

Article

Effect of Different Zeolite Supports on the Catalytic Behavior of Platinum Nanoparticles in Cyclohexene Hydrogenation Reaction

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Abstract: In this study, 1 wt% platinum (Pt) nanoparticles were incorporated into five types of zeolites (HY, Beta, mordenite, ZSM-5, and ferrierite) with an impregnation technique. The synthesis strategy included the use of water as a solvent for the applied Pt source. Moreover, the incorporation process was performed at ambient conditions followed by calcination at 450 °C. The five prepared materials were characterized by different physical and chemical characterization techniques and the obtained results confirmed the formation of Pt nanoparticles with an average size of 5–10 nm. The catalytic performance of the prepared materials was evaluated in the hydrogenation of cyclohexene under a solvent-free system at room temperature. Pt nanoparticles supported on ZSM-5 zeolite exhibited the best catalytic performance. Moreover, the optimization of operational conditions such as temperature, pressure, and catalyst amount was investigated and the obtained results showed the possibility to convert 100% of cyclohexene within 35 min over Pt-ZSM-5. Finally, the reusability of the Pt-ZSM-5 catalyst was investigated in four consecutive runs without treatment and the obtained results showed a negligible activity loss.

Keywords: hydrogenation; zeolite; Pt nanoparticles; cyclohexene; impregnation



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1. Introduction

Hydrogenation reactions, which include the conversion of unsaturated double bonds into saturated bonds by using molecular hydrogen, play a crucial role in chemical industries [1,2]. Several daily-use commercial products are fabricated based on hydrogenation reactions, such as the variety of products which are based on margarine [3] and nylon [4,5]. One of the most interesting catalysts which has been deeply investigated in hydrogenation reactions is the Wilkinson catalyst [6]. However, due to the separation problem, which is associated with the use of homogeneous catalysts, scientists utilize heterogeneous catalysts in hydrogenation reactions. In addition to raney nickel [7], noble metals such as Pd [8], Pt [9], Rh [10] and Ru [11] were found to be superior in the heterogeneous activation of hydrogenation reactions. However, the high cost of noble metals motivated scientists to investigate several tactics to minimize the catalyst cost. One of these tactics is the use of well-distributed nanoparticles of the noble metal supported on porous material with high surface area [12–14]; the use of nanoparticles ensures the reaction activation with a minimum amount of noble metal [15].

Zeolites are naturally occurring crystalline porous materials with a large surface area [16]. Zeolites consist of tetrahedrally coordinated aluminosilicate with rigid anionic frameworks containing well-defined channels and cavities [17]. Natural zeolites have the general formula of $M_{2/n} \cdot Al_2O_3 \cdot xSiO_2 \cdot yH_2O$, where M stands for the extra-framework cation [18]. It was found that tetrahedrally coordinated AlO_4 and SiO_4 can share one, two, or three oxygen atoms, which creates a wide variety of possible structures as the network is extended in three dimensions. Currently, 40 types of natural zeolite have been discovered and more than 150 types have been synthesized. Zeolites have a high potential in industry since they are used in water treatment, catalysis, agriculture, animal feed additives, and in biochemical applications [19]. Therefore, zeolites are considered a good candidate to support noble metal nanoparticles in hydrogenation reactions [20,21].

Kubicka used Beta zeolite to support the Pt nanoparticles as a catalyst in the hydrogenation of phenol and cresols [22]. In another study, zeolite Y was applied to support the Pt nanoparticles and the prepared catalyst was used in the hydrogenation of benzene [23]. Moreover, Wang et al. [24] investigated the use of Ru nanoparticles supported by ZSM-5 in the hydrogenation of phenol. Mordenite was also reported to support Pt in the hydrogenation of cyclohexene [25]. However, few studies have been conducted to systematically compare the effect of different zeolite supports in hydrogenation.

In the current study, Pt nanoparticles were incorporated into five different types of commercial zeolites (Y, Beta, ZSM-5, mordenite, and ferrierite) [26] with an impregnation technique. The prepared materials were characterized by various physical and chemical techniques to reveal their structure. Their catalytic activity was evaluated in the hydrogenation of cyclohexene under a solvent-free system at room temperature. The obtained results in terms of activity, stability and recycling were compared and the findings were discussed.

2. Experimental

2.1. Materials

In Table 1, a list of the applied materials that were used in the experimental work of the current study is presented. The listed chemical materials were used as received without any further purification and/or treatment.

Table 1. A list of materials which were used in this work.

Materials	Molecular Formula	Assay%	Source
Zeolite H-Beta	SiO_2	>97	ZEOLYST
Zeolite NH_4 -ZSM-5	SiO_2, Al_2O_3 (Si/Al = 50)	>97	ZEOLYST
Zeolite NH_4 -MOR	SiO_2, Al_2O_3 (Si/Al = 20)	>97	ZEOLYST
Zeolite NH_4 -Ferrierite	SiO_2, Al_2O_3, Fe_2O_3 (Si/Al = 20)	>97	ZEOLYST
Zeolite H-Y	SiO_2	>97	ZEOLYST
Platinum II Chloride	$PtCl_2$	98	ALDRICH
Cyclohexene	C_6H_{10}	99	MTEDIA
Cyclohexane	C_6H_{12}	99	ACROS

2.2. Catalysts Fabrication

First, 1 wt% of Pt was incorporated into five zeolite samples using an impregnation technique. In the real experiment, 1 g of the applied zeolite sample was suspended in 50 mL of distilled water. Then, a stoichiometric amount of $PtCl_2$ was dissolved in the above-mentioned suspension and the overall mixture was vigorously stirred for 48 h. After stirring, the mixture was dried at 100 °C for 24 h to remove the water and the solid powder was collected and finally calcined for 4 h at 450 °C. The obtained solid powder was carefully grinded and sieved through a 65-micron particle sieve.

2.3. Catalysts Characterization

The five prepared catalytic samples were characterized by several techniques to understand their structure. Powder X-ray diffraction patterns were used to assess the crystallinity of the manufactured samples. CuK radiation ($\lambda = 0.1541$ nm) was used to obtain XRD patterns on a Shimadzu 6000 DX instrument diffractometer with a graphite monochromator. The samples were scanned in steps of 0.02° over a range of $5\text{--}80^\circ 2\theta$. ICP elemental analysis was used to determine the exact concentration of Pt in each sample. The samples were digested before being cooked in the microwave for 90 min. The digested samples were then filtered and washed numerous times. Finally, using inductively coupled plasma optical emission spectroscopy (Thermo scientific, ICAP 7000 series, component No: 1340910, Qtegra Software, Bremen, Germany), the concentration of Pt was determined. The textural parameters of the manufactured catalytic samples (i.e., total surface area, pore volume, and pore diameter) were determined using the N_2 sorption data. On a NOVA 2000e at 77 K, nitrogen adsorption/desorption isotherms were obtained. The Barret–Joyner–Halenda (BJH) model was used to derive the pore size distribution from the adsorption branch. The samples had previously been evacuated for 16 h at 623 K. The surface area (S_{BET}) of the samples was calculated using the BET method, while the pore volume (V_{pore}) was estimated using Lippens and Boer's t-plot approach. Using an Agilent Cary 630 FTIR Spectrometer, the produced catalytic samples were studied using Fourier transform infrared (FTIR) spectroscopy. At ambient conditions, the spectra were taken in the range $4000\text{--}400\text{ cm}^{-1}$ with a spectral resolution of 4 cm^{-1} . The morphological structure of the catalysts was investigated using SEM. The elementary decomposition and the purity of the samples were studied using EDX, and a semi-quantitative study of the elements that made up the catalysts was also performed. After coating them with gold, SEM micrographs were obtained using the Jeol Model (6360 LVSEM, Peabody, MA, USA). Furthermore, an EDX study was performed utilizing the Jeol Model (6360 LVSEM, Peabody, MA, USA). Using high-resolution transmission electron microscopy, the size and distribution of the Pt on the various supports were investigated (HR-TEM). The analysis was carried out using a JEOL-JEM-2100 with a 200 KV accelerating voltage. By sprinkling a few drops of ground sample suspension in ethanol on a carbon polymer grid with copper support and drying at room temperature, the samples were deposited and a LINK EDX system was employed.

2.4. Catalytic Activity Study

The hydrogenation of cyclohexene was performed in a 300 mL semi-batch Parr reactor at room temperature and 5 atm of H_2 gas for 1 h. In a typical experiment, 25 mL of cyclohexene and 0.25 g of catalyst were placed inside the reactor to form a suspension. The suspension was vigorously stirred at a constant rate of 1000 rpm to reduce the external mass transfer limitation, if present. After closing the reactor carefully, it was degassed with nitrogen gas and finally pressurized to 5 atm with hydrogen gas (99%). After elapsing the reaction time, the reactor was flushed with nitrogen gas and finally a sample of 0.5 mL was sent to GC for analysis. The applied GC was SHIMADZU GC-17, and the applied capillary column was RTX-5, $30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$. Finally, the applied detector was a flame ionization type (FID).

The conversion of cyclohexene (CXE) was calculated as follows:

$$\text{Conversion} = \frac{[CXE]_0 - [CXE]_t}{[CXE]_0} \times 100 \quad (1)$$

where $[CXE]_0$ is the concentration of cyclohexene at zero time and $[CXE]_t$ is the concentration of cyclohexene at (t) time.

Moreover, the turnover frequency (TOF) was calculated as follows:

$$\text{TOF} = \frac{[CXE]_0 - [CXE]_t}{[Pt] \times \text{time}(s)} \quad (2)$$

where $[Pt]$ is the concentration of Pt , and the time of reaction was calculated in seconds.

3. Results

3.1. The Characterization Data

The exact amount of Pt was determined with ICP analysis. Table 2 shows a comparison between the intended Pt loading and the obtained loading in the final solid product.

Table 2. The ICP analysis of exact amount of Pt in each sample.

Sample	Technique	Intended Loading (%)	Obtained Loading (%)	Incorporation Efficiency (%)
Pt-ZSM-5	Impregnation	1	0.766	76.6
Pt-Beta	Impregnation	1	0.597	59.7
Pt-Y	Impregnation	1	0.562	56.2
Pt-MOR	Impregnation	1	0.588	58.8
Pt-FERR	Impregnation	1	0.673	67.3

The obtained result shows that a considerable amount of Pt was lost during the fabrication. This can be explained by the nature of the pore system of zeolite materials. The small pore volume partially allows Pt solution to access the entire zeolite channels. Moreover, the hydrophobic nature of silica in Y and $Beta$ types hinders the accessibility of Pt solution to the zeolite channels. ZSM-5 exhibited the maximum impregnation efficiency, in which almost 76.6% of the Pt amount was obtained in the final solid product. While zeolite Y exhibited the lowest impregnation efficiency, only 56.2% was obtained in the final product.

The formation of Pt nanoparticles incorporated into the different applied supports was investigated using the XRD technique. Figure 1 shows the XRD analysis of the Pt -incorporated zeolite materials.

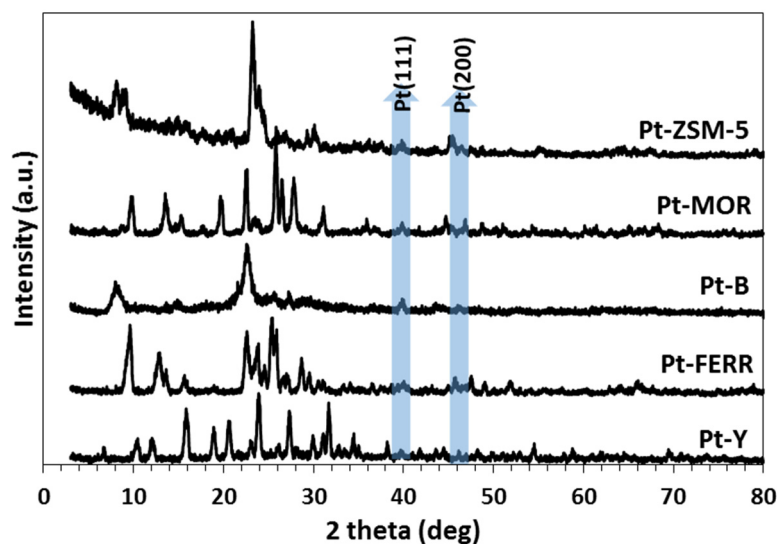


Figure 1. XRD patterns of the Pt -incorporated different zeolite materials.

The XRD patterns of the fabricated catalysts were dominated by the characteristic peaks of zeolite materials, as stated in the atlas of the zeolite framework [27]. Small peaks could be observed in the patterns at 2θ of 39.7° and 46.2° . As indicated in the reference (JCPDS card no 04-0802) of Pt nanoparticles, the positions and intensities of these peaks can be assigned to (111) and (200) of the metallic Pt nanoparticles [28]. The results showed that all the Pt was transformed directly into Pt^0 nanoparticles during the synthesis, which eliminated the need for a further hydrogenation step to generate the Pt^0 active sites.

N₂ sorption measurements were applied to determine the textural properties (total surface area, pore volume, and pore diameter) of the prepared materials. The obtained results are listed in Table 3.

Table 3. The texture properties of the prepared samples as determined using N₂ sorption analysis technique.

Sample	Surface Area (m ² /g)	Pore Volume (cm ³ /g)	Pore Size (nm)
Pt-Y	436.9	0.07	8.6
Pt-Beta	491.9	0.14	5.5
Pt-MOR	414.4	0.13	1.2
Pt-FERR	309.9	0.10	1.5
Pt-ZSM-5	402.9	0.16	7.2

The surface area of the entire prepared samples ranged from 309 to 491 m²/g. The maximum surface area of the Pt-incorporated mesoporous materials was obtained in the Pt-Beta sample, while Pt-FERR exhibited the smallest surface area between the Pt-incorporated zeolite samples. It was noticed that the total surface area was higher than the corresponding bare commercial samples. However, this can be related to the presence of Pt nanoparticles which increase the measurement of the surface area. On the other hand, the pore volume of the prepared samples ranged from 0.07 to 0.16 cm³/g. Surprisingly, only two applied commercial zeolites were found to have pore sizes in the range of microporous materials: Pt-MOR and Pt-FERR. However, three zeolite materials were found to have pore sizes in the range of mesoporous materials: Pt-Y, Pt-Beta, and Pt-ZSM-5. To explain this finding, there is a possibility that the producer applied some additional tactics to improve the pore size of the commercial zeolites to be suitable in the different industrial applications notable in the reactions which deal with high organic molecules. The N₂ isotherms can give additional information about the porous systems of the prepared samples. Figure 2 presents the N₂ sorption isotherms for the Pt-incorporated zeolite samples. The N₂ sorption isotherms of Pt-incorporated zeolites are a mixture of type IV and type III as an indication of the dual nature of the pore system in the zeolite samples.

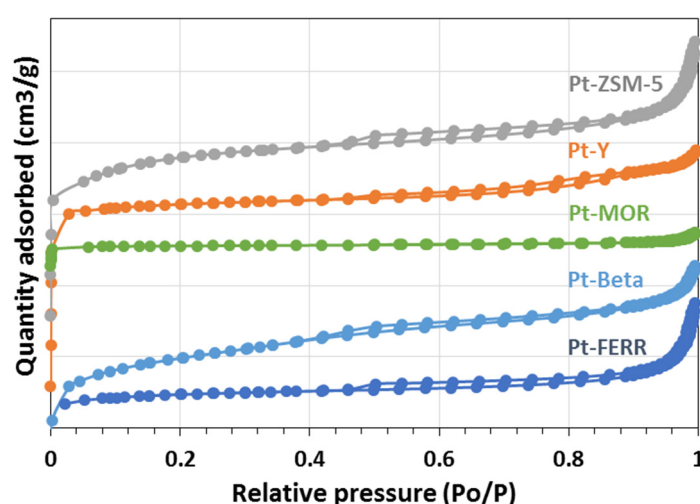


Figure 2. The nitrogen isotherms of the prepared Pt-incorporated zeolite materials (Y, Beta, MOR, FERR, and ZSM-5).

FTIR analysis was performed to investigate the changes which occurred in the zeolite framework as a result of Pt incorporation. The collected FTIR spectra for the samples are presented in Figure 3. The spectra of bare supporting zeolite samples are dominated

by two prominent bands at 1047 and 799 cm^{-1} which can be assigned to the stretching asymmetric and symmetric modes of the Si–O–Si lattice, respectively [28]. The addition of Pt^0 nanoparticles, which—most likely—increases the asymmetric vibration of the siliceous network, caused the intensity of the 1047 cm^{-1} band to be higher than that of the bare sample [29,30]. Finally, due to the presence of Pt^0 nanoparticles in the zeolite lattice, the shoulder around 1215 cm^{-1} , which also referred to the external asymmetric Si–O stretching mode in the bare support, was displaced to a smaller wavenumber. However, the obvious change in the entire spectra before and after Pt incorporation was the change in the two peaks of 2350 and 2880–2900 cm^{-1} , which can be attributed to the CO_2 and OH surface silanol groups, respectively. The reason for such a change is not clear and needs further investigation.

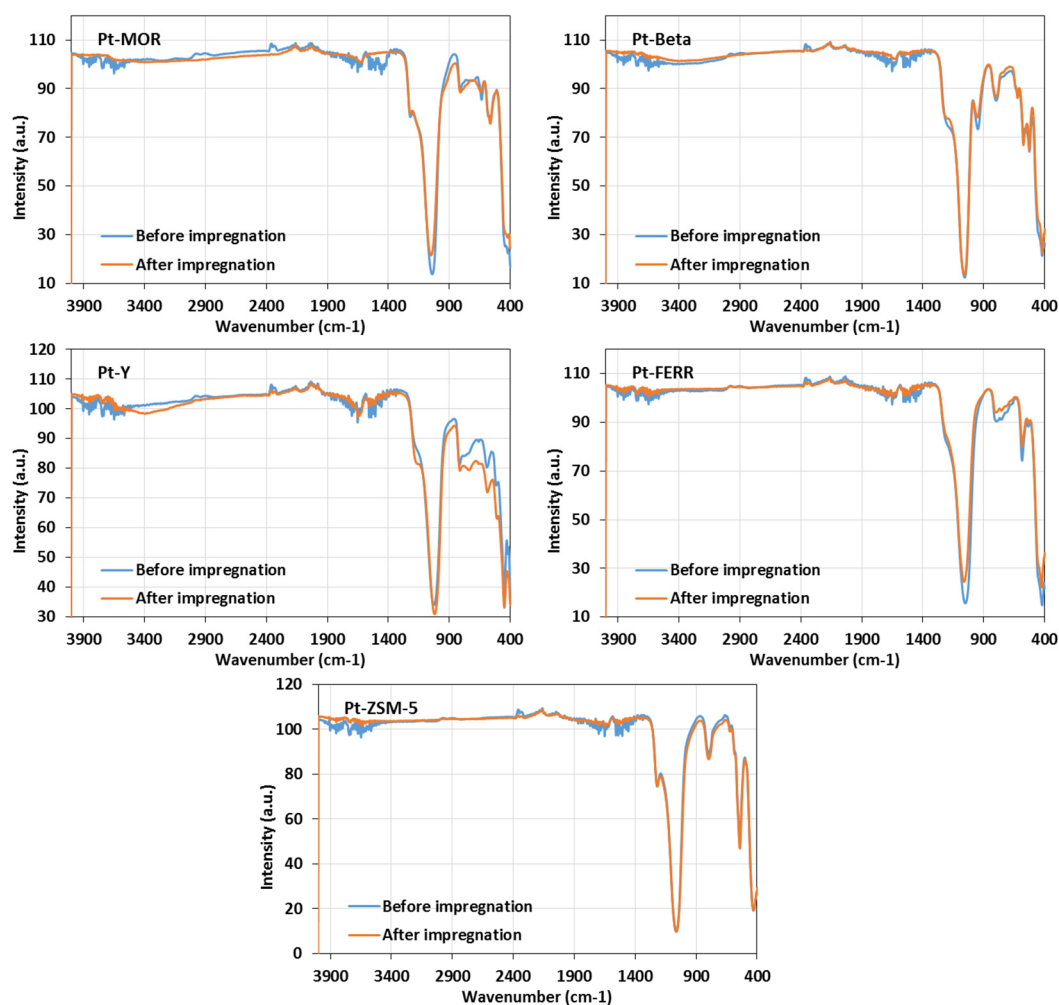


Figure 3. The FTIR spectra of the prepared Pt-incorporated zeolite materials (Y, Beta, MOR, FERR, and ZSM-5) before and after Pt incorporation.

The morphological structure of the prepared samples was investigated by SEM analysis. Figure 4 presents the SEM micrographs of the fabricated samples. Pt-Y exhibited a highly crystalline phase with partially replicated octahedral crystals (average size between 1 and 1.5 μm) with a few aggregates [30]. Pt-Beta showed a sphere-like morphology with a broad average size of 0.2–1 μm . Pt-MOR exhibited fused and aggregated prism-like crystals with an average crystal size of 1–1.5 μm [31]. Finally, Pt-ZSM-5 exhibited the aggregates' hexagonal crystal structure [32]. The average crystal size was hard to detect due to the high aggregation. More importantly, no Pt-separated phase could be detected in any micrograph, as an indication for the total incorporation of the Pt metal into the zeolite matrix. Moreover,

because water and Pt source were used only in the sample preparation, no carbon or carbonized species could be detected in the micrographs, which is an indication for the purity of the prepared samples.

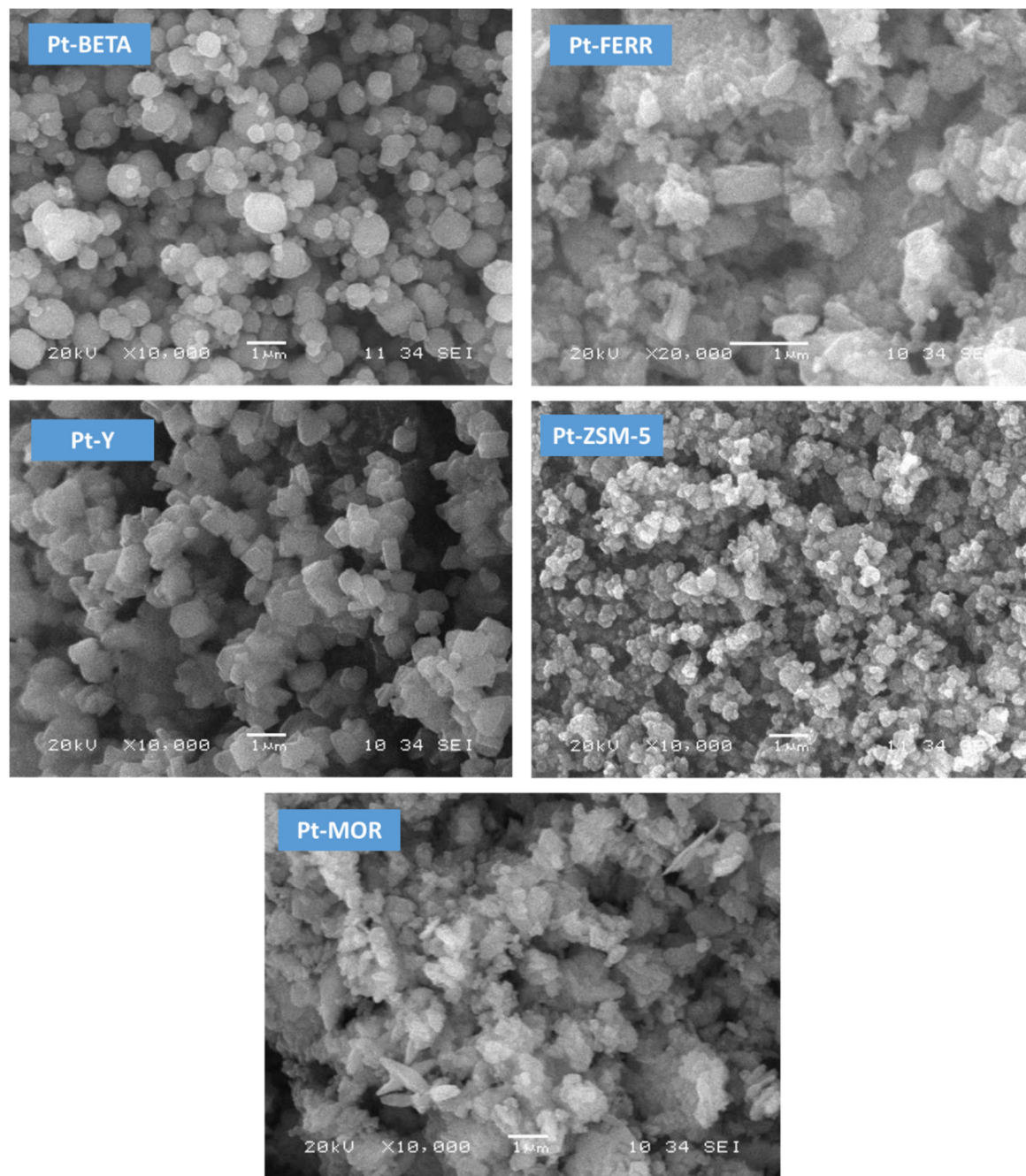


Figure 4. SEM micrographs with the same magnification for Pt-incorporated zeolite samples.

EDX analysis coupled with SEM analysis was carried out to reveal the chemical composition of the prepared catalytic samples. Figure 5 shows the obtained results of the EDX analysis for the Pt-incorporated zeolite materials.

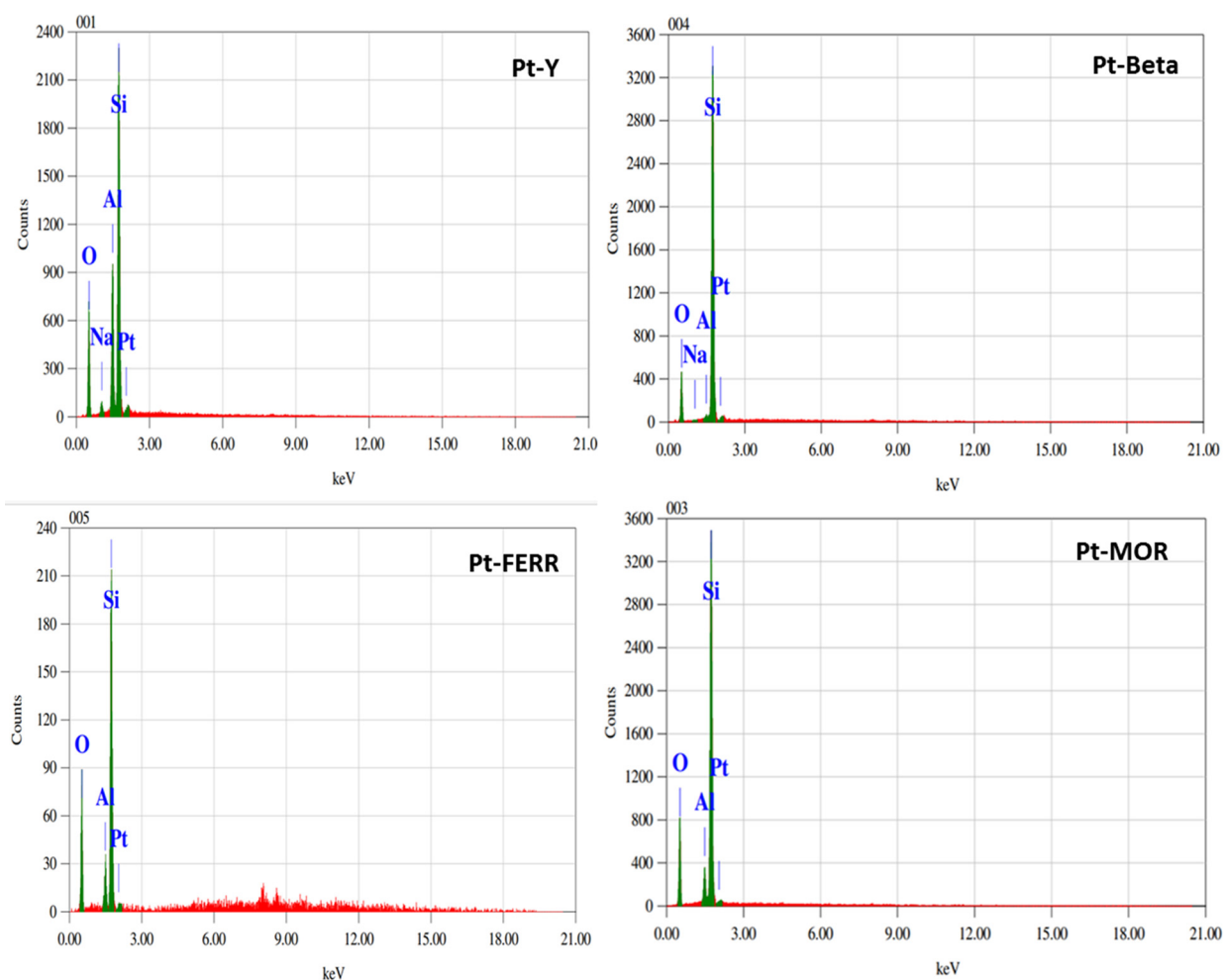


Figure 5. The EDX analysis of the prepared Pt-incorporated zeolite materials (Y, Beta, MOR, and FERR).

The Pt-incorporated zeolite materials showed peaks of Si, O, Al and Pt only. No other elements could be detected as an indication of the high purity of the prepared samples. Moreover, Na was detected in Pt-Y and Pt-Beta samples, which can be related to the chemicals which were used in the synthesis of the bare zeolite samples.

HR-TEM analysis was performed to investigate the incorporation and distribution of Pt nanoparticles into the different zeolite samples. Figure 6 presents the obtained micrographs with different magnification powers.

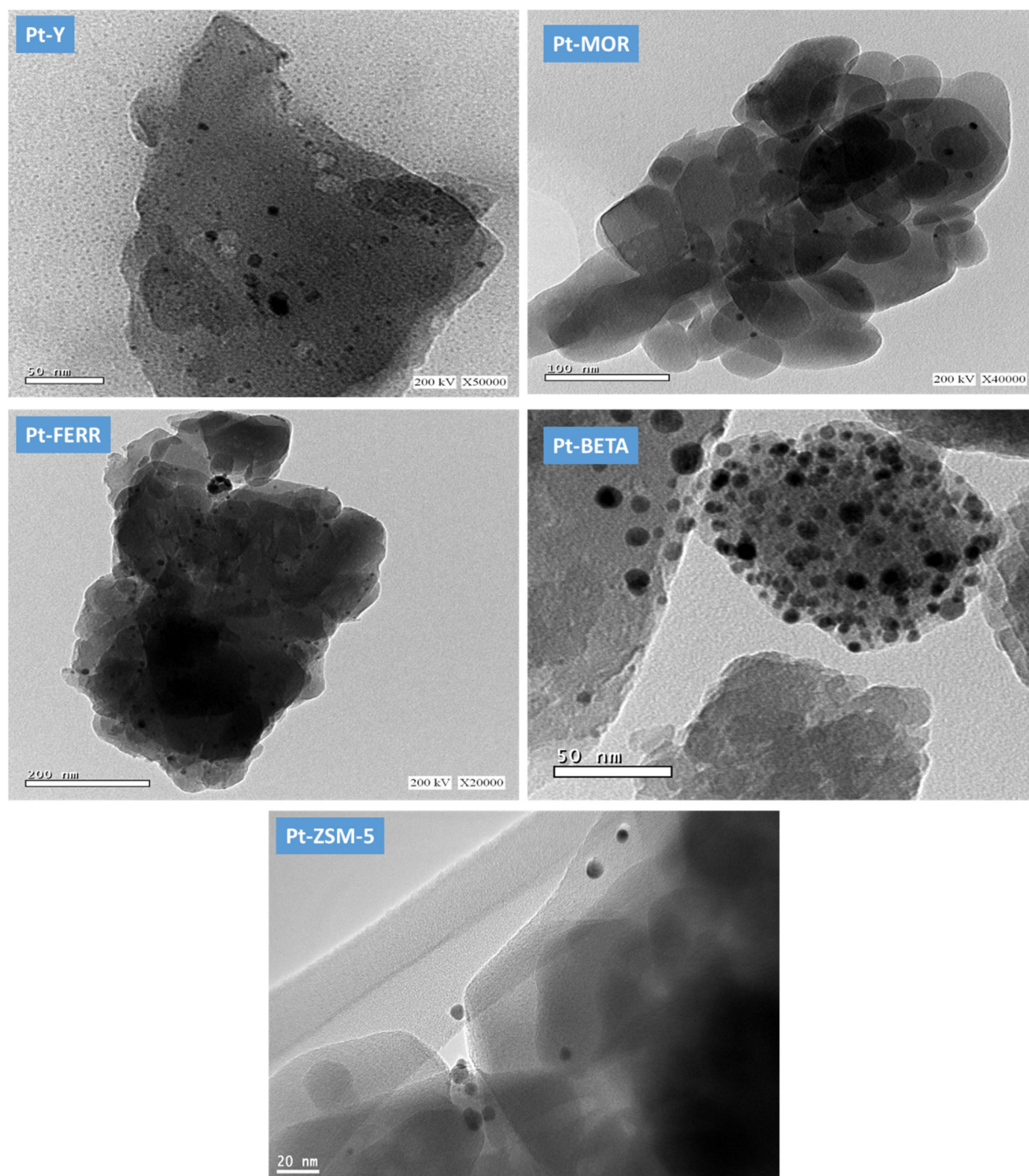


Figure 6. HR-TEM micrographs for Pt-incorporated different zeolite samples.

The micrographs of the entire samples show the Pt nanoparticles with an average size of 5–10 nm incorporated into the different supports with high distribution. Moreover, no bulky Pt particles could be observed, nor other bulky crystals, indicating the high efficiency of the synthesis method to incorporate Pt nanoparticles into the different zeolite samples.

3.2. The Hydrogenation of Cyclohexene

The catalytic performance study of the prepared catalysts was carried out in the reduction of cyclohexene by hydrogen gas to produce cyclohexane as a model reaction. The reactions were performed under solvent-free conditions and at room temperature by applying 5 atm of hydrogen pressure in a Parr reactor. The catalytic performance of each

catalyst was monitored by gas chromatography and the obtained results are reported in this section. In the beginning of the catalytic performance study, several blank experiments (normally called zero reactions) were performed. The aim of these experiments was to investigate the effect of different parameters such as self-catalysis, bare support, bulk catalyst, etc., on the chosen model reaction. The obtained results of the blank reactions are plotted in Figure 7.

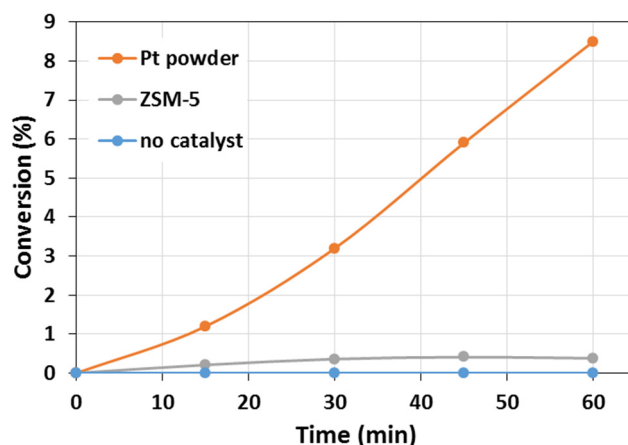


Figure 7. The conversion profiles of cyclohexene in the blank reactions as a function in the applied reaction time.

The model reaction proceeded without any catalyst to ensure that the reaction could not be catalyzed by the stainless steel of the Parr reactor or by the stirring rod. The obtaining conversion % was zero as an indication of the need for a catalyst to perform the reaction. In other experiments, the bare supports (without Pt active sites) were applied to catalyze the model reaction. The obtained results showed that a negligible % of conversions were obtained. Both supports could not convert more than 1% of cyclohexene. Moreover, bulk non-porous zero-valent Pt metal was applied to catalyze the reaction. The obtained results showed that only 8.5% of cyclohexene was converted into cyclohexane under the same reaction conditions. Finally, the reduction of cyclohexene into cyclohexane was performed at lower pressure, i.e., 1 and 3 atm, and catalyzed by bulk Pt particles. Almost no conversion could be detected. The results of the blank experiments clearly show that cyclohexene cannot be self-converted, there is no effect for the support, and the reaction can be proceeded only under 5 atm and at room temperature by using a metallic catalyst.

The catalytic performance of the Pt-incorporated zeolite samples is presented in Figure 8. Pt ZSM-5 exhibited the best catalytic performance, in which 22.4% conversion of cyclohexene was obtained with a total TOF of 0.63 s^{-1} . The Pt-Beta sample was able to convert 12.4% of cyclohexene with a total TOF of 0.44 s^{-1} . Similar catalytic behavior was observed with Pt-MOR and Pt-FERR samples, and almost the same TOF, 0.3 s^{-1} , was obtained. Finally, Pt-Y exhibited the lowest activity: only 6% of cyclohexene was converted with a total TOF of 0.23 s^{-1} .

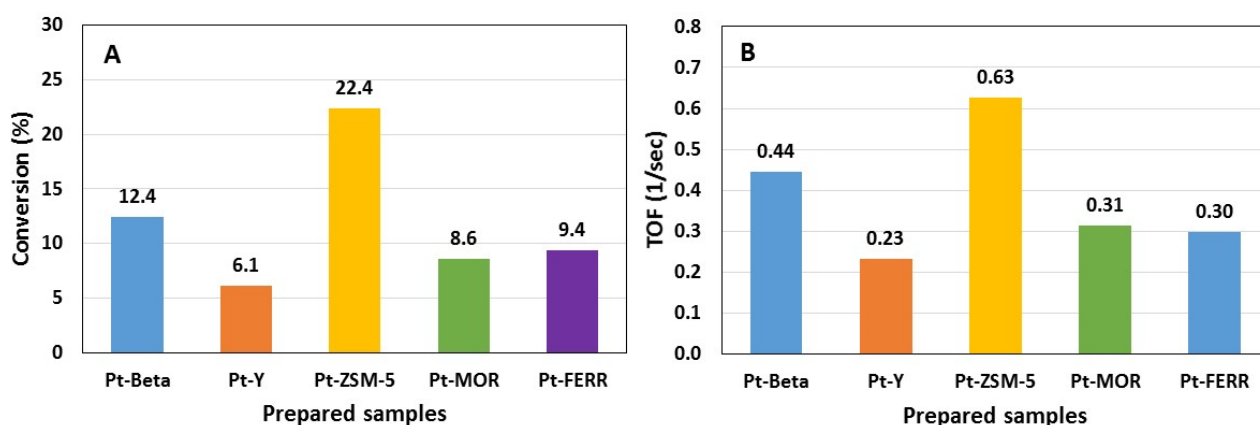


Figure 8. (A) The obtained conversion (%) of cyclohexene over Pt-incorporated zeolite materials (Beta, Y, ZSM-5, MOR, and FERR). (B) The corresponding TOF.

To have a fair comparison between the supports, the amount of Pt must be normalized, and hence the TOF s^{-1} is the correct parameter for comparison rather than conversion rate. Several parameters can affect the behavior of support, such as the geometrical configuration, texture properties, hydrophobicity, presence of contamination, and/or adsorption behavior. Moreover, the applied zeolites samples were ZSM-5, Y and Beta with three-dimensional pore systems, while MOR and FERR have two-dimensional pore systems. Therefore, it was expected that ZSM-5, Y and Beta would exhibit the highest activity, which was correct to a great extent. It was also expected that MOR and FERR would exhibit the minimum activity due to the small pore size, hindering the accessibility of cyclohexene to the Pt active sites in addition to the two-dimensional pore systems in both supports. The comparison between ZSM-5, Y and Beta (the three-dimensional pore system) also shows that ZSM-5 is the only support which contains alumina in the framework, which might improve the adsorption of the reactants.

The hydrogenation reaction over Pt-ZSM-5 was successfully performed under room temperature and, therefore, the study was extended to run the reaction under elevated temperatures up to 60 °C. The aim of this study was to calculate the kinetics of the hydrogenation reaction in addition to the activation energy calculation. The conversion % of cyclohexene over Pt-ZSM-5 at different reaction temperatures is plotted in Figure 9. The obtained results showed a typical improvement in the catalytic performance when the reaction temperature was increased. The conversion of cyclohexene reached 100% over Pt-ZSM-5 at 50 °C after 45 min, and at 60 °C after 35 min. Moreover, Pt-ZSM-5 did not suffer from thermal deterioration, and the structure of ZSM-5 was maintained and did not collapse as a result of applying 5 atm pressure and 60 °C temperature.

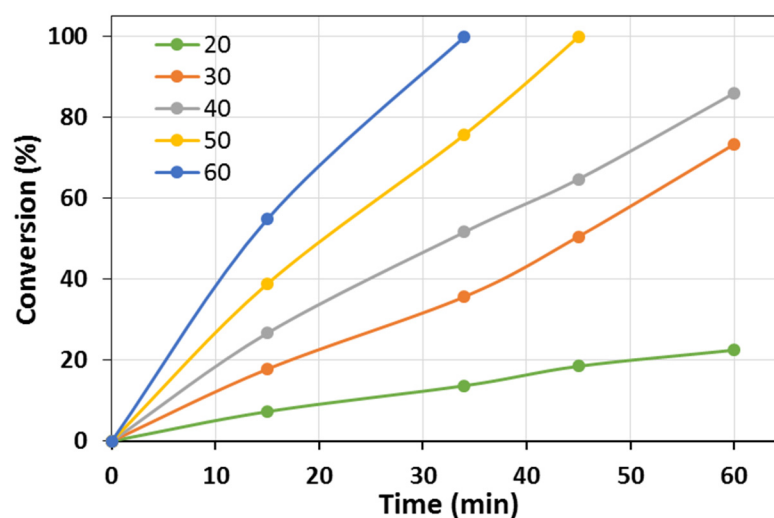


Figure 9. The conversion % profiles of cyclohexene over Pt-ZSM-5 at different temperatures as a function of the applied reaction time.

In order to identify the order of the hydrogenation reaction of cyclohexene over Pt-ZSM-5, several kinetic models were investigated. According to the literature [33], the zero-order reaction model was the most commonly used model to calculate the rate constants [K] of cyclohexene hydrogenation at various applied temperatures [34]. In this model, the concentration of cyclohexene is plotted against reaction time to obtain a straight line with a slope = $-K$.

The zero-order kinetic model of cyclohexene conversion over Pt-ZSM-5 at different reaction temperatures is plotted in Figure 10. The figure shows that all obtained conversion data are perfectly fit with the model, and the coefficient of determination (R^2) values in both graphs (ten data sets) are greater than 0.984. It is also observed that the rate constants increased with the increase in applied reaction temperature, and the maximum value was 0.0072 mol/min Pt-ZEM-5 at 60 °C.

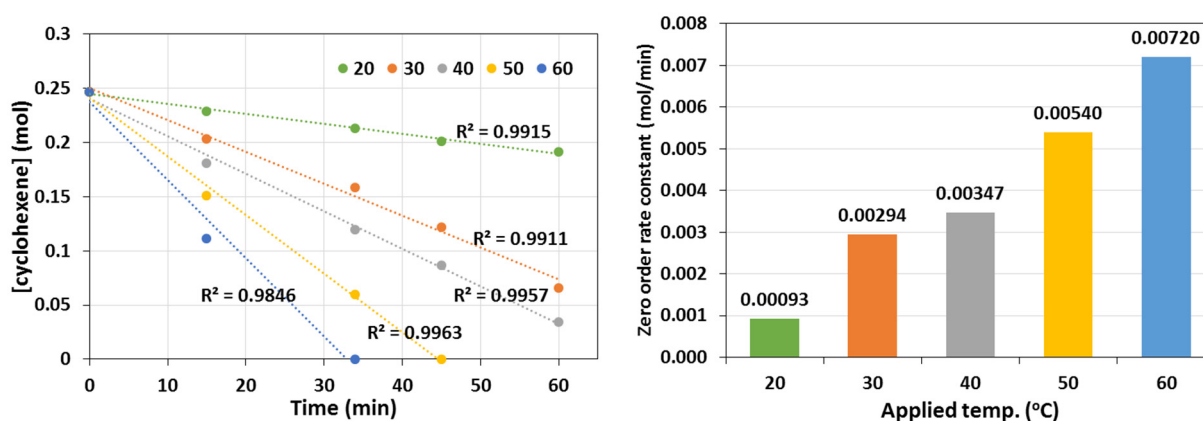


Figure 10. (Left) panel: The zero-order kinetic model for the hydrogenation of cyclohexene over Pt-ZSM-5 at different reaction temperatures. (Right) panel: comparison between the calculated zero-order rate constants.

To calculate the activation energy of the applied reaction, the Arrhenius equation was applied in which the plot of $\ln(K)$ against $1/T$ (kelven⁻¹) should give a straight line with a slope equal to $-E_a/R$, where R is the universal gas constant (Figure 11). The calculated activation energy (E_a) was 88.95 KJ/mol for Pt-ZSM-5.

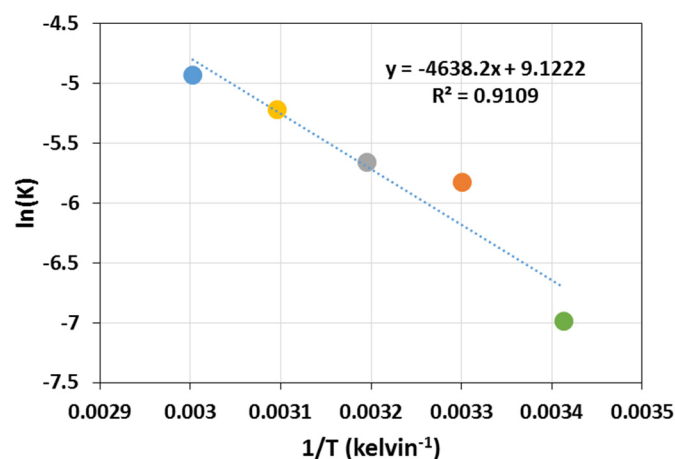


Figure 11. Arrhenius plot to calculate the activation energy (E_a) for Pt-ZSM-5 catalyst.

Furthermore, to confirm the exothermic nature of the hydrogenation reaction, the change in the reactor temperature was measured (Figure 12) for the Pt-ZSM-5 catalyst. It is clear that the reactor temperature is increasing as an indication of the exothermic nature of the hydrogenation reaction.

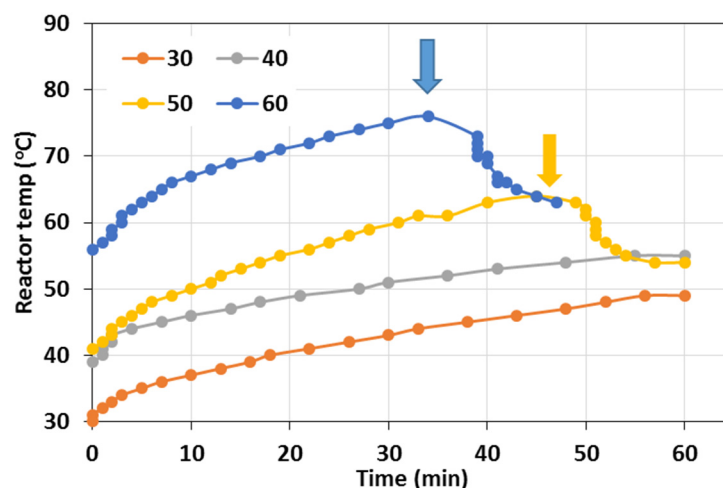


Figure 12. Change in the reactor temperature during the hydrogenation of cyclohexene over Pt-ZSM-5. Arrows are pointing to the 100% conversion of cyclohexene.

The reusability of the Pt-ZSM-5 was investigated by performing four consecutive runs using the same catalytic sample without any treatment, and a fifth run after thermal treatment at 300 $^{\circ}\text{C}$ for 180 min. The obtained results expressed by the conversion % of cyclohexene of the different runs are plotted in Figure 13. It is obvious that the Pt-ZSM-5 sample was able to activate the five runs at a good efficiency. Without treatment, the activity of Pt-ZSM-5 was reduced by 10% after four runs compared to a fresh sample. This is most likely due to the accumulation of organic species onto the surface of the catalysts, while after thermal treatment, only 7.1% loss in activity was obtained. This result clearly shows that Pt-ZSM-5 exhibited good stability after five runs.

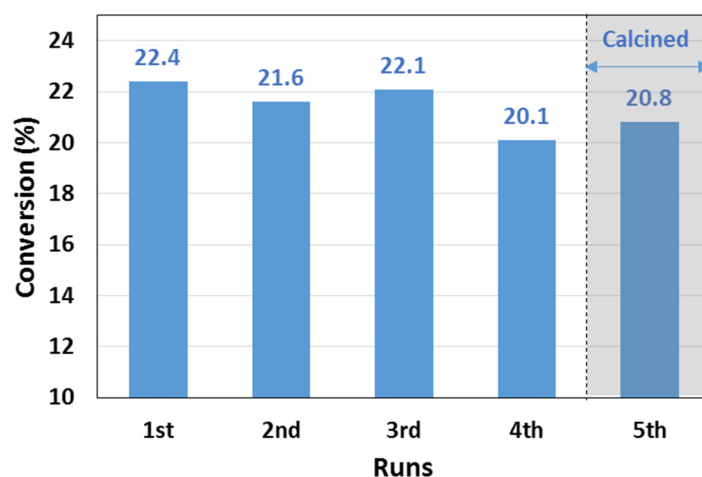


Figure 13. The cyclohexene conversion % over the same samples of Pt-ZSM-5 for four consecutive runs without treatment and one run after thermal treatment (calcination).

4. Conclusions

The current study presents—for the first time—a systematic comparison between the effects of five different zeolite supports on the catalytic performance of Pt nanoparticles in a hydrogenation reaction. Pt nanoparticles were incorporated into five different zeolites (HY, Beta, mordenite, ZSM-5, and ferrierite) using only water in a wet impregnation procedure. The incorporation efficiency differs from one sample to another. The zeolites which contained only silica, such as Beta and HY, exhibited the poorest incorporation efficiency (58% of Pt was incorporated into the zeolite framework). On the other hand, ZSM-5, which contains aluminum, exhibited the best incorporation efficiency (76%). The characterization data confirmed the presence of Pt nanoparticles with a size ranging from 5 to 10 nm. The five different catalysts were applied to activate the hydrogenation of the cyclohexene reaction at room temperature. Pt-ZSM-5 exhibited the best catalytic performance in which 22.4% conversion was achieved, while Pt-MOR and Pt-FERR exhibited the lowest activity (no more than 10% was obtained). This can be related to the three-dimensional framework of ZSM support which offers high accessibility to/from the Pt active sites. Moreover, the presence of Al^{3+} centers in ZSM-5 most likely facilitates the adsorption of the substrates onto the surface of the solid catalyst. The obtained activity at different temperatures fit perfectly with the zero-order kinetic model and the activation energy was calculated. Pt-ZSM-5 catalyzed five different reactions without significant loss in activity.

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References

1. Stanislaus, A.; Cooper, B.H. Aromatic hydrogenation catalysis: A review. *Catal. Rev. Sci. Eng.* **1994**, *36*, 75–123. [[CrossRef](#)]
2. Stoffels, M.A.; Klauck, F.J.R.; Hamadi, T.; Glorius, F.; Leker, J. Technology trends of catalysts in hydrogenation reactions: A patent landscape analysis. *Adv. Synth. Catal.* **2020**, *362*, 1258–1274. [[CrossRef](#)] [[PubMed](#)]

3. McGlynn, S.E.; Glass, J.B.; Johnson-Finn, K.; Klein, F.; Sanden, S.A.; Schrenk, M.O.; Ueno, Y.; Vitale-Brovarone, A. Hydrogenation reactions of carbon on Earth: Linking methane, margarine, and life. *Am. Mineral.* **2020**, *105*, 599–608. [\[CrossRef\]](#)
4. Lee, Y.; Park, H.; Han, J.; Lee, J. Economically-feasible production of a nylon monomer using RANEY[®] catalysts. *React. Chem. Eng.* **2021**, *6*, 225–234. [\[CrossRef\]](#)
5. Spiccia, N.D.; Border, E.; Illesinghe, J.; Jackson, W.R.; Robinson, A.J. Preparation of a nylon-11 precursor from renewable canola oil. *Synthesis* **2013**, *45*, 1683–1688.
6. Jourdant, A.; González-Zamora, E.; Zhu, J. Wilkinson's catalyst catalyzed selective hydrogenation of olefin in the presence of an aromatic nitro function: A remarkable solvent effect. *J. Org. Chem.* **2002**, *67*, 3163–3164. [\[CrossRef\]](#)
7. Fouilloux, P. The nature of raney nickel, its adsorbed hydrogen and its catalytic activity for hydrogenation reactions. *Appl. Catal.* **1983**, *8*, 1–42. [\[CrossRef\]](#)
8. Teschner, D.; Révay, Z.; Borsodi, J.; Hävecker, M.; Knop-Gericke, A.; Schlögl, R.; Milroy, D.; Jackson, S.D.; Torres, D.; Sautet, P. Understanding palladium hydrogenation catalysts: When the nature of the reactive molecule controls the nature of the catalyst active phase. *Angew. Chem.* **2008**, *120*, 9414–9418. [\[CrossRef\]](#)
9. Bratlie, K.M.; Lee, H.; Komvopoulos, K.; Yang, P.; Somorjai, G.A. Platinum nanoparticle shape effects on benzene hydrogenation selectivity. *Nano Lett.* **2007**, *7*, 3097–3101. [\[CrossRef\]](#)
10. Etayo, P.; Vidal-Ferran, A. Rhodium-catalysed asymmetric hydrogenation as a valuable synthetic tool for the preparation of chiral drugs. *Chem. Soc. Rev.* **2013**, *42*, 728–754. [\[CrossRef\]](#)
11. El Sayed, S.; Bordet, A.; Weidenthaler, C.; Hetaba, W.; Luska, K.L.; Leitner, W. Selective hydrogenation of benzofurans using ruthenium nanoparticles in Lewis acid-modified ruthenium-supported ionic liquid phases. *ACS Catal.* **2020**, *10*, 2124–2130. [\[CrossRef\]](#)
12. Alhanash, A.M.; Alqahtani, F.A.; Aldalbahi, A.; Rahaman, M.; Benaissa, M.; Hamdy, M.S. The hydrogenation of cycloalkenes over direct-synthesized well-defined zero-valent Pt nanoparticles incorporated TUD-1 mesoporous material. *Inorg. Chem. Commun.* **2021**, *127*, 108545. [\[CrossRef\]](#)
13. Benaissa, M.; Alhanash, A.M.; Mubarak, A.T.; Eissa, M.; Sahlabji, T.; Hamdy, M.S. Solvent-free hydrogenation of cyclohexene over Rh-TUD-1 at ambient conditions. *RSC Adv.* **2018**, *8*, 34370–34373. [\[CrossRef\]](#) [\[PubMed\]](#)
14. Alhanash, A.M.; Atran, A.A.; Eissa, M.; Benaissa, M.; Hamdy, M.S. Liquid Phase Hydrogenation of MIBK over M/CsPW (M = Ag, Ru, Pt, and Pd). *Catalysts* **2019**, *9*, 47. [\[CrossRef\]](#)
15. Chen, H.; Sun, J. Selective hydrogenation of phenol for cyclohexanone: A review. *J. Ind. Eng. Chem.* **2021**, *94*, 78–91. [\[CrossRef\]](#)
16. Chen, L.-H.; Sun, M.; Wang, Z.; Yang, W.; Xie, Z.; Su, B. Hierarchically structured zeolites: From design to application. *Chem. Rev.* **2020**, *120*, 11194–11294. [\[CrossRef\]](#)
17. Dusselier, M.; Davis, M.E. Small-pore zeolites: Synthesis and catalysis. *Chem. Rev.* **2018**, *118*, 5265–5329. [\[CrossRef\]](#)
18. Bogdanov, B.; Georgiev, D.; Angelova, K.; Yaneva, K. Natural zeolites: Clinoptilolite. *Rev. Nat. Math. Sci.* **2009**, *4*, 6–11.
19. Vermeiren, W.; Gilson, J.-P. Impact of zeolites on the petroleum and petrochemical industry. *Top. Catal.* **2009**, *52*, 1131–1161. [\[CrossRef\]](#)
20. Sidhpuria, K.B.; Patel, H.A.; Parikh, P.A.; Bahadur, P.; Bajaj, H.C.; Jasra, R.V. Rhodium nanoparticles intercalated into montmorillonite for hydrogenation of aromatic compounds in the presence of thiophene. *Appl. Clay Sci.* **2009**, *42*, 386–390. [\[CrossRef\]](#)
21. Liu, H.; Jiang, T.; Han, B.; Liang, S.; Zhou, Y. Selective phenol hydrogenation to cyclohexanone over a dual supported Pd–Lewis acid catalyst. *Science* **2009**, *326*, 1250–1252. [\[CrossRef\]](#)
22. Horáček, J.; Št'ávoň, G.; Kelbichová, V.; Kubička, D. Zeolite-Beta-supported platinum catalysts for hydrogenation/hydrodeoxygenation of pyrolysis oil model compounds. *Catal. Today* **2013**, *204*, 38–45. [\[CrossRef\]](#)
23. Wang, J.; Li, Q.; Yao, J. The effect of metal–acid balance in Pt-loading dealuminated Y zeolite catalysts on the hydrogenation of benzene. *Appl. Catal. A Gen.* **1999**, *184*, 181–188. [\[CrossRef\]](#)
24. Wang, L.; Zhang, J.; Yi, X.; Zheng, A.; Deng, F.; Chen, C.; Ji, Y.; Liu, F.; Meng, X.; Xiao, F.S. Mesoporous ZSM-5 zeolite-supported Ru nanoparticles as highly efficient catalysts for upgrading phenolic biomolecules. *ACS Catal.* **2015**, *5*, 2727–2734. [\[CrossRef\]](#)
25. Aboul-Fotouh, S.M. Cyclohexene Reactivity Using Catalysts Containing Pt, Re and PtRe Supported on Na-and H-Mordenite. *J. Chin. Chem. Soc.* **2003**, *50*, 1151–1158. [\[CrossRef\]](#)
26. Baerlocher, C.; McCusker, L.B.; Olson, D.H. *Atlas of Zeolite Framework Types*; Elsevier: Amsterdam, The Netherlands, 2007.
27. Qin, H.; Qian, X.; Meng, T.; Lin, Y.; Ma, Z. Pt/MO_x/SiO₂, Pt/MO_x/TiO₂, and Pt/MO_x/Al₂O₃ Catalysts for CO Oxidation. *Catalysts* **2015**, *5*, 606–633. [\[CrossRef\]](#)
28. Wang, C.; Wu, C. Electrical sensing properties of silica aerogel thin films to humidity. *Thin Solid Films* **2006**, *496*, 658–664. [\[CrossRef\]](#)
29. Wu, R.; Sun, Y.; Lin, C.; Chen, H.; Chavali, M. Composite of TiO₂ nanowires and Nafion as humidity sensor material. *Sens. Actuators B Chem.* **2006**, *115*, 198–204. [\[CrossRef\]](#)
30. Shamzhy, M.; Opanasenko, M.; Concepción, P.; Martínez, A. New trends in tailoring active sites in zeolite-based catalysts. *Chem. Soc. Rev.* **2019**, *48*, 1095–1149. [\[CrossRef\]](#)
31. Ye, G.; Sun, Y.; Guo, Z.; Zhu, K.; Liu, H.; Zhou, X.; Coppens, M. Effects of zeolite particle size and internal grain boundaries on Pt/Beta catalyzed isomerization of n-pentane. *J. Catal.* **2018**, *360*, 152–159. [\[CrossRef\]](#)
32. Tamizhdurai, P. Isomerization of hydrocarbons over Pt supported on micro-mesoporous ZSM-5. *Polyhedron* **2018**, *154*, 314–324. [\[CrossRef\]](#)

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33. Singh, U.K.; Vannice, M.A. Kinetics of liquid-phase hydrogenation reactions over supported metal catalysts—A review. *Appl. Catal. A Gen.* **2001**, *213*, 1–24. [[CrossRef](#)]
 34. Li, G.; Zhao, Z.; Mou, T.; Tan, Q.; Wang, B.; Resasco, D. Experimental and computational kinetics study of the liquid-phase hydrogenation of CC and CO bonds. *J. Catal.* **2021**, *404*, 771–785. [[CrossRef](#)]