Coke Formation on the Surface of α-Al₂O₃ in the Catalytic Pyrolysis of Naphtha

Sang Mun Jeong, Young Chang Byun, Jong Hyun Chae and Won-Ho Lee[†]

Chemical Process & Catalysis Research Institute, LG Chemical Ltd./Research Park, 104-1,
Moonji-dong, Yusong-gu, Daejeon 305-380, Korea

Abstract—The catalytic pyrolysis of naphtha has been carried out in a quartz reactor loaded with 5 mm α-Al₂O₃ spheres. The yields of ethylene and propylene exhibit about 10% and 5% higher values compared to the thermal pyrolysis in the absence of α-Al₂O₃ spheres at the same reaction conditions. The coke formation on α-Al₂O₃ spheres increased continuously along with the axial length of the reactor as well as with reaction time. Results suggest that the concentration of the coke precursors in the gas phase may increase along with the axial length of the reactor. Coke filled up completely the internal pore of the sphere near the exit of the reactor after reaction for 4 hr. The coke film on the external surface of the sphere grew continuously thicker. The coke formation was influenced strongly by the physical properties of the α-Al₂O₃ spheres. Coke deposition was the least on the α-Al₂O₃ sphere with the lowest surface area and pore volume among the tested α-Al₂O₃ spheres.

Key words: Catalytic Pyrolysis, Naphtha, Coke, Olefin Yield, Physical Property

INTRODUCTION

Light olefins such as ethylene and propylene are the most important basic chemicals for the petro-chemical industry. A general method to manufacture light olefins from naphtha is the thermal cracking process in the presence of steam. This method has some drawbacks, such as the high temperature required for cracking reactions, and especially low selectivity in ethylene and other desired products [Lemonidou et al., 1989].

Build-up of coke inside of the pyrolysis tube is another problem to handle routinely in the thermal cracking of naphtha. It reduces the heat transfer and causes an increase of pressure drop across the reactor, which is detrimental for the olefin yield [Reyniers and Froment, 1995]. Therefore, there have been many studies on this issue to gain a better understanding of coke formation during the pyrolysis of hydrocarbons [Chan et al., 1998; Kumar and Kunzru, 1985; Ghosh and Kunzru, 1988; Albright et al., 1983].

Catalytic pyrolysis has been found as an alternative method to utilize the feedstock more effectively by producing light olefins at higher yields [Basu and Kunzru, 1992; Golombok et al., 2000]. However, it also has several problems to be resolved. One challenging problem associated with catalytic pyrolysis is also how to control the coke deposition on the catalyst which may cause the loss of catalyst activity and reactor plugging. There have been relatively a few studies to tackle these problems [Lemonidou et al., 1991; Kumar et al., 1997; Xanthopoulou, 1999] with little attention to the characteristics of coke formation on the catalysts.

It has been reported that KVO₃/α-Al₂O₃ with low surface area is a promising catalyst system for coke control in the catalytic pyrolysis of naphtha [Adel'son et al., 1988]. However, there have been only a few studies on coke formation on this catalyst system [Adel'son et al., 1985]. In this study, we have tried to find out the effect

of the physical properties of α-Al₂O₃, reaction time and the catalyst location in the reactor on the coke formation on the 5 mm α-Al₂O₃ spheres which were loaded in a quartz reactor. Also the morphology of coke on the catalyst surface has been investigated with scanning electron microscopy (SEM).

EXPERIMENTAL

1. Properties of Feed Material (Naphtha) and Catalyst (α-Al₂O₃)

The properties of naphtha, the mixture of C4-C10 hydrocarbons, used in this study are shown in Table 1. The average molecular weight of naphtha is found to be 80-85. As catalysts, α-Al₂O₃ spheres of 5 mm were used, which were obtained from Norton (USA). Their physical properties are summarized in Table 2. As can be seen, surface areas of all catalysts are below 1 m²/g except that of the α-Al₂O₃ sphere "J".

2. Experimental Procedure

Both non-catalytic and catalytic pyrolysis runs were conducted

Table 1. Properties of naphtha feed

Density (kg/m³)				660-680
Viscosity (cP)				0.33
Composition (wt%)	n-Paraffin	i-Paraffin	Naphthene	Aromatics
C4	1-3	0.5-0.7		0
C5	16-20	12-16	0	0
C6	11-12	11-13	1-1.5	1.2-2.0
C7	4-6	5-6	5-7	1.2-2.0
C8	1-2	2-3		0.5-2.0
C9	0.5-1.5	1-15	5-8	0.2-1.0
C10	0.2-0.5	0.5-0.7		0.1
Final boiling point (°C)				140-160
Total sulfur (wt. ppm)				200-500

[†]To whom correspondence should be addressed.
E-mail: whlee@lgchem.co.kr

Table 2. Physical properties of fresh α-Al₂O₃ catalysts

Catalyst	Surface area (m^2/g)	Pore diameter (μm)	Pore volume (cc/g)	Silica $wt\%$
A	0.008	130		12
B	0.04	15/150	0.2	11
C	0.05	18	0.21	12
D	0.05	20	0.27	12
E	0.25	3	0.26	0.3
F	0.29	4	0.3	6
G	0.3	50	0.43	12
H	0.75	1.2	0.28	0.05
I	0.82	1/10/250	0.54	0.1
J	7.6	11	0.69	6

in a tubular quartz reactor. A schematic diagram of the experimental apparatus is shown in Fig. 1. Naphtha and water were introduced by HPLC pump (L-7110, Hitachi, Japan) into the vaporizer. The flow rates of naphtha and water were 1.5 g/min and 0.75 g/min, respectively, to ensure a weight ratio of steam to naphtha of 0.5. In the vaporizer, which was operated at 300°C, naphtha and water were separately vaporized and then mixed at the outlet of the vaporizer. Thereafter, the mixed stream passed through a pre-heater which was maintained at 600°C and then entered into a tubular quartz reactor (ID 10.5 mm), where the height of catalyst bed was 180 mm. The furnace temperature was maintained at 880°C and was controlled by thermocouples which were connected to the on/off controllers.

The reactor effluent passed through two condensers connected in series to collect liquid products and water in a reservoir. The mixture of condensed liquid products and water were separated later and their weights were measured. The gaseous products were analyzed by an on-line gas chromatograph (HP6890, USA) equipped with TCD and FID detectors and then vented. A Chromosorb 102 column was used to determine the composition of gaseous products.

At the completion of the run, the reactor was flushed with nitrogen, and then the coked catalysts were taken out. The amount of
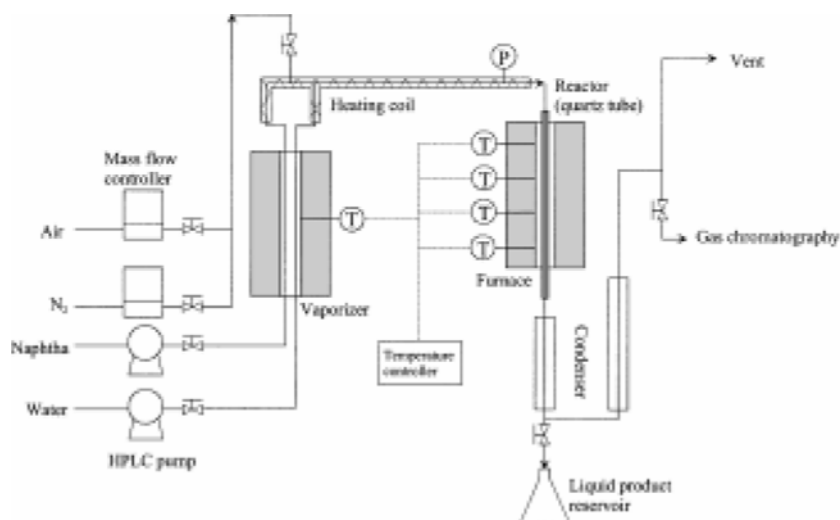
coke on catalyst was quantified by the method of the elemental analysis. A scanning electron microscope (JSM6340F, JEOL, Japan) was employed to observe the surface morphology of the coked catalyst.

RESULTS AND DISCUSSION

1. Olefin Yields in the Pyrolysis of Naphtha in the Presence of Catalyst (α-Al₂O₃)

Both non-catalytic and catalytic pyrolysis of naphtha were carried out at a temperature range of 800-880°C. During reaction, ethylene and propylene were the major gaseous products together with significant amounts of methane, butenes, and butadienes. Fig. 2 shows the temperature (furnace temperature) effect on the yields of ethylene and propylene. As can be seen, the ethylene yield increases with temperature for both non-catalytic and catalytic pyrolysis. However, the propylene yield in catalytic pyrolysis passes through the maximum with increasing temperature due to the secondary pyrolysis and polymerization reactions above the optimum temperature, whereas that in non-catalytic pyrolysis increases continuously with increasing temperature. The maximum propylene yield is expected to be observed at the higher temperature in non-catalytic pyrolysis [Basu and Kunzru, 1992]. It is noticeable that at the same temperature, the yields of ethylene and propylene in catalytic pyrolysis exhibit about 10% and 5% higher values compared to those in thermal pyrolysis, respectively. Enhancement in olefin yields in the presence of catalyst was attributed to the promotion of the initiation step of the free radical reaction, which is known to be the slowest step [Basu and Kunzru, 1992]. Another possibility is due to the enhancement of heat transfer through packing material. In this study, α-Al₂O₃ spheres from the reactor wall. Since the pyrolysis reaction is endothermic, the increase in heat transfer from the wall will result in an enhanced reaction. For the present system, the latter view seems to explain better the result that the olefin yield does not decrease significantly, even after coke covers almost all the surface of α-Al₂O₃ spheres.

2. Coke Formation on α-Al₂O₃ Spheres During the Pyrolysis of Naphtha

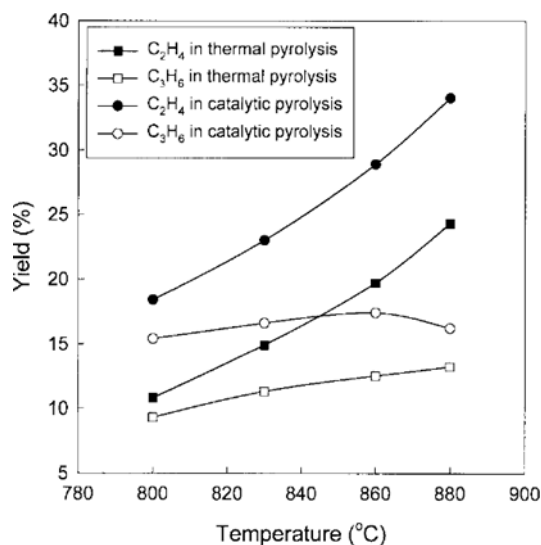**Fig. 1. Schematic diagram of the experimental apparatus.**

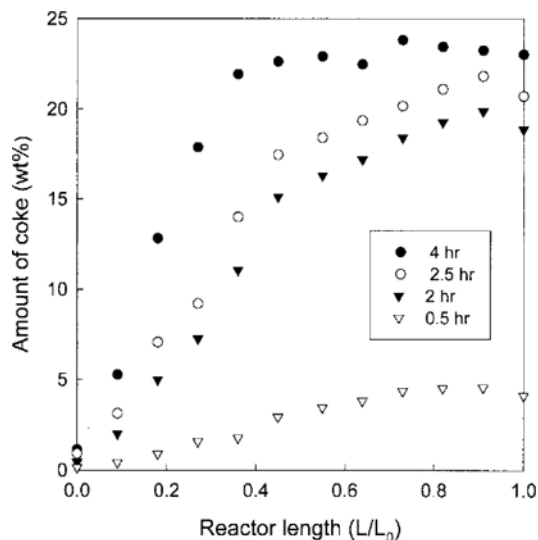Fig. 2. Effect of temperature on ethylene and propylene yields in the thermal and catalytic (E) naphtha pyrolysis.

Fig. 4. The amount of coke deposited on catalyst (E) as a function of reaction time.

Fig. 3. The amount of coke deposited on catalyst (E) as a function of reactor length with a variation of reaction time.

higher value of L/L_0. These results suggest that the concentration of the precursor for coke in the gas phase may increase along with the axial length of the reactor. Our finding well accords with the results of Zou et al. [1993] who report that the coke precursors in pyrolysis of hydrocarbon are aromatics and ethylene whose concentrations increase with increasing residence time. Coke formation is caused by a complex process involving both chemical reactions and thermodynamic behavior, such as the cracking of side chain from aromatic groups, condensation of aromatics and dimerization or oligomerization, etc. [Speight, 1998]. Changes in the slope for L/L_0=0.55 and 0.82 in Fig. 4 are probably due to the decrease in the inner surface area and pore volume of α-Al_2O_3 sphere as the pore plugging by coke progresses [Lee and Ha, 1998]. On the other hand, the coke formation on α-Al_2O_3 sphere at L/L_0=0.18 occurs still inside of the sphere predominantly after the 4 hr reaction.

3. Effect of Physical Properties on the Amount of Deposited Coke

The amount of coke deposited on α-Al_2O_3 spheres during the pyrolysis of naphtha was measured quantitatively after the pyrolysis of naphtha for 4 hr. The reactor was fully loaded with α-Al_2O_3 spheres of 5 mm in a row. Fig. 3 shows the profiles of coke deposition on α-Al_2O_3 sphere "E" (see Table 2) at various locations in the reactor for the different reaction time. There seem to be two regions in the reactor. Up to the middle of the reactor, coke deposition increases with the axial length of the reactor at a higher rate, after which the rate of increase is lower for the second region. The amount of coke increases with reaction time regardless of the location of the reactor. Kumar et al. [1997] also observed the increase in coke formation with increasing reaction time for the system of calcium aluminate catalyst for pyrolysis of n-heptane. The amount of coke deposited at L/L_0=0.18, 0.55, and 0.82 was plotted as a function of reaction time in Fig. 4. It is evident that the slope is steeper at a
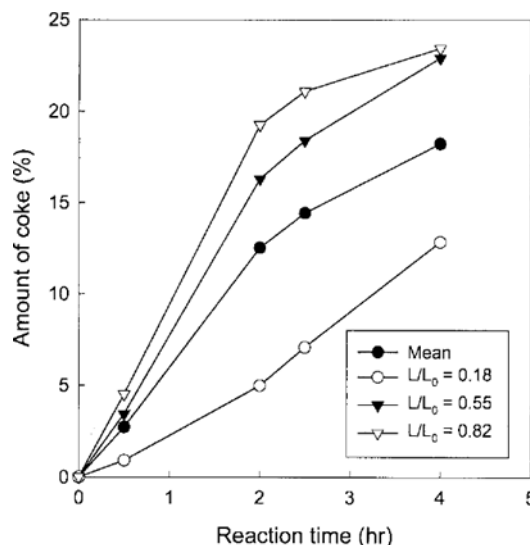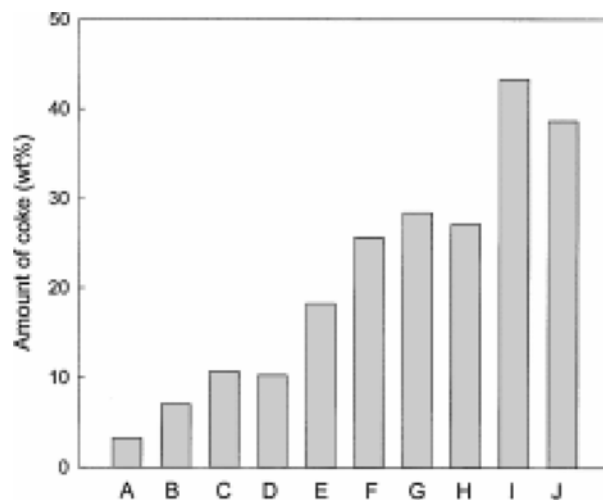

Fig. 5. The amount of coke deposited on various catalysts after naphtha pyrolysis for 4 hr.

Various efforts have been reported to suppress the coke deposition during the catalytic pyrolysis of hydrocarbons [Kumar et al., 1997; Mukhopadhyay and Kunzru, 1993; Golombok et al., 2000]. One effective method was to add the alkali metals such as K and Na on the catalyst, which catalyze the gasification reaction of coke deposited on the catalyst during pyrolysis [Mongkhonsi et al., 1998; Sri-hiranpullop et al., 2000]. On the other hand, not easily available in the open literatures were data on the effect of physical properties of the catalyst such as surface area and pore volume on coke forma-

tion during the catalytic pyrolysis of naphtha. In this study, spheres of α-Al_2O_3 having various physical properties as listed in Table 2 were tested in order to find the best support for suppressing coke formation.

After pyrolysis reaction for 4 hr, α-Al_2O_3 spheres charged into the quartz reactor were taken out and the amount of coke deposited was measured (Fig. 5). As can be seen in Fig. 5, the amount of coke ranges from 3 to 45 wt%, depending on the sample. The coke deposition was the least on catalysts A and B. The amount of coke
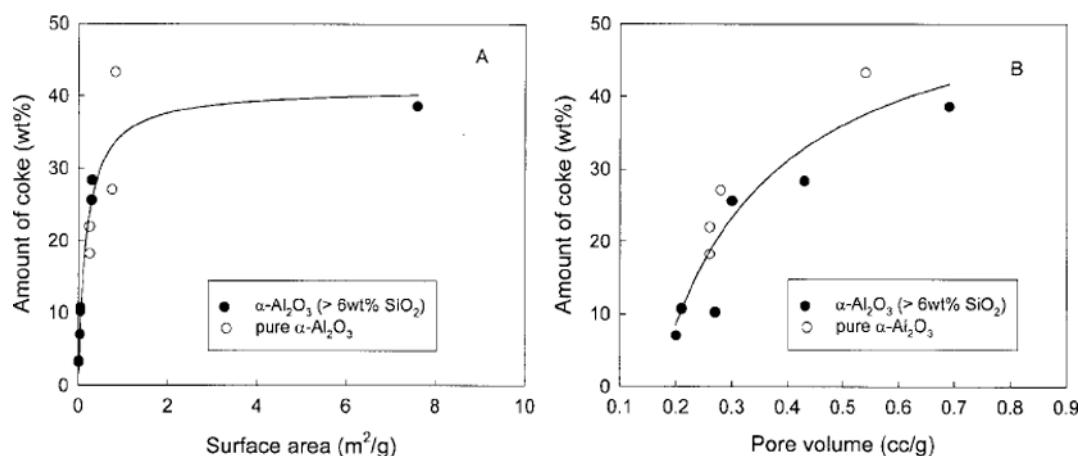

Fig. 6. The effect of (A) surface area and (B) pore volume on the amount of coke deposited on catalyst after naphtha pyrolysis for 4 hr.
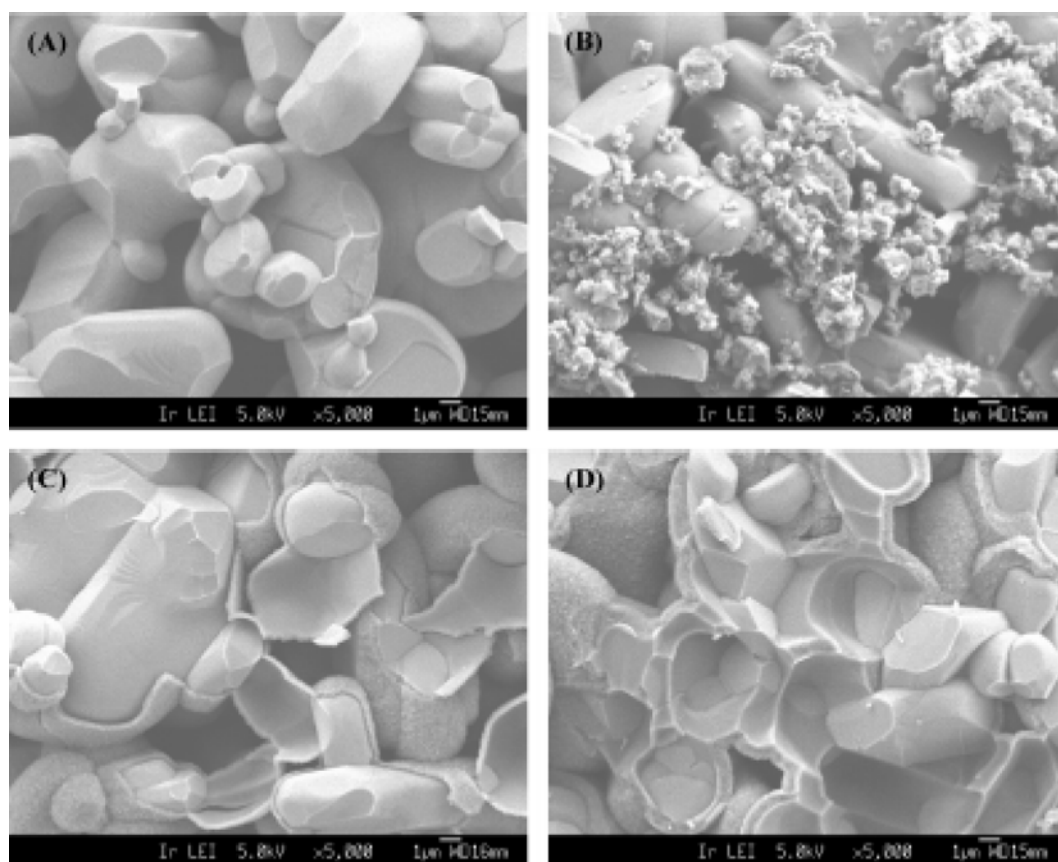

Fig. 7. SEM photographs of the catalyst at different bed locations after naphtha pyrolysis for 4 hr; (A) fresh catalyst, (B) inlet, (C) middle and (D) outlet points.

deposition increased in the order A<B<C≈D<E<F≈H<G<J<I. Fig. 6 shows the relationships between the amount of coke deposition and the surface area (A) and pore volume (B). The amount of coke on α-Al₂O₃ spheres increases sharply with increasing surface area up to 1 m²/g and then remains constant with further increase in the surface area of α-Al₂O₃ spheres (Fig. 6A). It is evident that a correlation also exists between the amount of coke and pore volume of α-Al₂O₃ spheres (Fig. 6B). If the precursor of coke forms in the gas-phase from the pyrolysis of hydrocarbons and adsorbs on the internal surface of α-Al₂O₃ spheres as well as the external surface, the results are rather expected. That is, coke forms more on α-Al₂O₃ spheres with the lager pore volume and surface area. Therefore, α-Al₂O₃ spheres having low surface area and pore volume are preferred for the support. It appears that there is no significant effect of silica (SiO₂) in α-Al₂O₃ on the coke deposition during naphtha pyrolysis (Fig. 6).

4. Scanning Electron Microscopy (SEM) Photograph of Coke

A scanning electron microscope (SEM) was employed to observe the surface morphology of the coked α-Al₂O₃ sphere "E," whose mean pore diameter is about 3 μm (see Table 2). Fig. 7 shows SEM photographs for α-Al₂O₃ spheres taken out at various locations of the reactor after reaction for 4 hr. In order to observe the inside of spheres, they were cut into the half. Fig. 7(A) is the SEM photograph for the inside of a fresh α-Al₂O₃ sphere. Fig. 7(B) is the SEM photograph for the α-Al₂O₃ spheres near to the inlet of the reactor. It shows that coarse coke particles less than 1 μm formed on the surface of α-Al₂O₃ particles. In case of the α-Al₂O₃ sphere in the middle of the reactor, it is evident that the α-Al₂O₃ particles inside the sphere were covered with the coke films (C). Some coke films were destroyed due to the impact given when the sphere was cut into the half. The thickness of film is about 0.2 μm. The internal pores still remain. The coke deposition may result from the adsorption of complexes of the reaction products, which are considered to be intermediates in the coke formation [Guéret et al., 1995], onto the surface of α-Al₂O₃ particles. In case of α-Al₂O₃ sphere near the exit of the reactor, thick coke films of the thickness of about 0.7-1 μm covered the α-Al₂O₃ particles (D). Because of the impact on cutting the α-Al₂O₃ sphere into the half, some α-Al₂O₃ particles escaped and only broken coke films were left like empty nut shells in half. It is

evident from the photograph that pores are filled up completely with the grown coke films. This result agrees well with that in Fig. 3. That is, the formation of coke occurs more severely along with the axial length of the reactor, which is attributed to increasing concentration of heavy products and coke precursors toward the exit of the reactor.

Fig. 8 shows the thick film of coke formed on the external surface of α-Al₂O₃ sphere near the exit of the reactor after naphtha pyrolysis of 4 hr. The thickness of coke film exhibits about 5 μm, which is a much higher value compared with a film in the internal pore (about 0.7-1 μm) of α-Al₂O₃ sphere [Fig. 7(D)]. That is, the coke film on the outer surface of α-Al₂O₃ sphere grows up continuously even after internal pores are plugged by the deposited coke. This result suggests that coke deposition comes from condensation of the gas phase products [Guéret et al., 1995].

CONCLUSIONS

The catalytic pyrolysis of naphtha has been carried out in a quartz reactor loaded with 5 mm α-Al₂O₃ spheres. The yields of ethylene and propylene exhibit about 10% and 5% higher values compared to the thermal pyrolysis in the absence of α-Al₂O₃ spheres at the same reaction operation conditions. The coke formation on α-Al₂O₃ spheres increased continuously along with the axial length of the reactor as well as with reaction time. Results suggest that the concentration of the coke precursors in the gas phase may increase along with the axial length of the reactor. Coke filled up completely the internal pore of the sphere near the exit of the reactor after reaction for 4 hr. The coke film on the external surface of the sphere grew continuously thicker. The coke formation was influenced strongly by the physical properties of the α-Al₂O₃ spheres. Coke deposition was the least on the α-Al₂O₃ sphere "A" of this study, which has the lowest surface area and pore volume among the tested α-Al₂O₃ spheres.

ACKNOWLEDGEMENT

REFERENCES

Adel'son, S. V., Zhagfarov, F. G., Rudyk, E. M. and Smirnova, G. Y., "Effect of Vanadium Catalyst Phase Composition on its Poisoning and Activity during the Pyrolysis of Naphtha," Zh. Fiz. Khim., 62, 2216 (1988).

Adel'son, S. V., Rudyk, E. M., Smirnova, G. Y. and Zhagfarov, F. G., "Study of the Kinetics of Coking of a Vanadium Pyrolysis Catalyst," Neftepererab. Neftekhim., 4, 21 (1985).

Albright, L. F., Crynes, B. L. and Corcoran. W. H., "Pyrolysis-Theory and Industrial practice," Academic Press, London (1983).

Basu, B. and Kunzru, D., "Catalytic Pyrolysis of Naphtha," Ind. Eng. Chem. Res., 31, 146 (1992).

Chan, K. Y. G., Inal, F. and Senkan, S., "Suppression of Coke Formation in the Steam Cracking of Alkanes: Ethane and Propane," Ind.
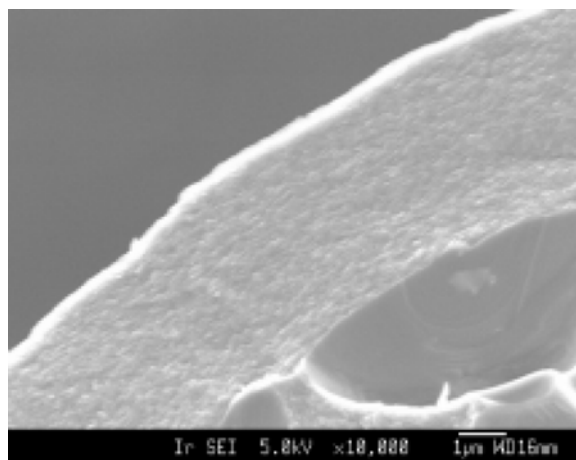

Fig. 8. SEM photograph for the external surface of coked catalyst.

Eng. Chem. Res., **37**, 901 (1998).

Ghosh, K. K. and Kunzru, D., "Reduction of Coke Formation during Naphtha Pyrolysis Using Triethyl Phosphite," *Ind. Eng. Chem. Res.*, **27**, 559 (1988).

Golombok, M., Kornegoor, M., van den Brink, P., Dierickx, J. and Grotenbreg, R., "Surface-Enhanced Light Olefin Yields during Steam Cracking," *Ind. Eng. Chem. Res.*, **39**, 285 (2000).

Guéret, C., Billaud, F., Fixari, B. and Le Perchec, P., "Thermal Coupling of Methane, Experimental Investigations on Coke Deposits," *Carbon*, **33**, 159 (1995).

Kumar, P. and Kunzru, D., "Kinetics of Coke Deposition in Naphtha Pyrolysis," *Can. J. Chem. Eng.*, **63**, 598 (1985).

Kumar, V. A., Pant, K. K. and Kunzru, D., "Potassium-Containing Calcium Aluminate Catalysts for Pyrolysis of n-Heptane," *Applied Catalysis A: General*, **162**, 193 (1997).

Lee, K.-H. and Ha, B.-H., "Catalytic Cracking of Vacuum Gas Oil on Alumina/Zeolites Mixtures-Effects of Precipitation pH of Alumina and Zeolite Type on Product Distribution," *Korean J. Chem. Eng.*, **15**, 533 (1998).

Lemonidou, A. A. and Vasalos, I. A., Hirschberg, E. J. and Bertolacini, R. J., "Catalyst Evaluation and Kinetic Study for Ethylene Production," Ind. *Eng. Chem. Res.*, **28**, 524 (1989).

Lemonidou, A. A., Koulouris, A. P., Varvarezos, D. K. and Vasalos, I. A., "Mechanistic Model for the Catalytic Cracking of n-Hexane over

Calcium Aluminate Catalysts for Producing Light Alkenes," *Applied Catalysis*, **69**, 105 (1991).

Mongkhonsi, T., Prasertdham, P., Saengpoo, A., Pinitniyom, N. and Jaikaew, B., "Roles of Pt and Alumina during the Combustion of Coke Deposits on Propane Dehydrogenation Catalysts," *Korean J. Chem. Eng.*, **15**, 486 (1998).

Mukhopadhyay, R. and Kunzru, D., "Catalytic Pyrolysis of Naphtha on Calcium Aluminate Catalysts. Effect of Potassium Carbonate Impregnation," *Ind. Eng. Chem. Res.*, **32**, 1914 (1993).

Reyniers, M.-F., S. G. and Froment, G. F., "Influence of Metal Surface and Sulfur Addition on Coke Deposition in the Thermal Cracking of Hydrocarbons," *Ind. Eng. Chem. Res.*, **34**, 773 (1995).

Speight, J. G., "The Chemistry and Physics of Coking," *Korean J. Chem. Eng.*, **15**, 1 (1998).

Srihiranpullop, S., Prasertdam, P. and Mongkhonsi, T., "Deactivation of the Metal and Acidic Functions for Pt, Pt-Sn and Pt-Sn-K Using Physically Mixed Catalysts," *Korean J. Chem. Eng.*, **17**, 548 (2000).

Xanthopoulou, G., "Oxide Catalysts for Pyrolysis of Diesel Fuel Made by Self-Propagating High-Temperature Synthesis. Part I: Cobalt-Modified Mg-Al Spinel Catalysts," *Applied Catalysis A: General*, **182**, 285 (1999).

Zou, R., Lou, Q., Mo, S. and Feng, S., "Study on a Kinetic Model of Atmospheric Gas Oil Pyrolysis and Coke Deposition," *Ind. Eng. Chem. Res.*, **32**, 843 (1993).