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Synthesis of spherical and size-controlled Pt dendrimer-encapsulated nanoparticles for SCR of NO_x

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Highly active and selective alumina-supported Pt dendrimer-encapsulated nanocomposite materials were successfully prepared and evaluated for the selective catalytic reduction (SCR) of NO_x using methane as reductant. The physicochemical properties of the prepared samples were investigated with X-ray diffraction (XRD), Brunauer Emmett Teller (BET) surface area, inductively coupled plasma mass spectrometry (ICP-MS), and transmission electron microscopy-energy-dispersive X-ray analysis (EDX) techniques. The resulted metallic Pt₄₀ particles are spherical and well separated from each other. As derived from the transmission electron microscopy images, the average particle diameter of dendrimer-encapsulated nanoparticles (DENs) is 2.4 nm. The diffraction profiles of fresh and used catalysts indicated that the prepared materials are highly stable after 40 h of time-on-stream reaction. For DENs Pt/Al₂O₃ sample, the distribution of platinum particle size ranged between 2 and 20 nm. In the present investigation, the N₂ selectivity is attained more than 85% at 400 °C. In addition, the time-on-stream results revealed that the DENs Pt/Al₂O₃ catalysts are very effective on the reduction of NO_x under wide temperature window.

Keywords: size-controlled synthesis; Pt dendrimer-encapsulated nanocomposites; PAMAM; Pt/Al₂O₃; DeNO_x

1. Introduction

Recently, research in nanoparticles has become more attractive topic, and the synthesis and characterization of nanoparticles have received considerable attention from both fundamental and applied research. Various preparative methods have been extensively investigated to synthesize the nanoparticles [1]. However, the chemical reduction of metal salts is the most convenient method where metal ions are reduced by reducing agents. In general, the obtained colloids tend to aggregate in solution due to their small size. An effective strategy to avoid agglomeration is dendrimer-encapsulated synthesis. It was proved that dendrimer-encapsulated nanoparticles (DENs) endowed different nanometal particle sizes and distributions compared to conventional preparation [2]. Using the DENs, it is easy to prepare stable and size-controlled reduced metal particles by varying the synthesis parameters [3–10]. Recently, Crooks and coworkers have also demonstrated the activity of dendrimer-stabilized metallic nanoparticles [5,11]. However, the use of these metal nanoparticles is not fully studied. Furthermore, synthesis of supported catalysts using DENs as a precursor seems to be an interesting approach.

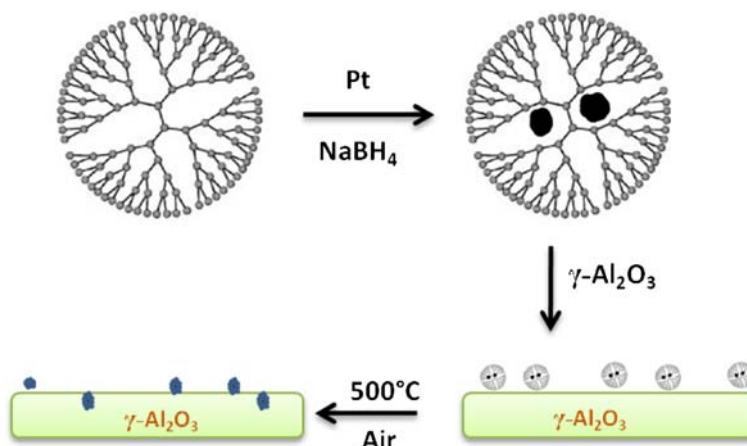
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Pt-based materials which have significant low temperature activity toward the selective catalytic reduction (SCR) of NO_x by hydrocarbons are extensively investigated. In general, these materials are prepared by various conventional methods requiring high amounts of platinum loading. Unfortunately, these catalysts also have limitations in the practical application such as narrow temperature window and tend to form higher amount of N₂O [11,12]. Therefore, the present investigation was undertaken to exploit the beneficial features of the DENs-supported materials. For this poly(amidoamine) (PAMAM) G4OH-encapsulated Pt nanoparticles were synthesized by complexation method followed by reduction with NaBH₄ [6,7,11]. The obtained DENs were deposited on the commercial alumina support. The physicochemical properties of the prepared samples were investigated with X-ray diffraction (XRD), Brunauer Emmett Teller (BET) surface area, inductively coupled plasma mass spectrometry (ICP-MS), and transmission electron microscopy (TEM)-energy-dispersive X-ray analysis (EDX) techniques and evaluated for SCR of NO_x.

2. Experimental

2.1. Catalyst synthesis

Pt DENs were prepared by complexation process as reported by Crooks et al. [5]. Prior to use the hydroxyl-terminated G4OH poly(amidoamine; PAMAM) dendrimer (Aldrich), methanol was evacuated at room temperature under N₂ flow. Aqueous solution of 0.1-mM G4OH dendrimer was prepared by using milli-Q deionized water (18 MΩ cm). In order to synthesize the G4OH-DENs, 4.0 mM of K₂PtCl₄ solutions were mixed with 50 mL of 0.1-mM PAMAM dendrimer. This solution was allowed to ligand exchange reaction for 24 h with stirring in air atmosphere. To evaluate zerovalent Pt₄₀G4OH, an eightfold excess of 0.5 M NaBH₄ (Aldrich) solution was added drop wise at room temperature. This Pt-G4OH solution was allowed to stand in a closed vial for 5 h to insure complete reduction of Pt. Finally, the solutions were dialyzed using a cellulose dialysis sack having a molecular weight cutoff of 12,000 Da to remove impurities. The obtained Pt₄₀G4OH solution was wet impregnated on γ-Al₂O₃ at room temperature. After impregnation, the resulted solid samples are subjected to heat treatment in air atmosphere at 500 °C for 2 h followed by reduction with H₂/He mixture gas at 300 °C for 1 h. Scheme 1 represents the complete synthesis procedure of DENs preparation and dispersion of DENs over alumina. For comparison, 0.5 wt.% platinum loaded on γ-Al₂O₃



Scheme 1. Synthesis procedure of Pt dendrimer-encapsulated nanoparticles.

was prepared by wet-impregnation method, the resulted sample was dried at 120 °C and calcined at 500 °C for 2 h.

2.2. Catalyst characterization

Scanning transmission electron microscopy (STEM) and transmission electron microscopy (TEM) images and the corresponding EDX data were obtained from FEI TECNAI G2 F20 instrument at an operating voltage of 200 kV. The samples were supported on a carbon grid by dropping ethanol suspensions containing the uniformly dispersed powders. The catalysts were analyzed by powder X-ray diffractometer (Bruker-8), and the spectra were recorded using Ni-filtered Cu K α radiation operated at 40 kV and 20 mA. The fine powder was scanned for a 2-h period at $2\theta = 10\text{--}90^\circ$. The BET surface area of the samples was measured from the N₂ adsorption isotherms at -196°C using a Micromeritics (ASAP 2000) analyzer. The elemental analysis was performed on Agilent inductively coupled plasma-optical emission spectroscopy (ICP-OES) 710 series.

2.3. Catalytic activity

The catalytic activity was evaluated in a vapor phase fixed-bed flow-type quartz reactor at normal atmospheric pressure. Prior to the reaction, about 0.3 g of catalyst was pretreated with 10% H₂ in He gas flow at 300 °C for 1 h. All the gases were regulated with mass flow controllers before entering into the reactor. The exhaust contains 500 ppm of NO_x, 500 ppm of CH₄, and balance of He. Total flow rate of the reaction gas mixture is 500 ml min⁻¹ at a space velocity of 60,000 h⁻¹. The NO_x concentrations were analyzed with online Non-Dispersive Infra-Red Fuji NO analyzer. The other reactants and products were analyzed online by using a VARIAN Micro GC equipped with thermal conductivity detector.

3. Results and discussion

3.1. Catalyst characterization

The TEM images of Pt₄₀G4OH, RT-dried, and 500 °C calcined DENs Pt/Al₂O₃ sample are presented in Figure 1(A), (B&C), and (D), respectively. Figure 1(A) presents the small and unique particle size of Pt₄₀G4OH. It is also clearly seen that the most of the platinum particles are spherical in shape and well separated from each other. The quantitative estimation of particle sizes for Pt-DENs indicates a narrow range distribution with an average particle size of 2.4 nm. The narrow distribution of reduced platinum particles is attributed to the use of specific PAMAM dendrimer and the method of preparation adopted. In general, the ability to control dendrimer interior/exterior functionalities and the macromolecular architecture of PAMAM dendrimers (open spaces within the interior) also creates an ideal environment for trapping guest species like Pt. In addition, dendrons have greater steric requirement for their stronger rigidity, and therefore larger localized area may be used for the controlled growth and stabilization of metal nanoparticles. As seen from Figure 1(B&C), the platinum particles distributed over alumina surface with a mean particles size of 3.6 nm. However, for the dispersed and dried Pt₄₀G4OH over Al₂O₃, there is no drastic hike in the particle size, the electronic images once again revealed the narrow particle dispersion over alumina support. In contrast to this, the STEM image of Figure 1(D) showed the different Pt clusters, the grain sizes were ranged between 2 and 20 nm. The chemical composition of the selected position is detected by EDX. Presumably, in the absence of solvent, the dendrimer collapses onto the

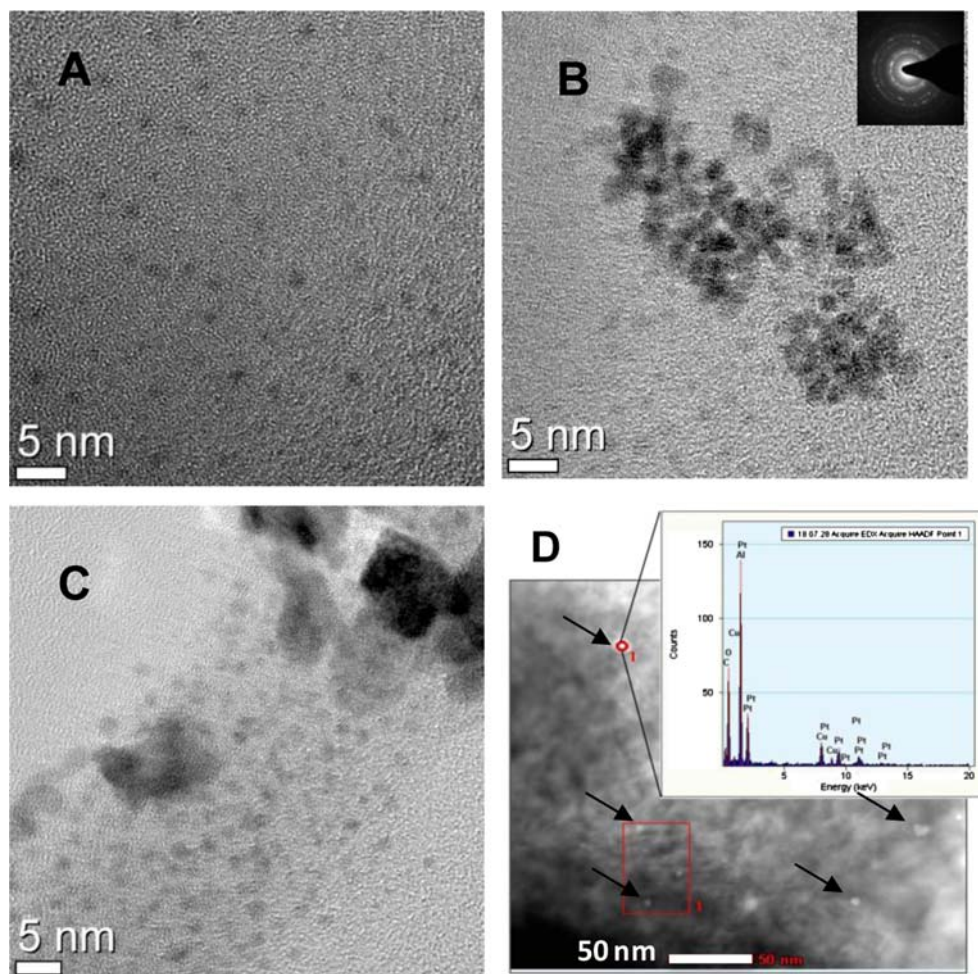


Figure 1. TEM images of (A) Pt₄₀G4OH (after dialysis); (B&C) Pt DENs on alumina (RT dried); and (D) STEM and corresponding EDX data of DENs Pt/Al₂O₃ sample calcined at 500 °C.

nanoparticle, preventing even small substrates from accessing the metal surface [8–10,13]. It is also found from literature that the amide bonds of the PAMAM dendrimers are largely destroyed after aerial oxidation without a solvent. Activation conditions for these supported DENs were chosen on the basis of thermal decomposition, which cause the increase in the particle diameter [14,15]. However, the thermally treated DENs Pt/Al₂O₃ catalyst showed enhanced deNO_x at broad temperatures, details are presented in the activity studies. STEM image of Imp Pt/Al₂O₃ sample calcined at 500 °C is presented in Figure 2. As could be seen from the image, Pt particles were not homogeneously distributed, but nano-sized particles less than 4-nm scale were detected. However, comparing to the Imp sample, DENs have lower mean particle size. After the time-on-stream, the Imp Pt/Al₂O₃ sample showed large platinum clusters due to sintering of platinum over alumina.

The XRD patterns of pure Al₂O₃, fresh and used DENs Pt/Al₂O₃ sample calcined at 500 °C are presented in Figure 3. From Figure 3, the broad reflections at $2\theta = 32^\circ$, 45° , and 67° assigned to γ -alumina and the lines at 39.7° , 46.2° , and 67.4° are due to the characteristic lines of the cubic Pt⁰ (JCPDS 4-802), indicating that the present synthesis method facilitates

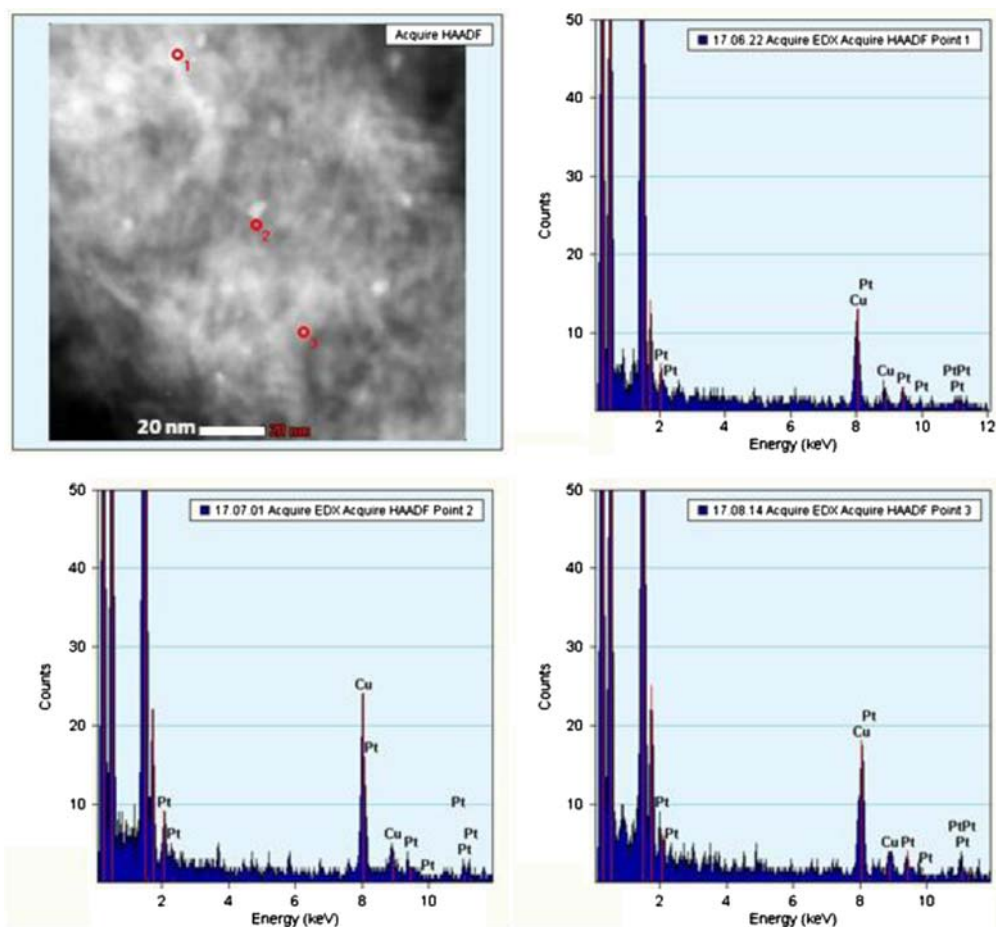


Figure 2. STEM and corresponding EDX data of Imp. Pt/Al₂O₃ sample.

to make the stable reduced metal particles over alumina support. The low intense lines correspond to platinum is attributed to the lower amounts of metal loading. The XRD patterns for used sample (after 40 h of time-on-stream reaction) clearly evidenced the thermal stability of materials under drastic reaction conditions. Few small intense diffraction lines at $2\theta = 34.8^\circ$, 42.5° , and 54.9° were attributed to the presence of Pt²⁺ species (JCPDS 42-866). The metal amounts were measured with ICP-MS. The total content of platinum in DENs Pt/Al₂O₃ sample is ~ 0.5 wt.%. This is well correlated with the theoretical calculations of Pt amount. The BET surface area measurements for DENs Pt/Al₂O₃ calcined at 500 °C showed high-surface area of 230 m²g⁻¹ with total pore volume 0.72 m³g⁻¹.

3.2. Catalytic activity

The deNO_x catalytic activity of DENs Pt/Al₂O₃ catalysts was evaluated using methane as reductant, the relative conversion and selectivity to N₂ results are displayed in Table 1. For better understanding, the number of millimoles of NO converted to N₂ was plotted as function of temperature in Figure 4. As shown in Table 1, an increase in NO_x conversion with the increase in reaction temperature was observed. In parallel to this, the methane conversion

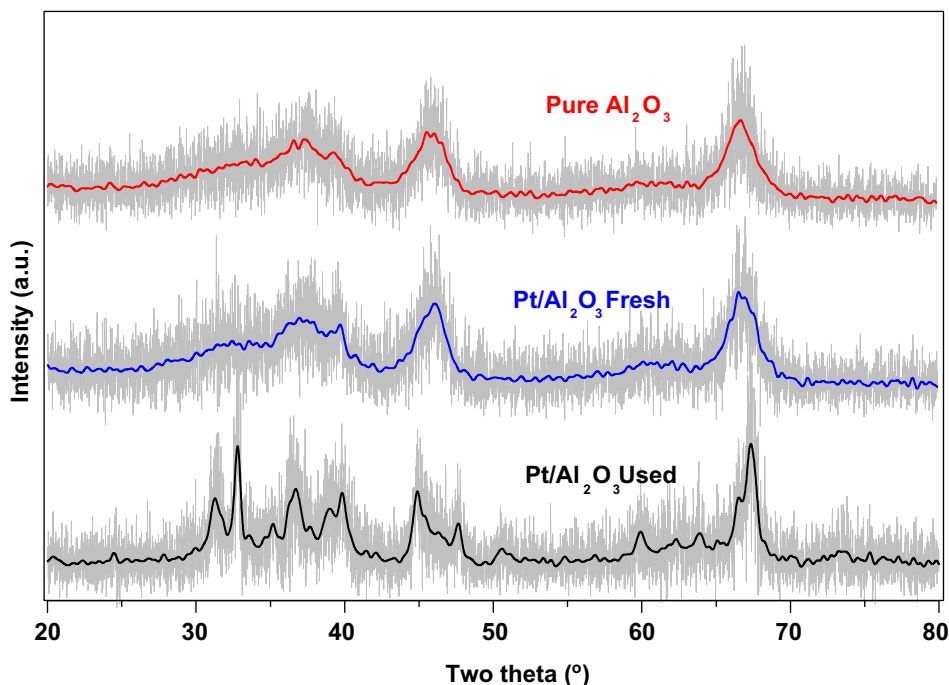


Figure 3. XRD profiles of pure alumina; fresh and used (after 40 h of time-on-stream) DENs Pt/Al₂O₃ sample.

Table 1. NO_x and CH₄ conversions (%), N₂ selectivity (%) of DENs Pt/Al₂O₃ and conventional impregnated 0.5wt.% Pt/Al₂O₃ samples at different temperatures, respectively.

Temp. (°C)	DENs Pt/Al ₂ O ₃			Imp. Pt/Al ₂ O ₃		
	NO _x conv.	N ₂ selec.	CH ₄ conv.	NO _x conv.	N ₂ selec.	CH ₄ conv.
300	0	0	4	0	0	0
350	98	75.5	30	0	0	2
400	100	89	52	95	65	40
450	100	94	53	100	74	60
500	100	95	57	100	77	65

is also increased with temperature. However, the impregnated Pt/Al₂O₃ sample exhibited NO_x conversion from 350 °C. The NO_x conversions for both samples reached more than 80% with an increase in the reaction temperature from 350 to 400 °C. Interestingly, in case of DENs Pt/Al₂O₃ in accordance with NO_x conversion, the selectivity of N₂ (desired product) was also enhanced to about 95%. The different Pt particle size distributions are expected to be the reason for the higher deNO_x conversions [1]. Burch et al. [2] reported the same phenomenon on Pt impregnated on Al₂O₃ and ZrO₂ systems. Furthermore, the present investigated materials have been showed excellent conversion as well as selectivity at low temperature at nominal loading of platinum (about 0.5 wt.%) as compared to the traditional impregnated Pt/Al₂O₃ sample. Based on literature [1–3], it is known that the Pt based catalysts typically exhibit around 50% selectivity to N₂O. However, in the present investigation, the selectivity to N₂

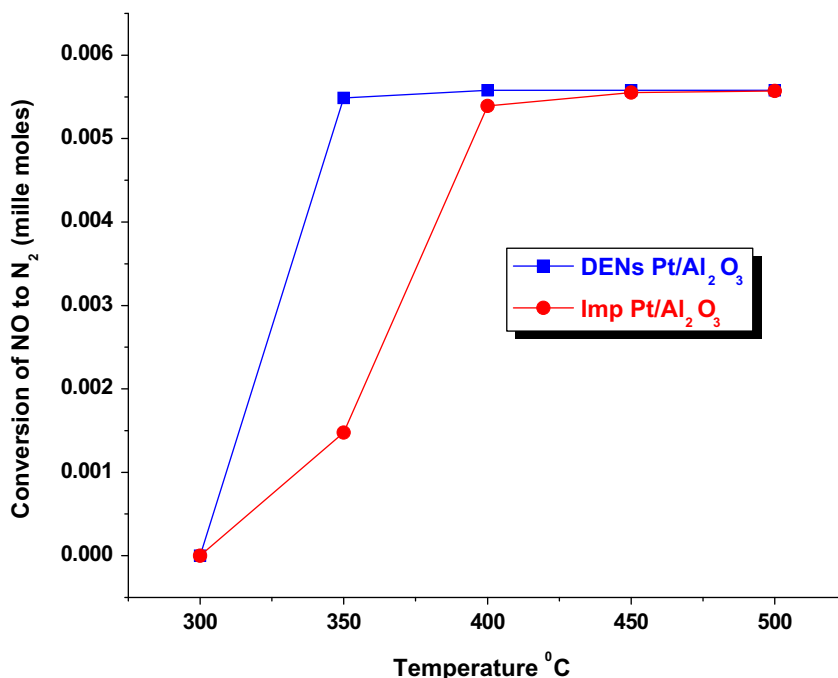


Figure 4. Number of millimoles of NO converted to N₂ as function of temperature on DENs Pt/Al₂O₃ and Imp 0.5 wt.% Pt/Al₂O₃ materials at different temperatures, respectively. (Reaction conditions: catalyst = 0.3 g, CH₄ = 500 ppm, NO = 5.58×10^{-3} millimole, Total flow = 500 ml min⁻¹.)

was more than 85% from 400 °C, whereas the Imp sample showed around 65–77%. The N₂O selectivity for both the DENs and Imp samples found to be less than 6% from 400 °C. Therefore, the activity results of the present work revealed that the Pt DENs-supported catalysts are very effective on the reduction of NO_x under wide temperature window.

A fast catalyst deactivation is often encountered on most of the platinum-supported catalytic systems due to sintering of metal particles as well as coke formation. Thus to study the influence of time and high temperature on the performance of catalysts, a series of time-on-stream measurements were examined from 350 to 1000 °C with continuous three cycles. The corresponding results of NO_x reduction activities of the catalysts as a function of time are depicted in Figure 5. In the inset, a temperature ramp over time used for this study is provided. As can be observed from the figure, the DENs-supported samples showed significant increase in the NO_x conversion and exceptional stability over 40 h of time-on-stream. Whereas the Imp sample exhibited similar activity at higher temperature, but at temperature below 350 °C the material was almost inactive. Further, from second the cycle NO_x conversions were slightly dropped, which indicates the Imp samples are not enough stable at high temperature. Interestingly, the DENs Pt/Al₂O₃ sample exhibited substantial thermal stability and catalytic activity. However, the ongoing studies will be focused on detailed investigation of how Pt species have been stabilized and their involvement in the mechanism. In conclusion, it is clear that the investigated samples are highly selective and stable at low loading of Pt and can also operated at wide temperatures.

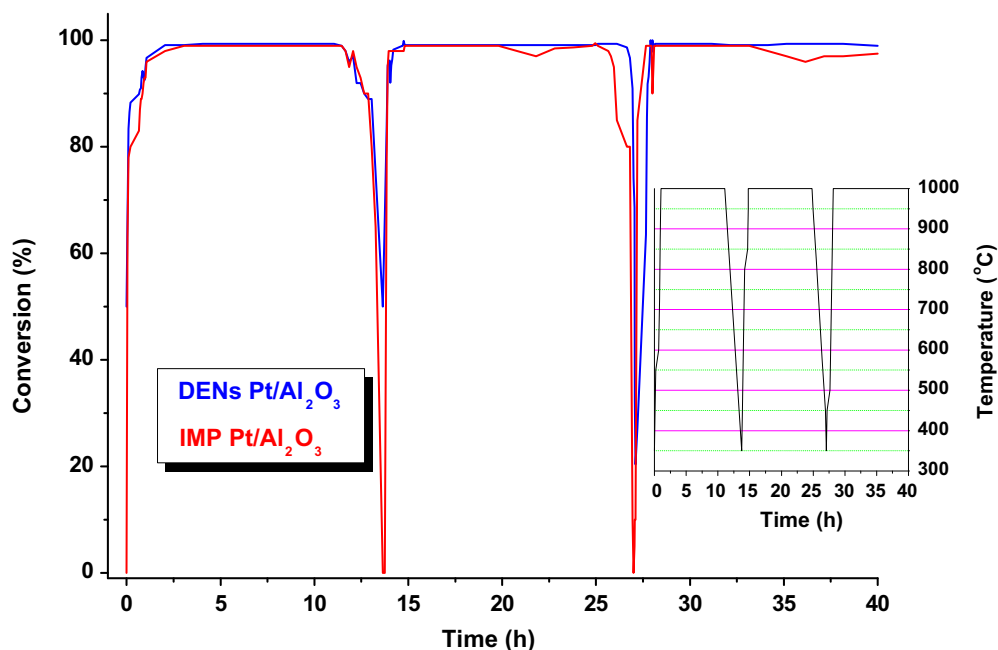


Figure 5. Time-on-stream studies of prepared DENs Pt/Al₂O₃ and Imp. Pt/Al₂O₃ samples (Inset: profile of temperature ramp).

4. Conclusions

Pt DENs were prepared by complexation and co-complexation method. The obtained nanoparticulates were dispersed over Al₂O₃ using wet-impregnation method (Scheme 1) and evaluated for SCR of NO_x. The calcined samples showed high-specific surface area (230 m²/g) and pore volume (0.72 m³/g). The STEM results revealed that the distribution of Pt particles over the alumina was broad and ranges between 2 and 20 nm. XRD and BET surface area results indicated that the prepared materials exhibited high-surface area and thermal resistance for the drastic reaction conditions. However, the synthesized catalysts exhibited higher activity and stability on the 40 h of time-on-stream studies. Their superior durability and light-off characteristics are mainly attributed to the bimodal platinum particle-size distribution as well as the synthesis procedure adopted. The present investigated samples seem to be superior for HC-SCR of NO_x, since at nominal loading of platinum (about 0.5 wt.%) they exhibited excellent conversion as well as selectivity at low temperature.

Acknowledgments

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