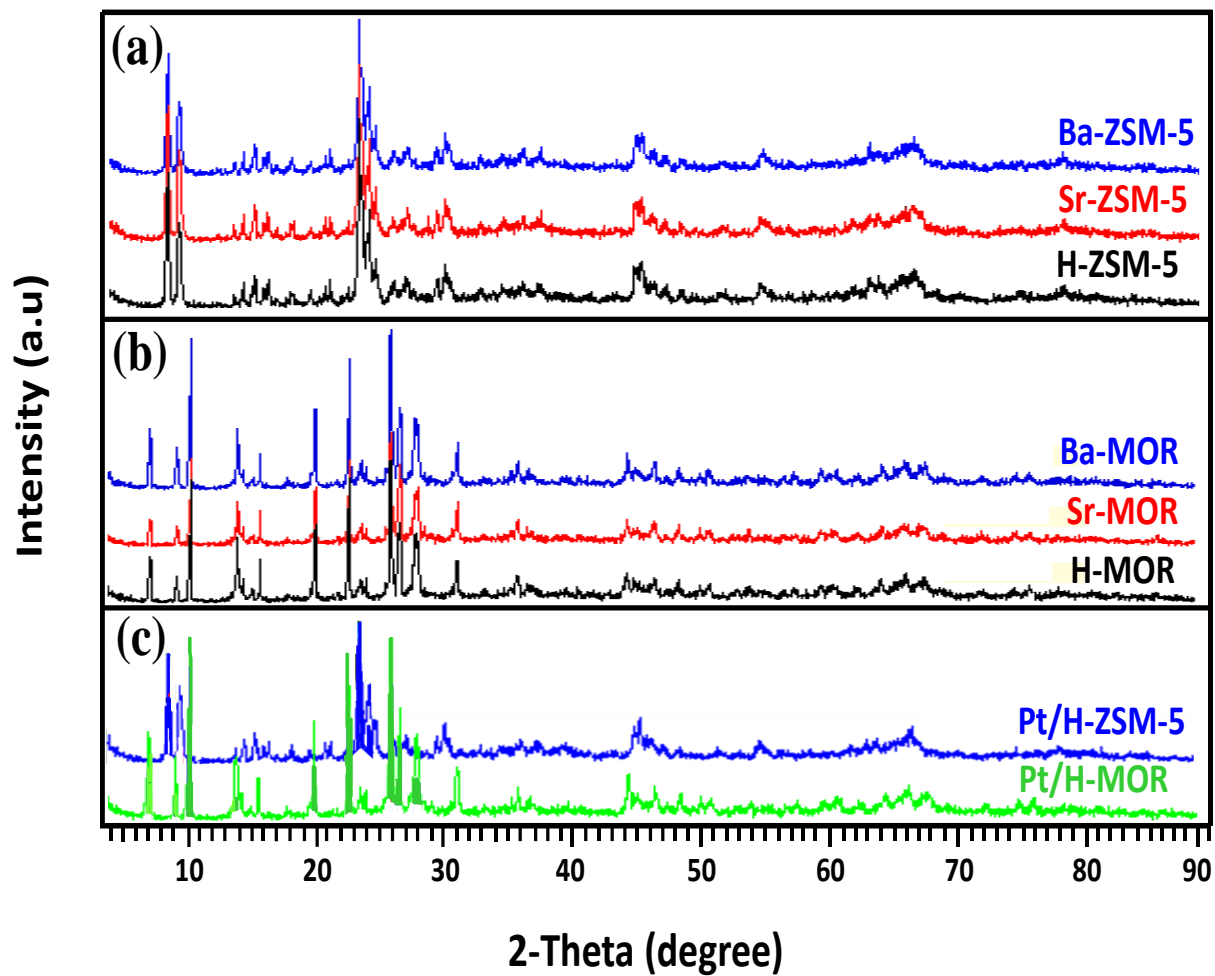
**Fig. 1.** The platinum contents in zeolite catalysts loading by supercritical carbon dioxide.



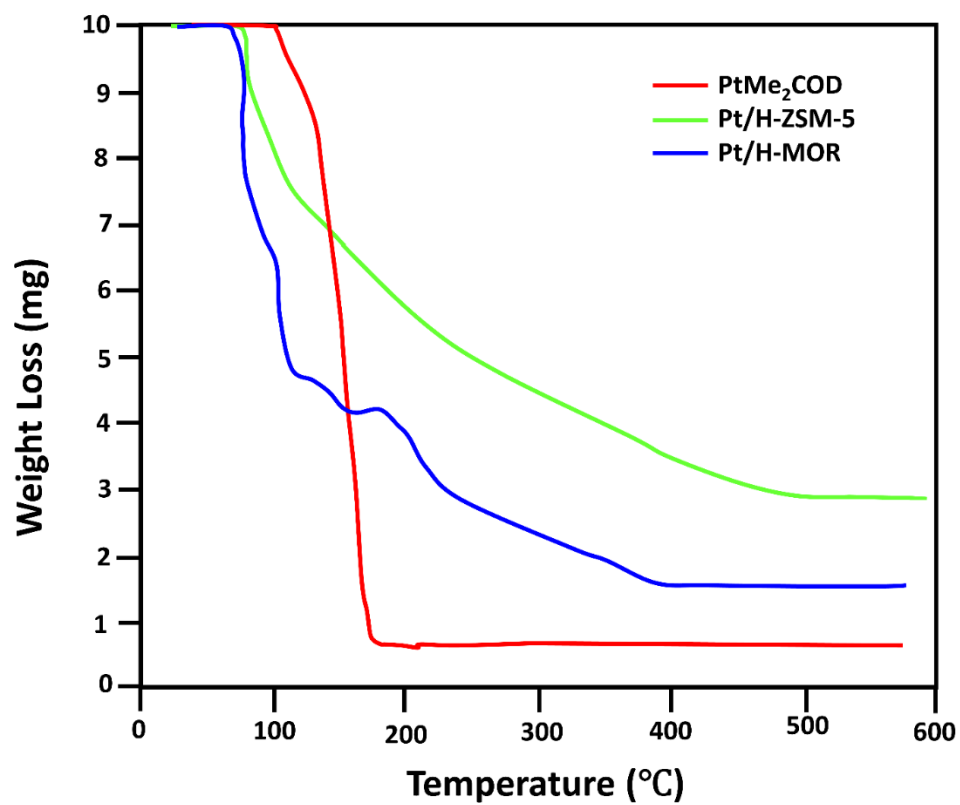
**Fig. 2.** The schematic flow diagram of hydro-isomerization of n-hexane; (1) Feeding tank, (2) Dosing pump, (3) Dryer, (4) Three-way valve, (5) Mass flow meter for gases, (6) One-way valve, (7) Three way connection, (8) Evaporator, (9) Reactor, (10) Oven, (11) Heat exchanger, (12) Back pressure regulator, (13) Separator, (14) GC, (15) Manual valve, (16) PC and (17) Control and power supply box.



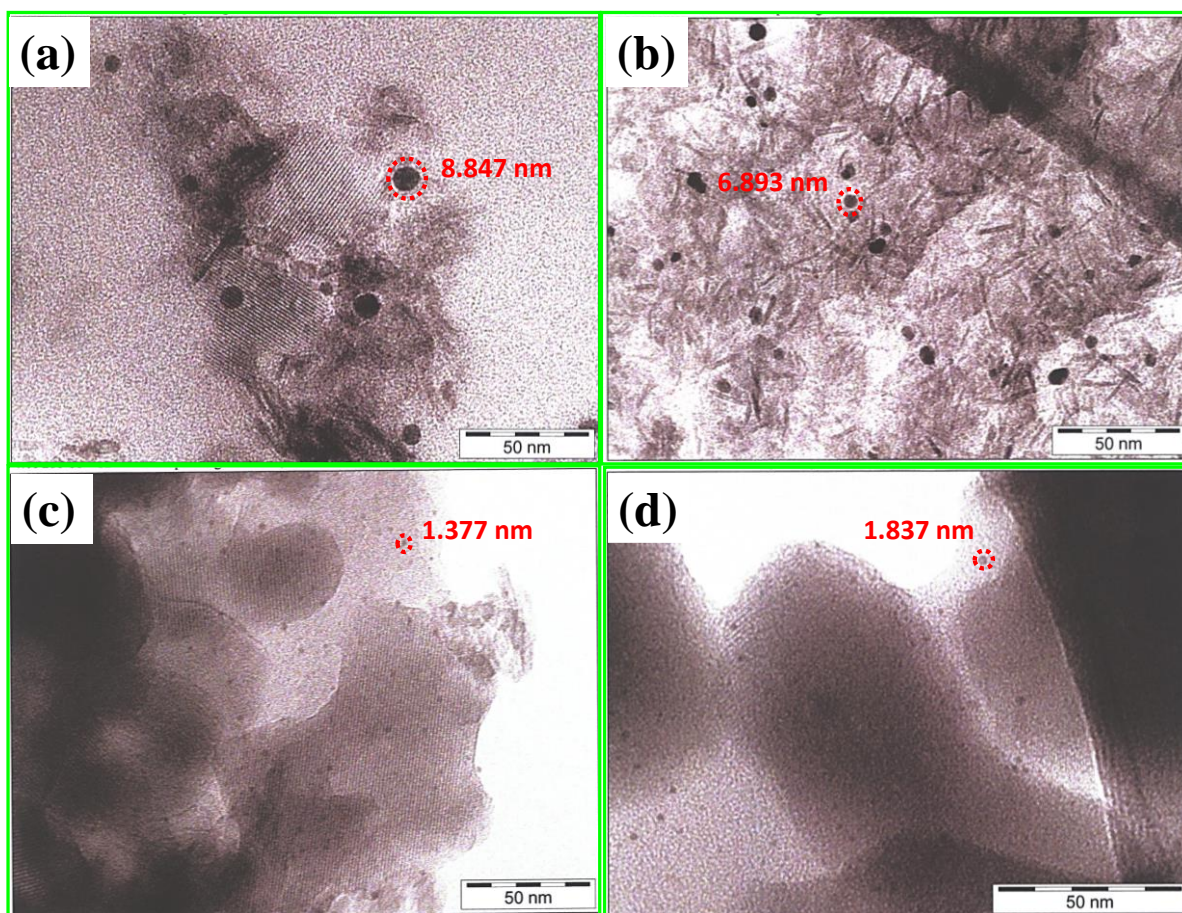
**Fig. 3.** The FT-IR spectra of zeolites catalyst before and after ion exchange with Ba and Sr over a) ZSM-5 and b) MOR zeolites.



**Fig. 4.** XRD spectra for different zeolite catalysts before and after ion exchange for a) ZSM-5, b) MOR, and c) Pt/H-ZSM-5 and Pt/H-MOR.

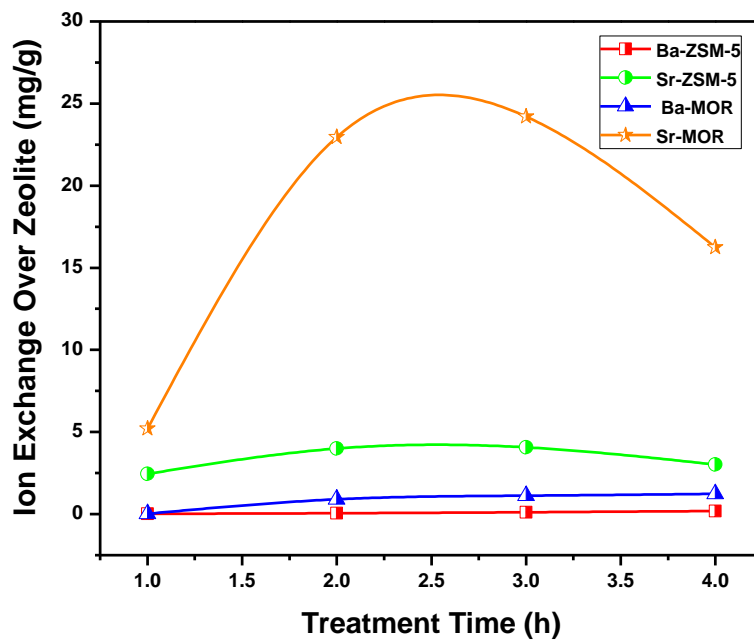


**Fig. 5.** The effect of temperature on the weight loss of pure and loaded zeolites by TGA thermograph.

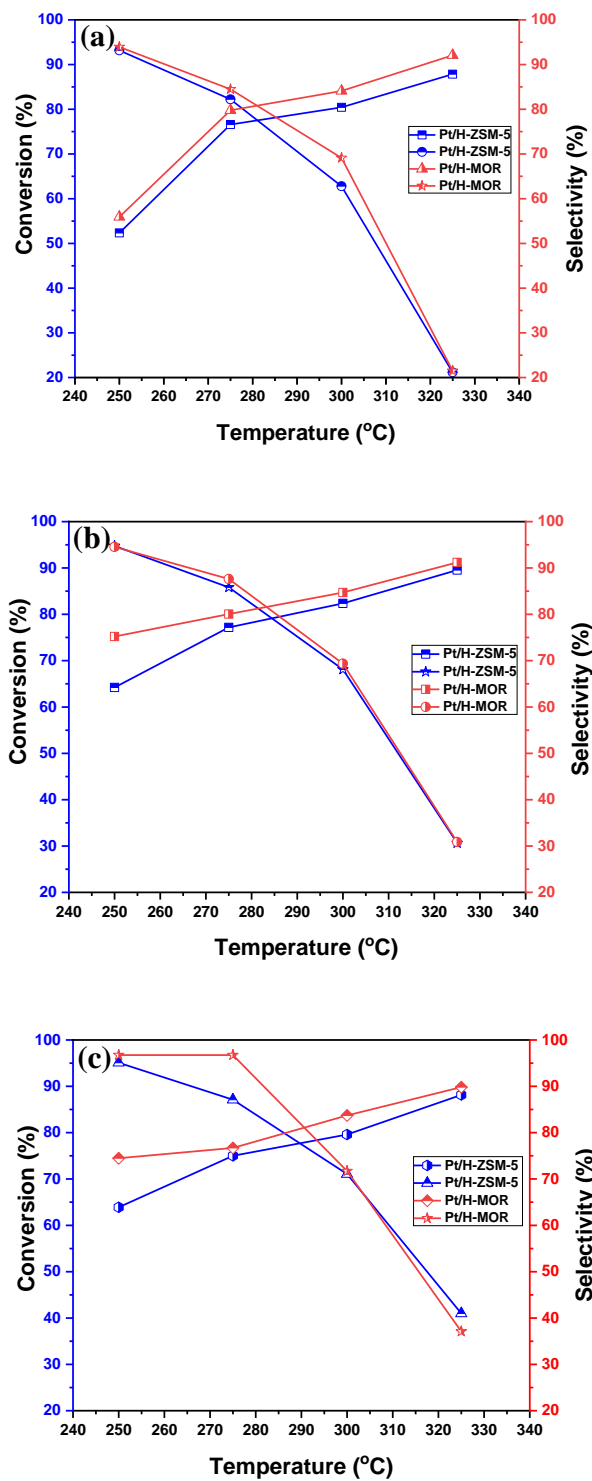


**Fig. 6.** The TEM micrograph for Pt loaded over different zeolites catalysts including; (a, b) H-ZSM-5 and H-MOR by impregnated method, (c, d) H-ZSM-5 and H-MOR by scCO<sub>2</sub> method at 280 bar and 80 °C.

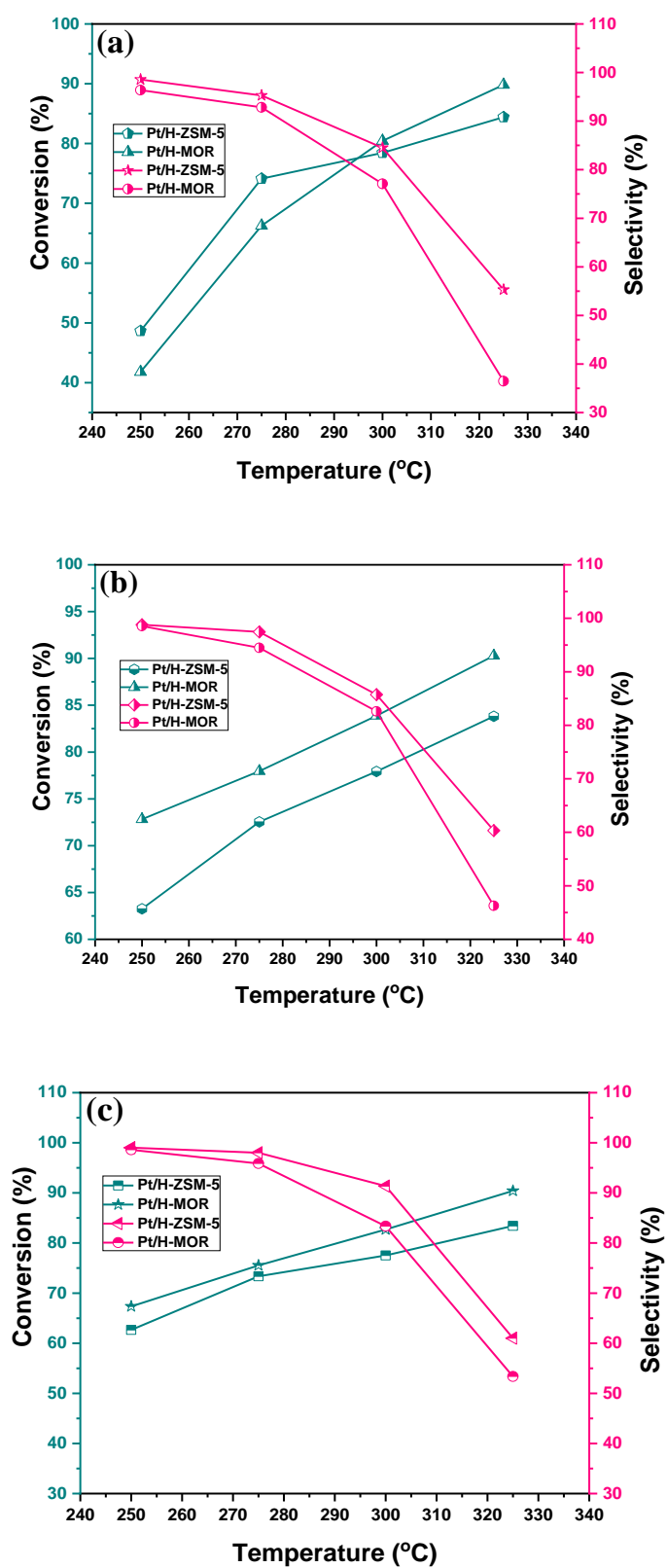




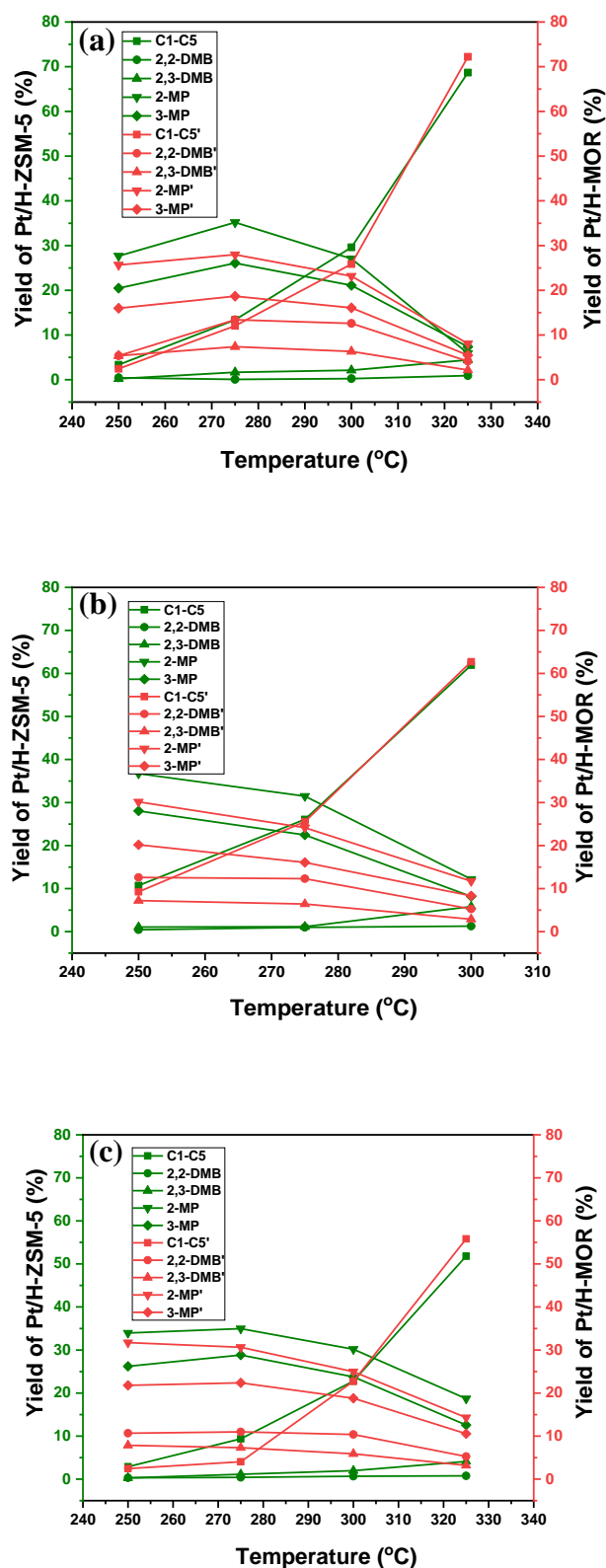
**Fig. 7.** The effect of treatment time for the ion exchange of Sr and Ba cations over different zeolites.



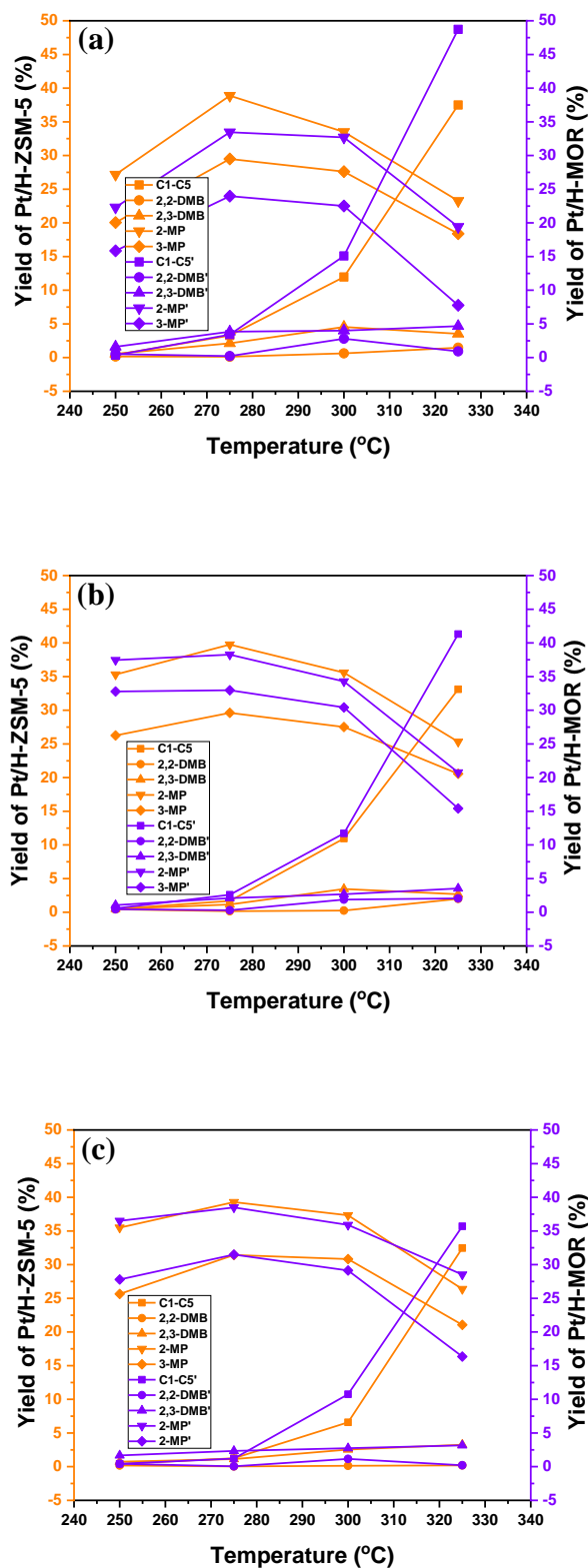
**Fig. 8.** The experimental results of selectivity and conversion for n-hexane isomerization at different temperatures and H<sub>2</sub>/HC ratios; (a) 3, (b) 6 and (c) 9 by an impregnated method.



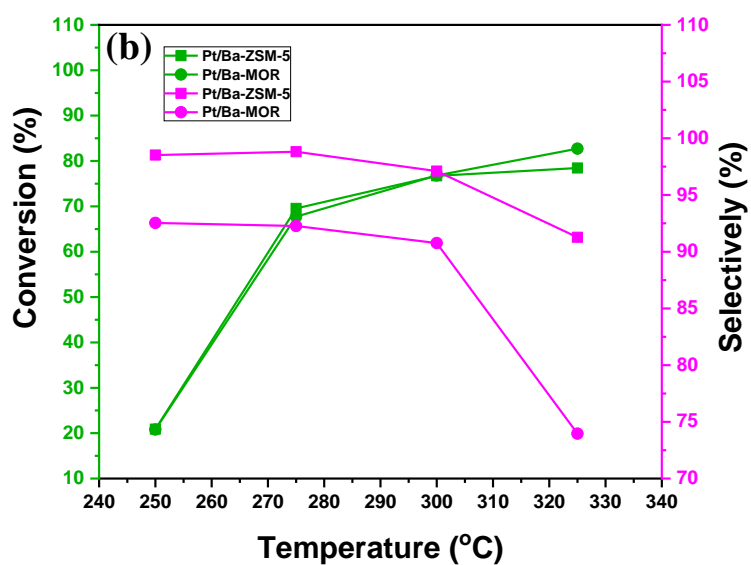
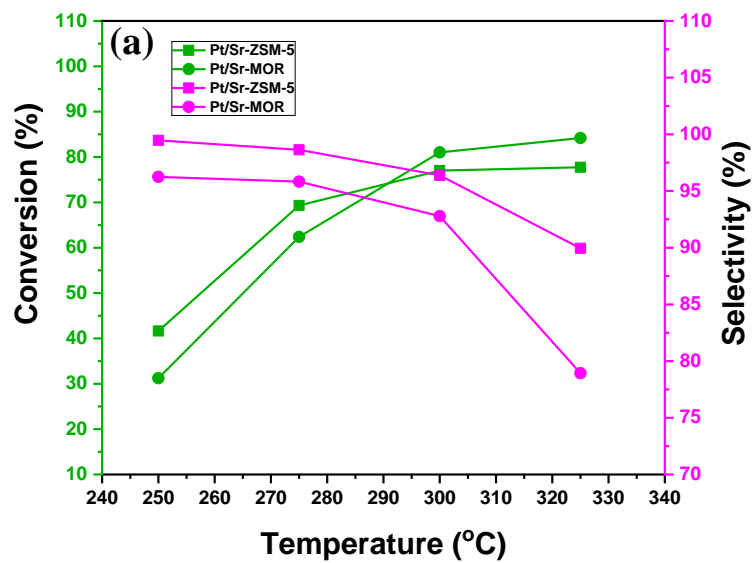
**Fig. 9.** The experimental results for hydroisomerization of n-hexane by Pt loaded over H-ZSM-5 and H-MOR by scCO<sub>2</sub> method at 5 bar and different temperatures and H<sub>2</sub>/HC ratios; (a) 3, (b) 6 and (c) 9.



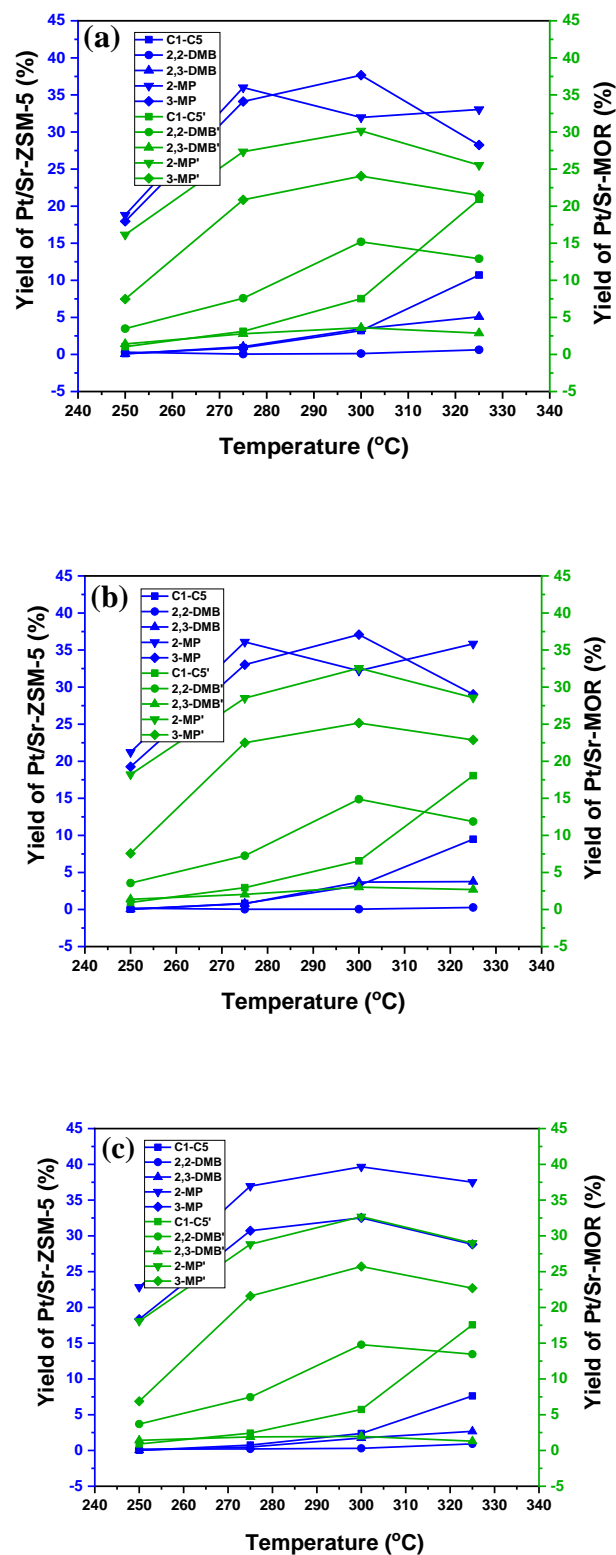
**Fig. 10.** The experimental results of yield percentage for n-hexane isomerization at different temperatures and H<sub>2</sub>/HC ratios; (a) 3, (b) 6 and (c) 9 for Pt loaded zeolites by an impregnated method.



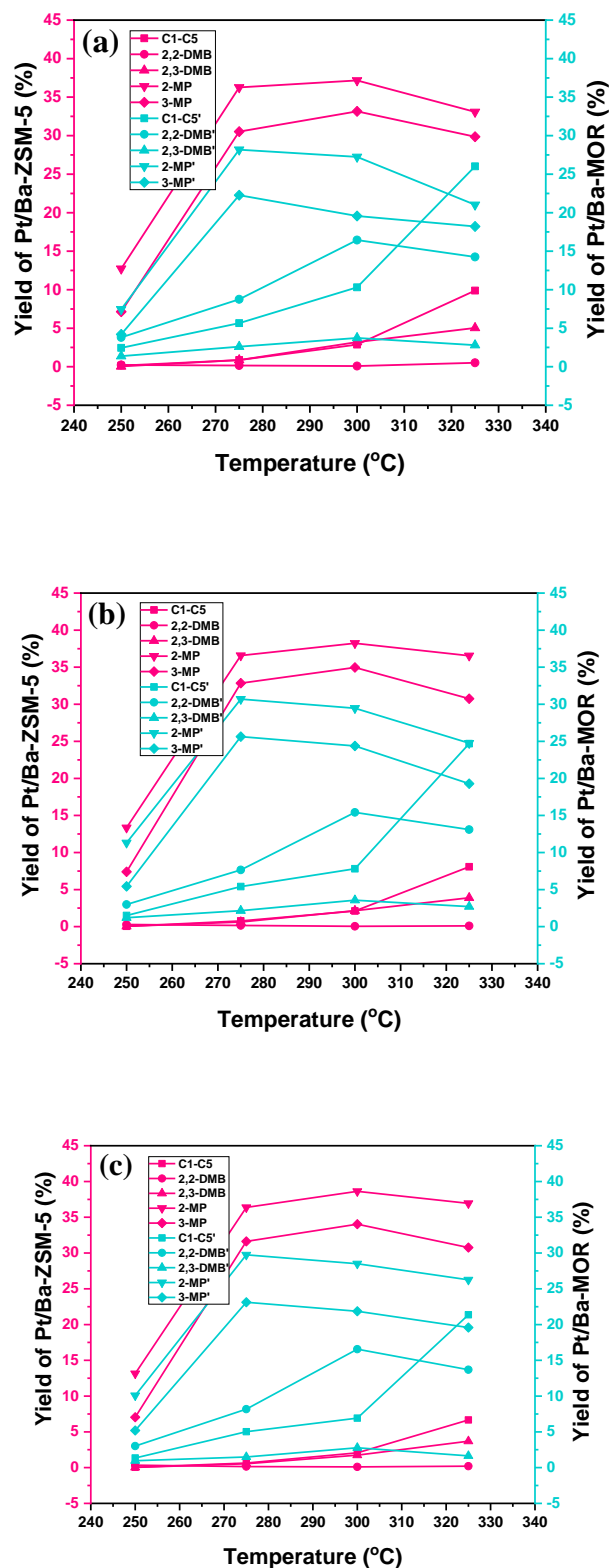
**Fig. 11.** The experimental results of yield percentage for n-hexane isomerization at different temperatures and H<sub>2</sub>/HC ratios; (a) 3, (b) 6 and (c) 9 for Pt loaded zeolites by scCO<sub>2</sub> method.



**Fig. 12.** The experimental results of selectivity and conversion for n-hexane isomerization by; (a) Sr modified zeolites and (b) Ba modified zeolites at different temperature and H<sub>2</sub>/HC ratio of 9.

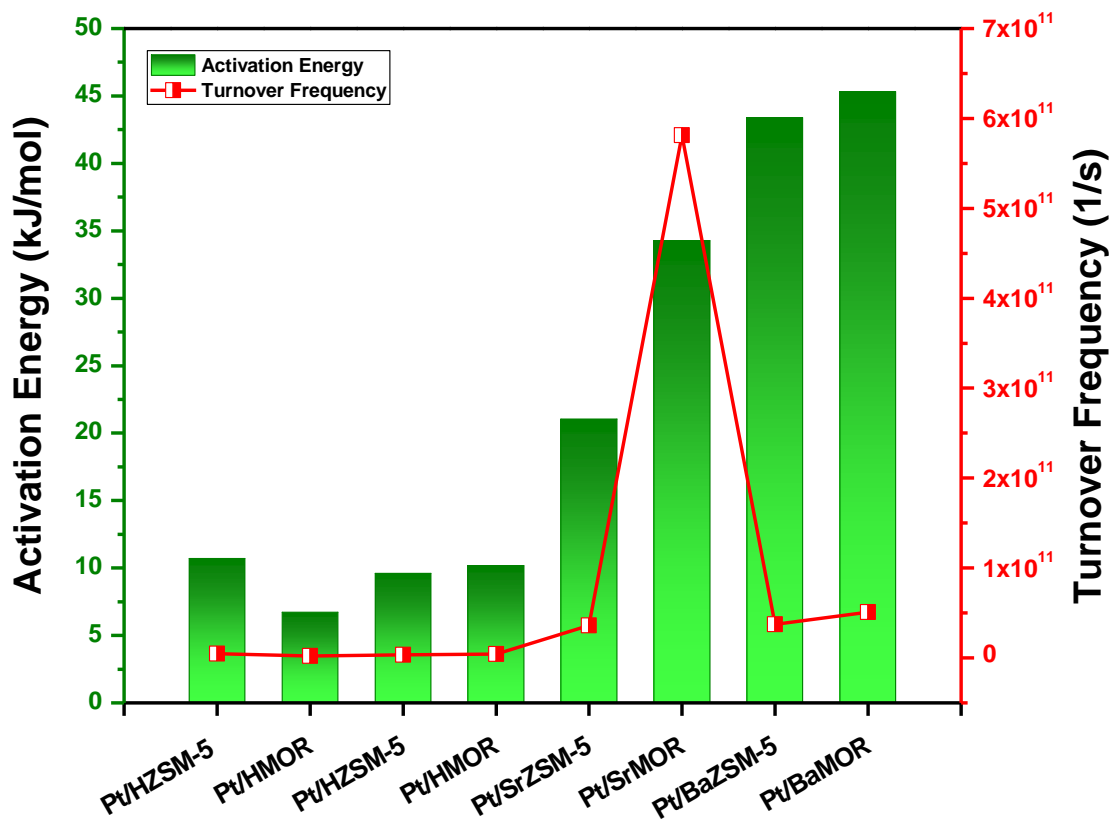


**Fig. 13.** The calculated findings for hydroisomerization of n-hexane over Pt/Sr-ZSM-5 and Pt/Sr-MOR (scCO<sub>2</sub> method) at 5 bar and different temperatures and H<sub>2</sub>/HC ratios (a) 3, (b) 6 and (c) 9.



**Fig. 14.** The findings for hydroisomerization of n-hexane by Pt loaded over Ba-ZSM-5 and Ba-MOR catalysts by scCO<sub>2</sub> method at 5 bar and different temperatures and H<sub>2</sub>/HC ratios; (a) 3, (b) 6 and (c) 9.





**Fig. 15.** The activation energy and turnover frequency of different Pt loaded zeolite catalysts for n-hexane isomerization.

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