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Catalytic pyrolysis of naphtha on the KVO_3-based catalyst

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Abstract

The catalytic pyrolysis of naphtha has been performed in a quartz reactor to produce the light olefins at high yields. The catalytic pyrolysis leads to 10 and 5% higher values in the yields of ethylene and propylene, respectively, compared to the thermal pyrolysis at the same operation condition. The enhancement of olefin yield in the presence of catalyst comes from the better heat transfer through the catalyst particles. KVO_3 plays role of a catalyst to accelerate the gasification of coke deposited on the catalyst surface and its optimum range is found to be more than 10 wt.%. An addition of B_2O_3 into KVO_3-based catalyst causes a strong interaction between metal oxide (KVO_3) and α-Al_2O_3 support, which decreases the loss by an evaporation of active phase.

Keywords: Catalytic pyrolysis; Naphtha; Olefin yield; Coke; Heat transfer; KVO_3

1. Introduction

The basic materials of the chemical industry such as ethylene and propylene are being produced in the cracking process. For the production of these kinds of materials, some hydrocarbons such as the naphtha, ethane, propane, *n*-butane and gas oil have been utilized as a feed material. Among these, naphtha produced by refining the crude oil has been world-widely used for the cracking process. The products from the naphtha cracking are moved to the downstream of chemical industry to make resins and synthetic chemical materials.

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 yield in ethylene and other desired products [1]. Since 1980s, the ethylene yield in the thermal cracking process remains constant without a further increase due to the technical limit.

Catalytic pyrolysis of naphtha has been found as an effective way to utilize the feedstock by producing light olefins at higher yields [2,3]. However, it has also several problems to be resolved. The most critical problem is the coke deposition on the catalyst particles which result in not only the activity loss of catalysts but also the reactor plugging.

There have been various efforts to suppress the coke deposition onto catalyst surface [2,4,5]. One effective method is to add alkali compounds on the catalyst, which is well known as a catalyst for the gasification of carbon [6]. Mukhopadhyay and Kunzru [4] reported that the loading of K_2CO_3 on $12CaO–7Al_2O_3$ reduced the coke deposited on the catalyst due to the gasification of coke and a significant amount of potassium loss from the catalyst occurred during the pyrolysis reaction. Also, it was reported that the physical properties

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of catalysts such as surface area and pore volume have an important effect on the coke formation [2].

KVO_3-based catalysts have been investigated with the goal of enhancing the olefin production and reducing the coke formation [6–10]. Several researchers reported that $KVO_3/\alpha\text{-}Al_2O_3$ with low surface area is effective for the coke control in the catalytic pyrolysis of naphtha [5]. However, very limited published data are available on the catalytic pyrolysis of naphtha using this catalyst system. Also, the role of each component in $KVO_3/\alpha\text{-}Al_2O_3$ with B_2O_3 as an additive is still unclear.

In the present study, using the $KVO_3/B_2O_3/\alpha\text{-}Al_2O_3$ catalyst system, we have studied the characteristics of catalytic pyrolysis of naphtha. Also, we have investigated the roles of KVO_3 as a catalyst and B_2O_3 as an additive in the catalytic pyrolysis.

2. Experimental

2.1. Catalyst preparation

The catalyst was prepared by impregnating a KVO_3 precursor solution into a low-surface ($<1\,m^2/g$) $\alpha\text{-}Al_2O_3$ support with 5 mm diameter that was obtained from Saint-Gobain NorPro (USA). A precursor solution for the impregnation was prepared as follows: vanadium oxide was completely dissolved in a KOH solution at 70 °C and then boric acid was added to this solution. After impregnation, the alumina support was dried at 120 °C for 24 h and then calcined at 750 °C under air atmosphere for 3 h. The uniformity of KVO_3 distribution in the calcined catalysts was verified by using SEM. The concentration of KVO_3 and B_2O_3 based on the dry $\alpha\text{-}Al_2O_3$ support was 10 and 1 wt.%, respectively.

2.2. Characterization of catalysts

Temperature programmed reduction (TPR) test was performed in a quartz reactor. Catalyst samples (200 ± 10 mg) were reduced in a quartz reactor with 5 vol.% H_2/Ar mixture (50 cc/min). All the catalysts were pretreated at 400 °C for 1 h in He atmosphere of 20 cc/min to desorb gas component adsrobed on the catalyst surface. All TPR tests were carried out in the range 100–900 °C with a heating rate of 10 °C/min. The H_2 consumption was measured by a thermoconductivity detecter (TCD) connected to a personal computer for data storage and processing. The oxidation state of each element in the fresh and reduced catalysts was examined with XPS technique, where all the spectra were calibrated against C 1s line from adventitious carbon (284.5 eV).

The amount of coke on catalyst was quantified with an elemental analyzer. Also, the weight fractions of K and V in the used catalysts are determined using inductively coupled plasma-atomic emission spectrometer (ICP-AES).

2.3. Experimental procedure

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

Table 1
Properties of naphtha feed

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

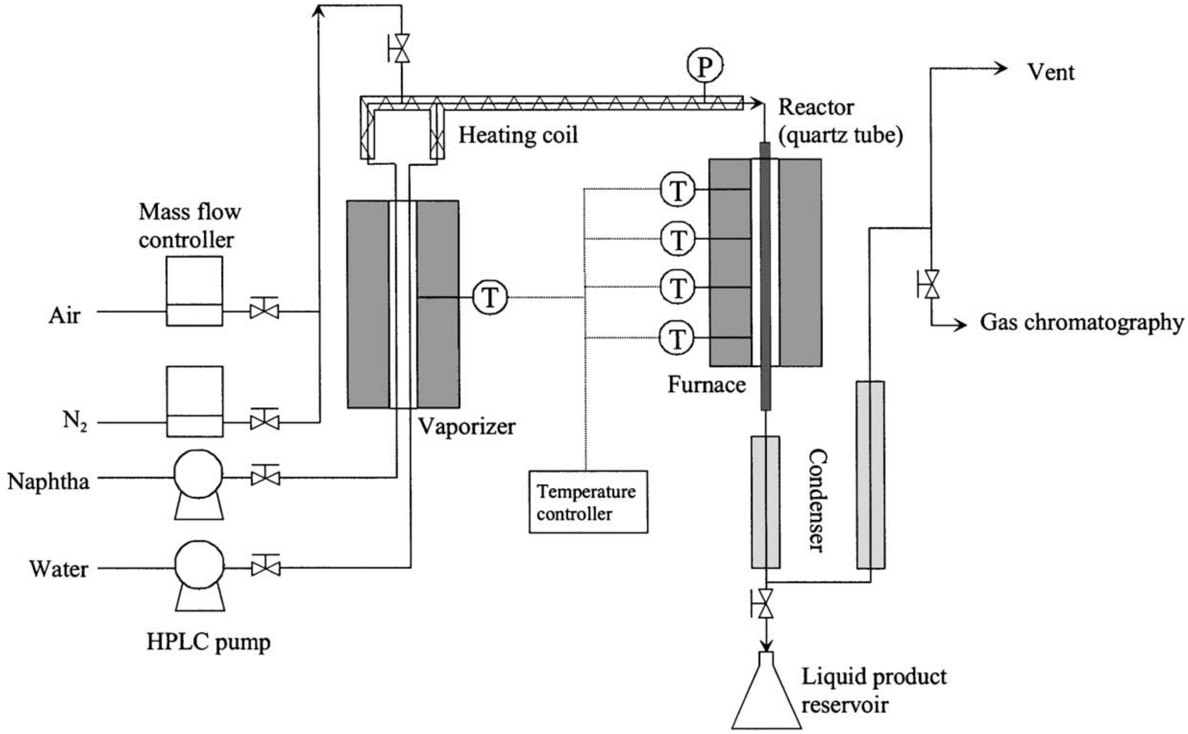

Fig. 1. Schematic diagram of the experimental apparatus.

be 80–85. Both non-catalytic and catalytic pyrolysis runs were conducted 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 into a vaporizer. The flow rates of naphtha and water were 1.5 and 0.75 g/min, respectively, to ensure the 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 vaporizer. Thereafter, the mixed stream passes through a pre-heater which was maintained at 600 °C and then enters a tubular quartz reactor (ID: 7.6 mm), where the height of catalyst bed was 450 mm. The furnace temperature 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 chromatography 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 for the analysis.

3. Results and discussion

3.1. Olefin yields in the naphtha cracking

In order to investigate the enhancement of olefin yield by the catalyst, both non-catalytic and catalytic pyrolysis of naphtha were carried out at temperatures ranging from 800 to 880 °C. Besides ethylene and propylene, significant amounts of methane, butenes, and butadienes were also detected. Fig. 2 shows the effect of temperature on the yields of ethylene and propylene. As can be seen, the ethylene yield in-

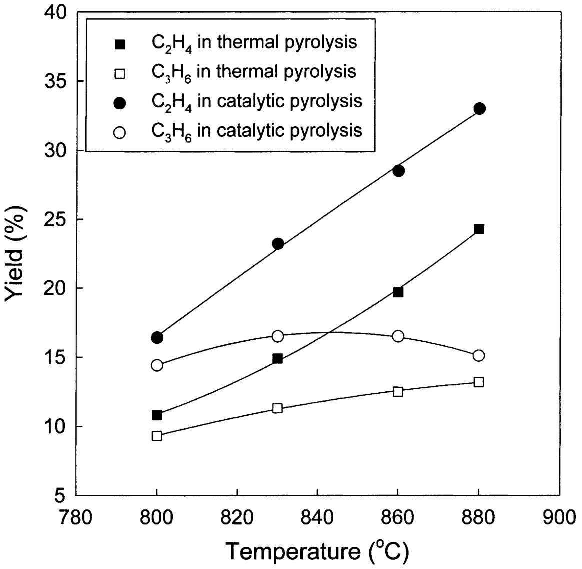

Fig. 2. Effect of temperature on ethylene and propylene yields in the thermal and catalytic naphtha pyrolysis.

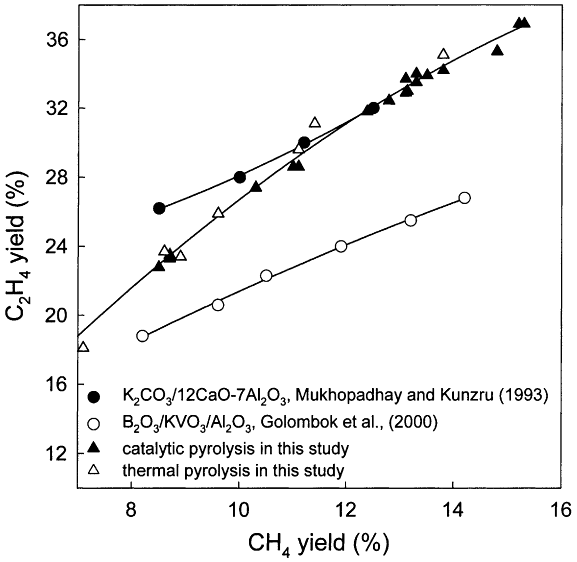

Fig. 3. C_2H_4 yield plotted versus severity measured by CH_4 yield.

creases 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 ethylene yield in the non-catalytic pyrolysis is expected to be observed at the higher temperature [3]. It is noticeable that at the same temperature, the yields of the ethylene and propylene in the catalytic pyrolysis exhibit about 10 and 5% higher values, respectively, compared to those in the non-catalytic pyrolysis. Basu and Kunzru [3] reported that the enhancement in olefin yields in the presence of catalyst is attributed to the promotion of initiation step of free radicals, which is known to be the slowest step. Golombok et al. [7] attributed the increase in ethylene yield to the surface volume effect resulting in the better heat transfer, which is not the catalytic effect. Since the pyrolysis reaction is endothermic, the increase in heat transfer from the reactor wall to the gas phase would result in the enhanced radical reaction.

In the naphtha cracking, the extent of cracking reaction can be usually defined by the severity parameter based on the methane yield. Thus, the ethylene selectivity can be compared by plotting the ethylene yields against the methane yields. Fig. 3 shows data reported in the literature [4,7] as well as data from this study. This result is in agreement with observation by other investigators [3] that the ethylene selectivity in the catalytic pyrolysis of naphtha exhibits a similar value obtained from the thermal pyrolysis performed in a vacant tube. On the other hand, it is contrary to the result obtained by Golombok et al. [7], who observed an increase in ethylene yield only but not methane. They concluded that the reaction kinetics are selectively influenced. In this study, both ethylene and methane yields increased.

Enhanced olefin yields obtained in this study can be explained by the increased heat transfer from the heat source (tube outside) to gaseous reactant via the catalyst particles, resulting in increase in the overall rate of pyrolysis reaction, especially the initiation step of free radical which is the rate determining step. Evidence also comes from the results that the decrease in the olefin yields was negligible even after the catalyst surface was covered by coke. If such enhancement in olefin yields were due to the surface catalytic effect, the olefin yields would be expected to decrease as the surface is progressively covered by coke.

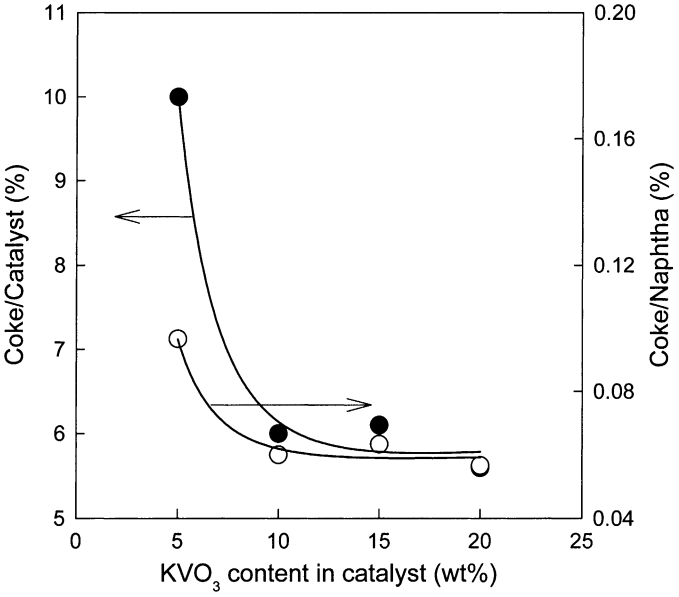

Fig. 4. The effect of KVO_3 content on the amount of coke deposited on the catalyst for 4 h run.

3.2. *Role of KVO_3 as a catalyst*

We measured the amount of coke deposited on the catalyst particles of various KVO_3 loading at the exit zone of the reactor after 4 h run, where we found previously [2] the coke deposition takes place the most severely. Fig. 4 shows the effect of KVO_3 loading on the coke deposition at 880 °C. The coke sharply decreases up to 10 wt.% KVO_3 and then remains constant with a further increase in the KVO_3 loading. This result indicates that the main role of KVO_3 is to suppress the coke formation on the catalyst, which is probably due to the steam gasification of coke. This coke gasification leads to the increase of CO_X concentration in the gas phase product, which was reported by others [4] and also confirmed in this study. It was also reported that the function of potassium in the catalyst is mainly coke suppression in a basis of the simple experimental data such as the weight change of total catalysts and the pressure drop across the cracking tube [7]. The suppression of coke formation during pyrolysis may lead to increase the olefin yield by the heat transfer effect and the conversion from naphtha to olefin not to coke. In this study, the optimum range of KVO_3 to control effectively the coke is found to be more than 10 wt.%.

3.3. *XPS study of catalysts*

Fig. 5 shows the XPS spectra for the fresh catalyst (a), the catalyst after the pyrolysis of naphtha (b) and the catalyst reduced in the H_2 stream (c). For the fresh catalyst, the binding energy and a shoulder of O 1s are found at 531.6 eV which is assigned to the oxygen atom of α-Al_2O_3 and 530 eV for the fresh catalyst (a), respectively. A shoulder at 530 eV is presumably due to the oxygen atoms supplied by alumina surface in order to form KVO_3 compound when the catalyst is calcined at high temperature, as a similar result was reported with vanadium impregnated α-Al_2O_3 previously [11]. The photoelectron intensity for spectrum (b) is considerably lower than those with the catalysts (a) and (c), which is attributed to the coke deposited on the catalyst surface during the pyrolysis of naphtha. Furthermore, the shoulder observed on the fresh catalyst disappears on the coked catalyst. It indicates that the catalyst be reduced possibly by hydrogen generating during the pyrolysis of naphtha. Such conclusion comes from the XPS result for the catalysts reduced in

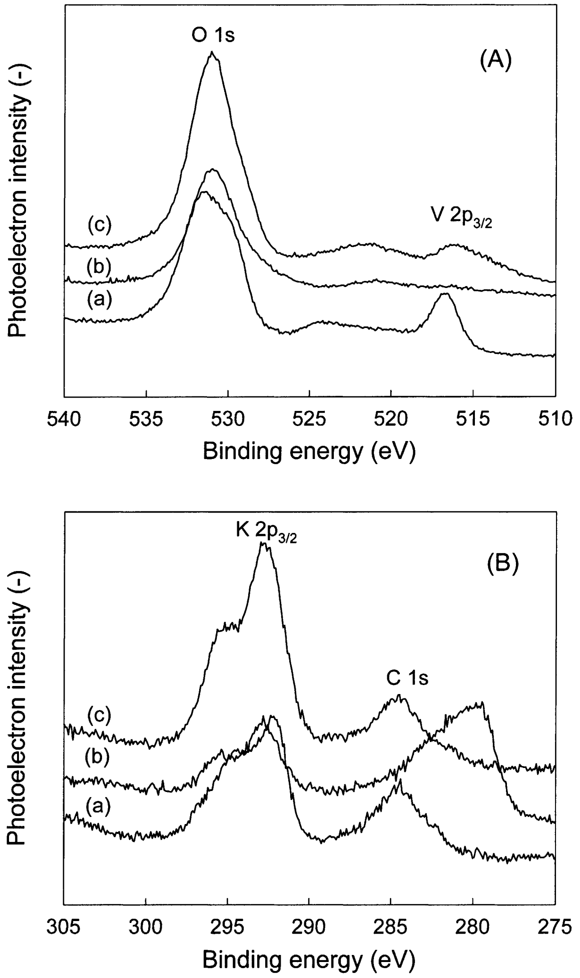

Fig. 5. XPS spectra of (A) O 1s/V 2p and (B) C 1s/K 2p of KVO_3-impregnated α-Al_2O_3 catalyst; (a) the fresh catalyst, (b) the catalyst after the pyrolysis of naphtha, and (c) the catalyst reduced in the H_2 stream.

the hydrogen stream (part (c) of Fig. 5A) showing that the shoulder disappears and the binding energy shifts to 531 eV in the O 1s signal indicating the reduction of V^{5+} and/or K^{1+} to the lower oxidation states.

V $2p_{3/2}$ binding energy is observed with symmetry at 516.7 eV for the fresh catalyst, which is somewhat lower than 517–517.5 eV for V_2O_5 in the previous publications [11,12]. This may be due to the difference in structural configuration between KVO_3 and V_2O_5. The reduction of catalyst by H_2 (c) causes the shift in the binding energy of V $2p_{3/2}$ from 516.7 to 516 eV and the decrease and broadening in V $2p_{3/2}$ signal which can be assigned to V^{3+} [11,12]. Although the V $2p_{3/2}$ peak for the catalyst (b) is very small due to the coke deposition on the catalyst surface, the peak shift to a value characteristic of V^{3+} is observed in the present study.

The same binding energy (292.7 eV) of K $2p_{3/2}$ for the coked catalyst (b) and the reduced catalyst (c), which is higher by 0.5 eV than 292.2 eV for the fresh catalyst (a), suggests again that the catalyst is reduced during the pyrolysis of naphtha. The results of TPR and XPS suggest that KVO_3 may be reduced to $KVO_{1.5–2.0}$ during the pyrolysis of naphtha.

The C 1s binding energy, 279.4 eV, for the coked catalyst (b) is about 5 eV lower than the fresh and the reduced catalyst. Such value is indicative of formation of the metal carbide on the coked catalyst (b) after pyrolysis of naphtha [13]. This implies that the deposited coke during pyrolysis is linked with metals on the catalyst surface to form the metal carbides as in other catalytic system [14].

3.4. *Role of B_2O_3 as an additive*

It has been reported that the significant amount of potassium loss occurs during the catalytic pyrolysis of hydrocarbons [4,7,15]. Mukhopadhyay and Kunzru [4] observed the 50.6% loss in the potassium content after a 4 h pyrolysis run at 780 °C. Also, Golombok et al. [7] concluded the considerable amount of K_2O evaporation based on the weight loss of KVO_3 catalysts after a 35 h run, although they did not quantify the potassium content in the catalyst. In order to measure the extent of KVO_3 loss and the effects of B_2O_3 loading in this study, the catalysts of various B_2O_3 loading were treated under the steam atmosphere at 880 °C for 4 h. Then, the amount of K and V in the fresh and treated catalysts has been measured with ICP-AES. The treatment under the steam only environment, which is different from the naphtha pyrolysis, was employed in order not to have complexity in the analysis due to coke formation. Nevertheless, the results suggests well the effect of B_2O_3 in the catalyst.

In B_2O_3-free catalyst, the loss of K and V occurs significantly as can be seen in Fig. 6. However, it is

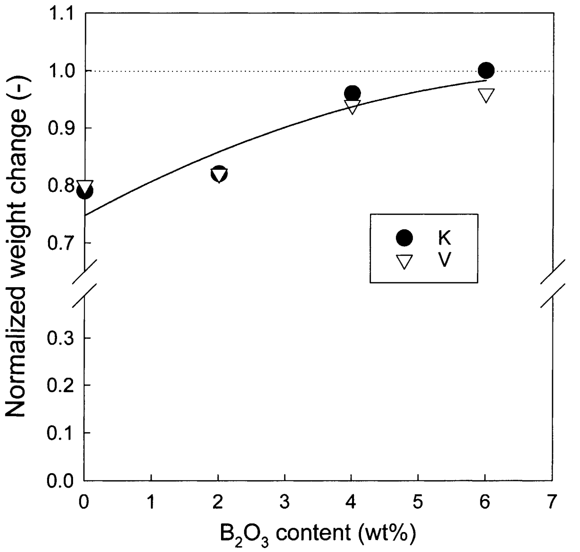

Fig. 6. The variation of K and V contents in the catalyst with the different amount of B_2O_3 loading before/after the steam treatment for 4 h.

evident that the loss decreases with increasing B_2O_3 loading. This result indicates that the addition of B_2O_3 may enhance the interaction between KVO_3 and the alumna support.

Such effect can be clearly seen through TPR results shown in Fig. 7. As expected, the fresh α-Al_2O_3 is not reduced under 5 vol.% H_2 atmosphere. However, the TPR profile of 10 wt.% KVO_3/α-Al_2O_3 shows a sharp main reduction peak with a maximum around 630 °C and a second symmetric peak at 690 °C as well as the broad peak between 400 and 580 °C. These peaks result from the reduction of K and V in the catalyst to the lower oxidation states of each elements. The quantitative analysis with respect to the hydrogen consumption suggests that KVO_3 may be reduced to $KVO_{1.5–2.0}$.

The TPR profile for 1 wt.% B_2O_3-promoted catalyst shows that the onset temperature of reduction and the temperatures of the first and second peaks shifts to the higher temperature by about 80 °C compared with the B_2O_3-free catalyst (Fig. 7). Also, more addition of B_2O_3 to 2 wt.% into the catalyst decreases significantly the peak heights indicating suppression in reducibility by H_2. From the TPR study on the interaction between V_2O_5 and various supports, Arena et al. [16] found that the strong interaction between better dispersed V_2O_5 and the support retards the reducibility of V_2O_5. Adel'son et al. [17] concluded, based on the results of SEM, that the addition of B_2O_3 leads to an even distribution and the decrease of crystalline size of KVO_3 on the catalyst surface. Therefore, the

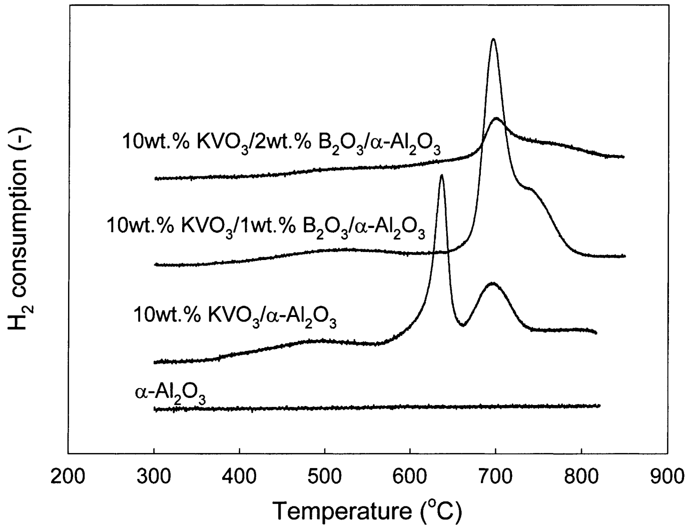

Fig. 7. Normalized TPR curves of various catalysts.

TPR results in this study suggest that the role of B_2O_3 be to increase the interaction between KVO_3 and α-Al_3O_3 support through the better dispersion of KVO_3 and thus decrease the loss of KVO_3.

4. Conclusions

The catalytic pyrolysis of naphtha has been carried out on KVO_3-based catalysts to produce the light olefin at high yields. Although the catalytic pyrolysis leads to 10 and 5% higher values in the yields of ethylene and propylene, respectively, compared to the thermal pyrolysis at the same operation condition, the evidence suggests that the effect be not catalytic but due to the enhanced heat transfer through the catalyst particles.

KVO_3 on the support plays a role to accelerate the gasification of coke deposited on the catalyst surface. The results of TPR and XPS suggest that KVO_3 be reduced to $KVO_{1.5–2.0}$ during the pyrolysis reaction. Addition of B_2O_3 into KVO_3-based catalyst causes a strong interaction between KVO_3 and α-Al_2O_3 support, which decreases the loss of KVO_3.

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