CHAPTER V

n-OCTANE AROMATIZATION ON Pt-CONTAINING ZEOLITES

II. EXTRA-LARGE PORE ALUMINOPHOSPHATE VPI-5

Siriporn Jongpatiwut, Thirasak Rirksomboon, and Somchai Osuwan

The Petroleum and Petrochemical College,
Chulalongkorn University, Bangkok, Thailand

and

Daniel E. Resasco*

School of Chemical Engineering and Materials Science,
The University of Oklahoma, Norman, OK 73019

In progress

*To whom correspondence should be addressed: e-mail: resasco@ou.edu

ABSTRACT

Platinum supported on unidimensional, extra-large pore aluminophosphate VPI-5 (Pt/VPI-5) was prepared by vapor phase impregnation method. The catalyst prepared was tested for the aromatization of n-octane at 500°C. The results show that the extra-large pore zeolite catalyst resulted in lower activity and total aromatics selectivity but it exhibited higher selectivity to C8-aromatics than the Pt/KL catalyst. XRD, SEM, TPD, and BET techniques were utilized to analyze the characteristics of the VPI-5 synthesized. After the reaction, nature and amount of coke formation were investigated by temperature programmed oxidation (TPO).

INTRODUCTION

It has been known for two decades that Pt-containing potassium form of L zeolite (Pt/KL) catalyst is highly active and selective for n-hexane aromatization. The important advantage is that Pt/KL, monofunctional catalyst, is free from acid support resulting in less undesired isomerization and cracking products. There have been many hypotheses for the unique property of Pt/KL. Tauster *et al.* [1] offered that over L zeolite, which is one-dimensional straight channel, n-hexane would preferentially adsorb onto the Pt cluster at a terminal carbon, which would favor ring closure to form benzene. Derouane and Vanderveken [2] reported that the space inside the L-zeolite was similar to that of a cyclic, six carbon species. Therefore, the aromatization is favorable inside the L-zeolite channel. Iglesia *et al.*[3] have shown that in the n-hexane aromatization reaction, the platinum that is well-dispersed inside the channels of the L zeolite is protected from bimolecular collision which leads to coke formation. However, we recently investigated the aromatization of n-octane over Pt/KL catalyst [4]. The catalyst deactivated fastly by coke formation. Moreover, the reaction testing resulted in undesired hydrogenolysis of C8-aromatics. We further studied the aromatization of n-octane over other large pore zeolites i.e. BEA, MAZ, and FAU. The results showed that the Pt/KL still exhibits highest activity and selectivity than other zeolite catalysts. VPI-5 zeolite is an alternative catalyst support. It was discovered in 1989 by Mark Davis [5]. VPI-5 is aluminophosphate,

unidimensional extra-large pore zeolite (12.7 A°). Later, the Pt/VPI-5 was prepared and studied for *n*-hexane aromatization by the dependent group [6, 7]. They found that the VPI-5 catalyst resulted in lower aromatization performance than that of Pt/KL catalysts. In this contribution, we have synthesized the VPI-5 zeolite and prepared Pt/VPI-5 for testing the aromatization of *n*-octane. A number of characterization techniques, including XRD, BET, SEM, and TPD were utilized to investigate the characteristics of the VPI-5 support and Pt/VPI-5 catalyst. After the reaction, the coke formation was analyzed by temperature programmed oxidation.

EXPERIMENTAL

__Synthesis of Aluminophosphate VPI-5__: The recipe for synthesis are psedo-boehmite (Catapal B, ca. 65% Al_2O_3, Lot# P10521, Condea Vista Co.), H_3PO_4 (ca. 85 wt. %, Aldrich), tetrabutylammoniumhydroxide (TBA-OH) solution (ca. 55-60% in water, Fluka), and distilled water. The amount of the recipes are based on $1 Al_2O_3$: $2H_3PO_4$: 1 TBA-OH: 50 H_2O molar ratio. The procedure of synthesis was reported elsewhere [5]. Briefly, pseudo-boehmite was dispersed in water and H_3PO_4 added. Then the mixture was stirred until homogeneous and aged for 2 h, without stirring. After that, TBA-OH was added to the mixture and stirred for 2 h. The mixture was then heated in a CEM MSP-1000 microwave oven with a Teflon vessel at 150°C for 20 h. The resultant was filtered, washed with distilled water, and dried at room temperature.

__Analysis of Synthesized VPI-5__: the VPI-5 prepared was tested the XRD pattern using a Rigaku RINT D/MAX 2200H with Cu Kα radiation. The physical morphology of the VPI-5 was inquired using a JEOL JSM-5200 scanning electron microscope. The measurement of surface area was performed by using nitrogen adsorption technique (BET) with a Quantachrome Autosorb-1. Prior to BET measurement, the sample was evacuated at room temperature for 30 min, and then the temperature was ramped to 300°C and held at this temperature for 5 h. XRD of the sample after the measurement, still, showed the majority of VPI-5. Temperature

programmed desorption of ammonia was carried out using a Micromeritics AutoChem 2910.

Catalyst Preparation: Prior to loading metal, the VPI-5 was calcined in air flow (100ml/min.g$_{zeol}$) at 600°C for 20 h. The Pt/VPI-5 was prepared by physically mixing weighed platinum (II) acetylacetonate (Alfa Aesar) and dry support under nitrogen atmosphere. The mixture was then loaded into the reactor tube under a He flow of 2 cm^3/min. The mixture was slowly ramped to 40°C and held there for 3 h, and ramped again to 60°C and held again for 1 h. After that, further ramped to 100°C, at which temperature the mixture was held for 1 h to sublime the Pt(AcAc)$_2$. After sublimation, the mixture was ramped to 130°C and held for 15 min to ensure that the entire precursor was sublimed. The reactor was cooled to room temperature. After that, it was ramped to 350°C in flow of air for 2 h and calcined at that temperature to decompose the Pt precursor. Finally, the Pt/VPI-5 was stored in a desiccator.

Catalytic Activity Measurement: The catalytic activity studies were conducted at atmospheric pressure in a 0.5-inch glass tube with an internal K-type thermocouple for temperature measurement. The reactor was a single-pass, continuous-flow type, with a catalyst bed of 0.20 g. Prior to reaction, the temperature was slowly ramped in flowing H$_2$ at 100 cm^3/min.g for 2 h up to 500°C and in situ reduced at that temperature for 1 h. *n*-Octane was added by injection from a syringe pump. In all experiments, the hydrogen to *n*-octane molar ratios was kept at 6:1. The products were analyzed in a Shimadzu GC-17A equipped with a capillary HP-PLOT/Al$_2$O$_3$ "S" deactivated column, using a temperature program to obtain optimal product separation.

Temperature Programmed Oxidation (TPO): Temperature programmed oxidation was employed to analyze the amount and characteristics of the coke deposits on spent catalysts. TPO of the spent catalysts was performed in a continuous flow of

2% O_2/He while the temperature was linearly increased at a heating rate of 12°C/min. Before conducting the TPO on a 0.03 g sample placed in a ¼" quartz fixed-bed reactor, the spent catalyst was dried at 110°C overnight and weighed. The catalyst was then flushed by 2% O_2 in He for 30 min before the temperature ramp was started. The CO_2 produced by the oxidation of coke species was further converted to methane by 15%Ni/Al_2O_3 catalyst in the presence of hydrogen at 400°C. The methane obtained was analyzed online by a FID detector. The amount of coke was calibrated by using 100 μl pulses of pure CO_2.

RESULTS AND DISCUSSION

Characterization of VPI-5 and Pt/VPI-5: the synthesized VPI-5 was tested by XRD technique. The XRD pattern obtained is shown in Fig. 1. The pattern showed that the zeolite prepared contains majority phase of VPI-5 zeolite. There is only small peak of $AlPO_4$-5 (2θ = 7.48°) observed. SEM images of VPI-5 support are shown in Fig. 2. Morphologies of the VPI-5 were needle-like, needle-like aggregate into bundles, and needle-like aggregate into spherurites as shown in Fig. 2a, b, and c respectively. The sizes and morphologies obtained are parallel to results from a previous study [8]. BET surface area of the VPI-5 is 242 m^2/g. TPD of adsorbed ammonia on VPI-5 compared to KL and SiO_2 is shown in Fig. 3. The result indicates that the VPI-5 exhibited higher acidity than SiO_2 and KL.
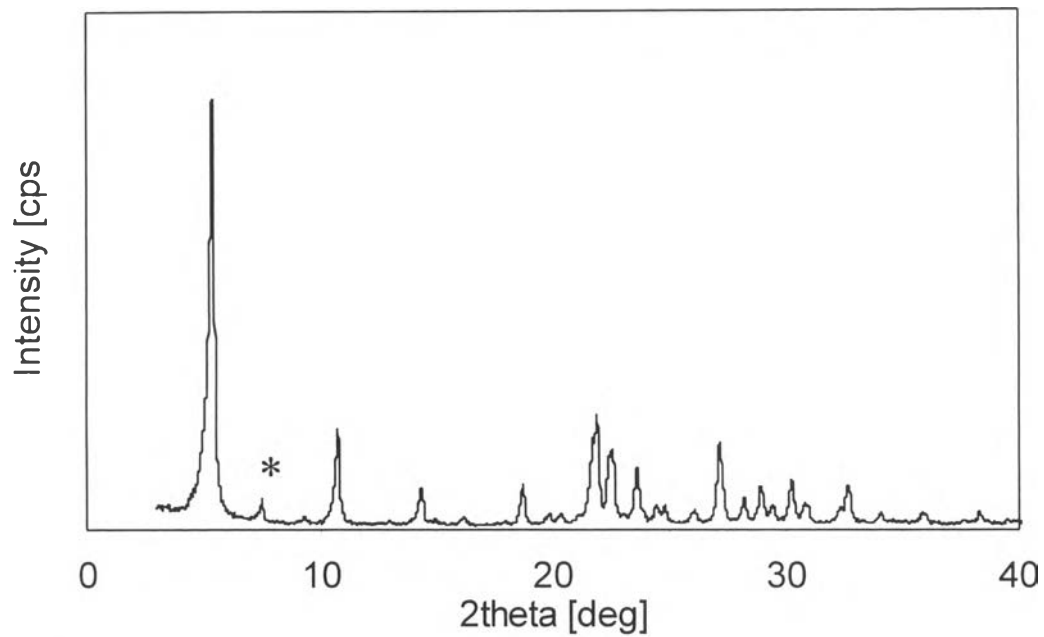
Fig. 1. XRD pattern of synthesized VPI-5. (Asterisk is due to $AlPO_4$-5 pattern.)
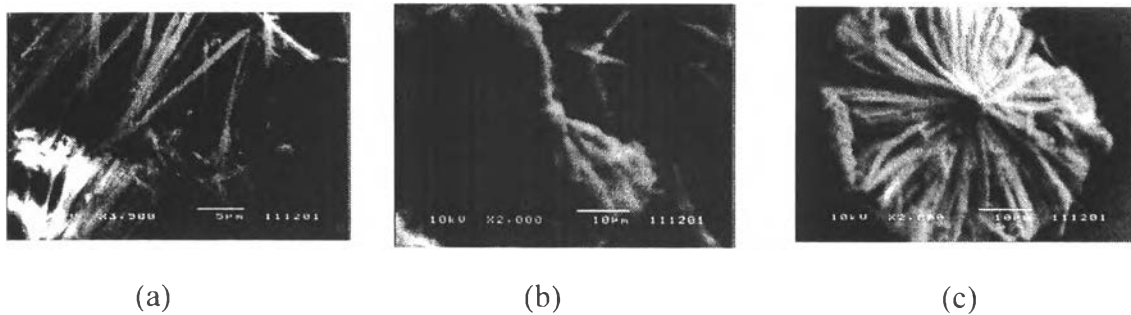

(a) (b) (c)

Fig. 2. SEM images of different morphologies of synthesized VPI-5 (a) needle-like, (b) needle-like aggregate into bundles, and (c) needle-like aggregate into spherurites.
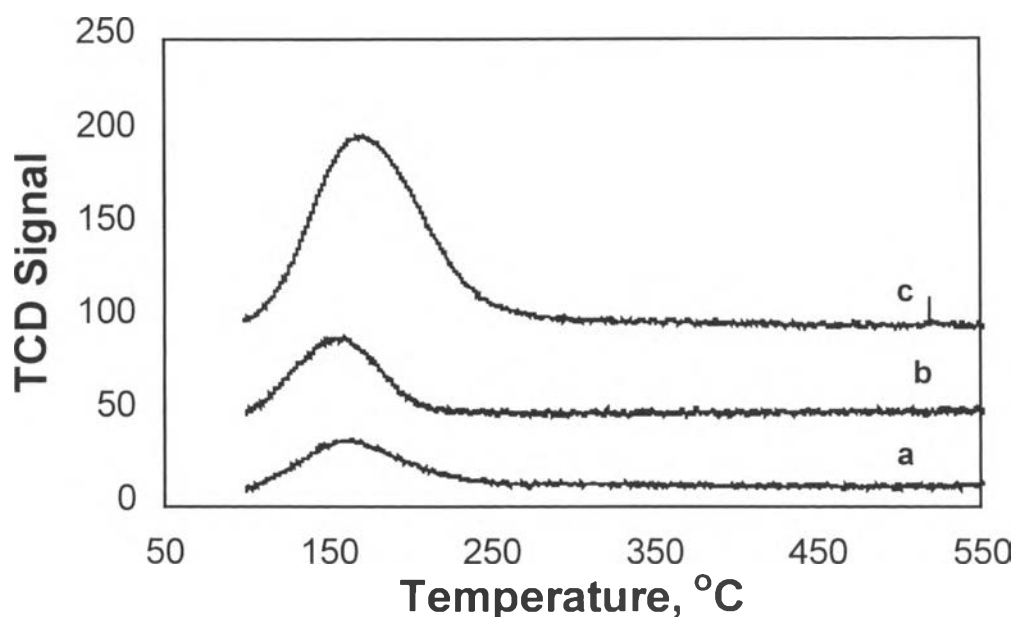
Fig. 3. TPD profiles of ammonia adsorbed on catalyst supports (a) SiO_2, (b) KL, and (c) VPI-5. The supports were exposed to a flow of $10\%NH_3/He$ at 100°C for 30 min and purged by He for 30 min.

After preparation of Pt/VPI-5, the resultant catalyst was re-analyzed by X-ray diffratometer. The XRD patterns of Pt/VPI-5 and bare VPI-5 are illustrated in Fig. 4a and b. It was found that the structure of VPI-5 support was significantly changed to $AlPO_4$-8. $AlPO_4$-8 zeolite is structurally similar to VPI-5 but the pore size of $AlPO_4$-8 (8.7 A°) is smaller than that of VPI-5 (12.7 A°). It was noted in previous studies [8, 9] that VPI-5 zeolite is thermally unstable, as remove water around 100°C, and atmospheric pressure transforms VPI-5 into $AlPO_4$-8. However, in an earlier report [10], the author offered that VPI-5 rapidly heated to at least 550°C can withstand exposure to steam at the elevated temperature with a little loss of structural integrity. In this work, even though we treated the VPI-5 zeolite as mentioned in the earlier report [10], the VPI-5 still exhibited significant change to $AlPO_4$-8. After the Pt/VPI-5 was tested for n-octane aromatization at 500°C for 20 h, the XRD pattern of spent Pt/VPI-5 was collected again. It was found that the structure of the spent Pt/VPI-5 was not much changed from the structure of fresh Pt/VPI-5 catalyst (as illustrated in Fig. 4b and c).
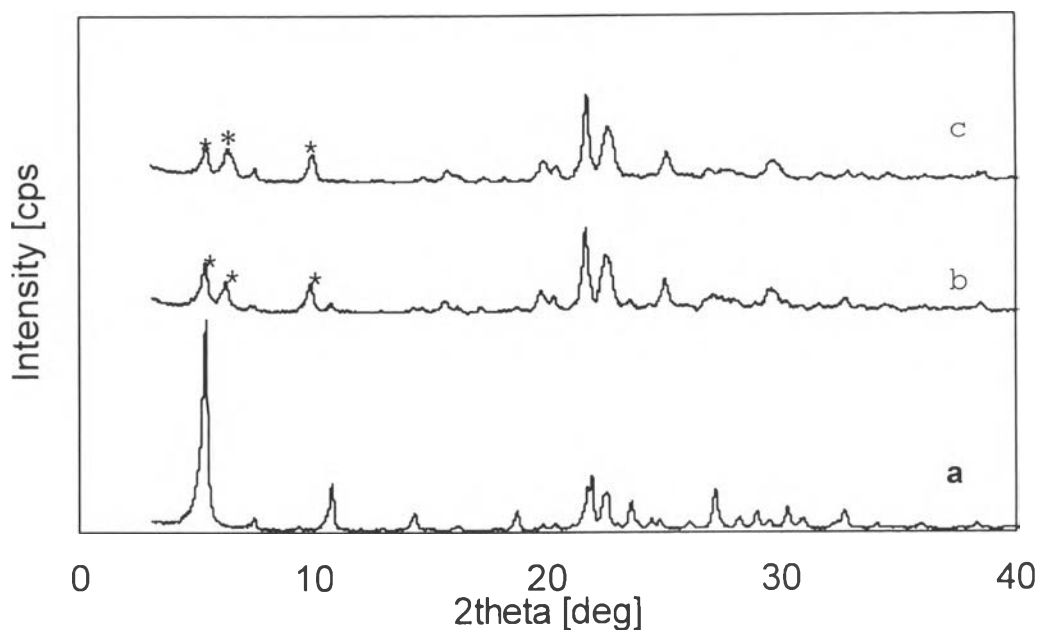
Fig. 4. XRD patterns of (a) synthesized VPI-5, (b) Pt/VPI-5, and (c) spent Pt/VPI-5, after reaction at 500°C for 20 h. (Asterisks are due to AlPO$_4$-8 pattern.)

Catalytic Activity Measurement: The *n*-octane conversion and total aromatics selectivity at 500°C on Pt/VPI-5, compared to Pt/KL and Pt/SiO$_2$ are shown in Fig 5a and b as a function of time on stream. Pt/VPI-5 exhibited slow drop of activity from 38% to 15% within first 8 h while the Pt/KL showed very high activity (70%) at the initial time then rapid drop to 25% in the same period. The Pt/KL also exhibited highest selectivity to aromatic among the catalysts tested. The activity of Pt/VPI-5 is comparable to that of Pt/SiO$_2$ but the total aromatics selectivity of Pt/VPI-5 is clearly higher.
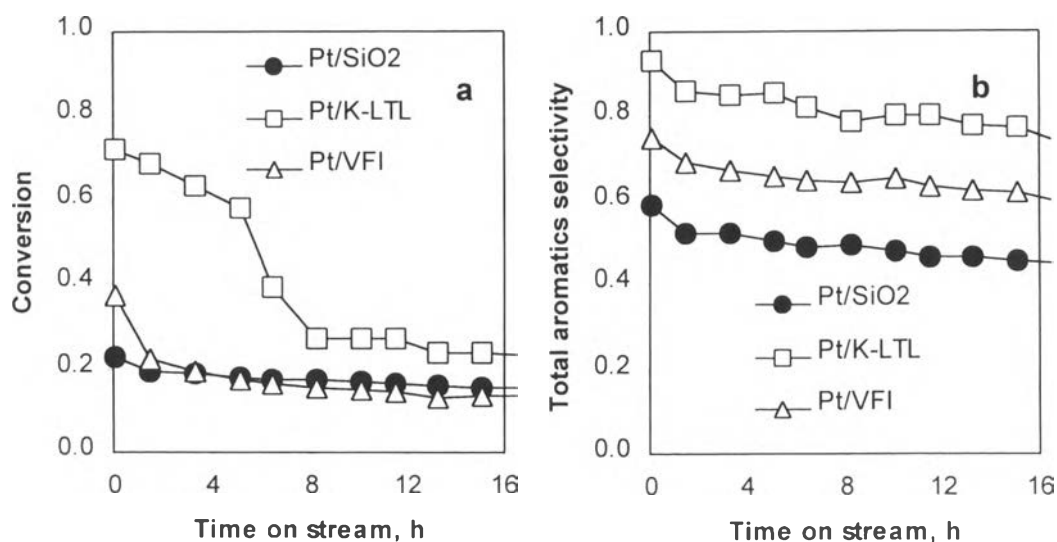
Fig. 5. (a) *n*-Octane conversion and (b) Total aromatics selectivity (mole basis) vs. time on stream over Pt/SiO$_2$, Pt/KL, and Pt/VPI-5 catalysts. Reaction conditions: 500°C, H$_2$/*n*-C6 (or *n*-C8) molar ratio 6:1, WHSV 5 h^{-1}.

The product distributions at 10 h on stream are listed in Table 1. Like Pt/SiO$_2$, Pt/VPI-5 resulted in more C8-aromatics and less hydrogenolysis products than Pt/KL catalyst. This can be explained that the pore of VPI-5 (with partial AlPO$_4$-8) are big enough to avoid the plugging of zeolite channel by coke formation. As ascribed previously [4], the pore plugging enhanced the secondary hydrogenolysis of C8-aromatics formed. Another possibility is that the Pt clusters are not stabilized in the zeolite channel of VPI-5 and they migrate outside the zeolite. Therefore, the reactions took place over platinum outside the channel, similar to that of Pt/SiO$_2$.

TABLE 1

Product distribution of *n*-octane aromatization on Pt/SiO₂, Pt/KL, and Pt/VPI-5 catalysts, after 10 h on stream. Reaction conditions; 500°C, H_2: *n*-C8 ratio 6:1, WHSV 5 h^{-1}

	Pt/SiO₂	Pt/KL	Pt/VPI-5
Conversion	16.8	37.7	15.0
Product selectivity, wt.%			
C1-C5	7.1	29.4	16.0
C6enes	4.3	1.2	4.6
C7enes	34.8	0.6	6.8
C8enes	5.4	1.9	10.6
Benzene	0.0	27.7	0.5
Toluene	0.9	28.2	25.9
EB	21.5	6.5	16.2
m-, p-Xylenes	1.5	1.4	2.7
o-Xylene	23.8	3.0	16.0
Total Aromatics	47.8	66.8	61.3
Total C8-aromatics	46.9	10.9	34.9
Total Olefins	44.5	3.7	22.0

Characterization of Spent Catalysts: After tested for *n*-octane aromatization, the spent Pt/VPI-5, Pt/KL, and Pt/SiO₂ were analyzed by temperature programmed oxidation technique to study the nature and amount of coke formed during the reaction. The TPO profiles are illustrated in Fig. 6. The results show that the profile of coke deposited on Pt/SiO₂ catalyst appeared mainly at 200-300°C whereas the profiles of coke from zeolite catalysts were shifted to higher temperature, ranging from 200-600°C. Pt/KL exhibited more pronounce of peak at 500°C. As mentioned earlier [11, 12], the peak at low temperature (200-300°C) is due to the oxidation of coke which is accelerated by platinum clusters. On the other hand, the profile at high

temperature is possible due to the plugging of zeolite pores, which would retard the platinum-catalyzed oxidation. Pt/VPI-5 exhibited less coke formation than Pt/KL catalyst. It is because on the extra-large pore zeolite, the pore plugging by coke could not be formed.
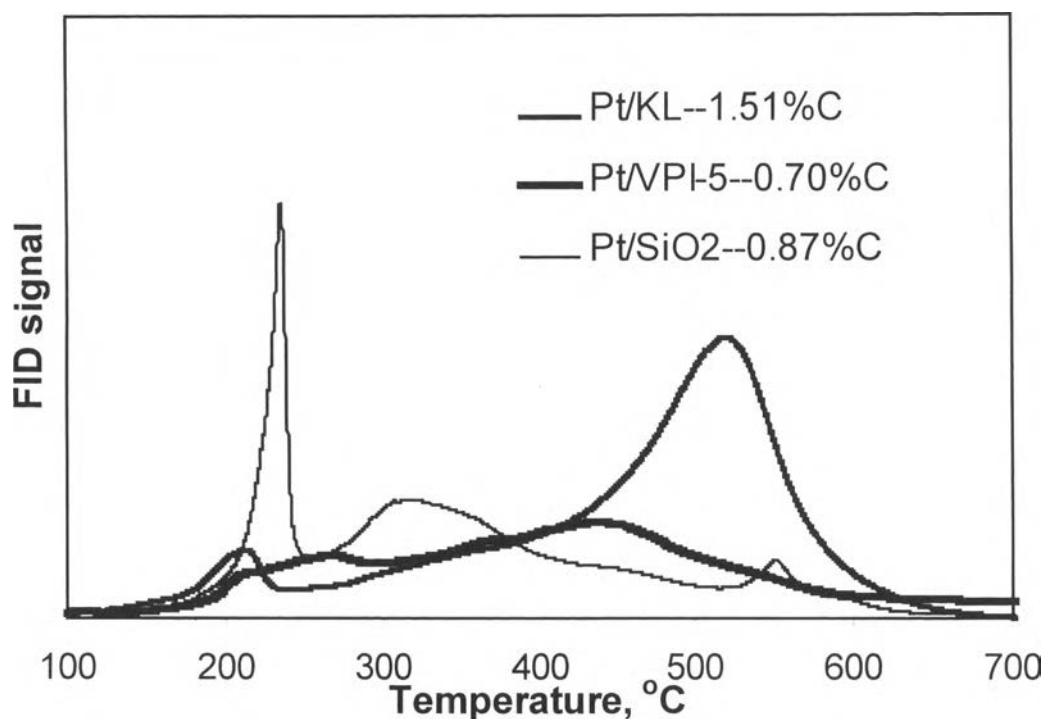

Fig. 6. TPO profiles of coke deposits on (a) Pt/SiO$_2$, (b) Pt/KL, and (c) Pt/VPI-5, after reaction at 500°C for 10 h on stream. The calculated amount of coke is included in each curve.

CONCLUSIONS

After procedure of loading platinum, VPI-5 is mostly transformed to AlPO$_4$-8. The aromatization of n-octane on the catalyst resulted in lower coke formation, higher selectivity to C8-aromatics than Pt/KL catalyst. However, Pt/KL still show higher activity and total aromatics selectivity than the Pt/VPI-5 catalyst.

ACKNOWLEDGEMENTS

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