Catalytic Pyrolysis of Naphtha on SHS Catalysts

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Abstract

High yield of light olefins by catalytic pyrolysis of naphtha on spinel-based catalysts is reported. The yields of ethylene and propylene reach over 50% and are at least 10% and 5% higher respectively than the yield using thermal Pyrolysis, under the same process conditions. The partial substitution of Mg by Co in $MgAl_2O_4$ and the incorporation of Al_2O_3, SiO_2, MgO, H_3BO_3 in the spinel and SHS synthesis of KVO_3 all increase the catalytic conversion efficiency while at the same time they suppress substantially the formation of coke. It was found that SHS-KVO_3 catalytically accelerates the gasification of coke deposited on the catalyst surface and its optimum values were found to be more than 10 wt.%. The addition of B_2O_3 into the KVO_3-based catalyst causes a strong interaction between KVO_3 and SHS support, which decreases the loss by evaporation of the active phase.

Introduction

Naphtha is used world-wide for the production of ethylene and propylene and is considered as one of the basic raw materials of the chemical and polymer industry. The main method of production of light olefins from naphtha is thermal (pyrolytic) cracking in the presence of steam.

The use of catalysts in the process of naphtha pyrolysis increases the yields of olefins, but the catalytic activity is often suppressed by the accumulation of coke on the catalyst surface. It has been reported [1-3], that KVO_3-based catalysts are effective for coke control and for increasing olefin production during pyrolysis of naphtha. It was found [4-6] that KVO_3 on the carrier plays a catalytic role and helps to accelerate the gasification of coke deposition on the catalyst surface. Furthermore, the addition of B_2O_3 into the KVO_3-based catalysts causes a strong interaction between KVO_3 and carrier, which decreases the loss of KVO_3.

Ideally, catalysts and carriers for naphtha pyrolysis should have relatively small specific area

$(1-5m^2/g)$ and good heat stability [7]. Such characteristics are found in catalysts produced by Self-Propagating High-Temperature Synthesis (SHS) since they are synthesised using a high temperature combustion process [8-10]. In addition, SHS catalysts have been reported previously to display high activity for pyrolysis of various hydrocarbons [9-10].

In the present study, we report on the catalytic pyrolysis of naphtha using SHS catalysts.

Experimental

Catalyst Preparation and Characterization

Modified Mg-Al-O spinel catalysts were synthesised by SHS. The initial SHS charges consisted of powder mixtures of Mg, Al, $MgSO_4·7H2O$, Co_3O_4, Al_2O_3 and in some cases, H_3BO_3, K_2SO_4, K_2CO_3, V_2O_5, MgO or SiO_2. After mixing the initial components in air, cylindrical samples were formed by uniaxial compaction at a pressure of up to 40MPa. Preheating of samples for SHS was carried out at $T_o = 500 – 1000$ °C

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(depending on the system) in a chamber furnace in air and the maximum combustion temperature was measured by an optical pyrometer and was found to reach about 1900 °C in some systems. Initiation of SHS combustion was done by a small amount of Mg on the top of each cylindrical specimen. The rate of synthesis (wave velocity) was determined by measuring the time taken for the SHS wave to traverse the sample from top to bottom and varied between about 0.1cm/s to 1.5cm/s. The resulting materials were characterised by mercury porosimetry, XRD and measurement of compressive strength.

Catalytic characterization

For catalytic activity characterization, the experimental set up that was used is shown in Figure 1. The naphtha flow rate during catalysis was 15 h^{-1} and the amount of catalyst tested was 10 cm^3 (3-5 mm particle size) in all cases. Pyrolysis products measured included methane, ethylene, propylene and coke. Quantitative determination of the pyrolysis gas products was carried out by a gas chromatograph. At the completion of each run, the reactor was flushed with nitrogen and then the coked catalysts were taken out for analysis. The amount of coke on the catalyst was quantified with an elemental analyzer.
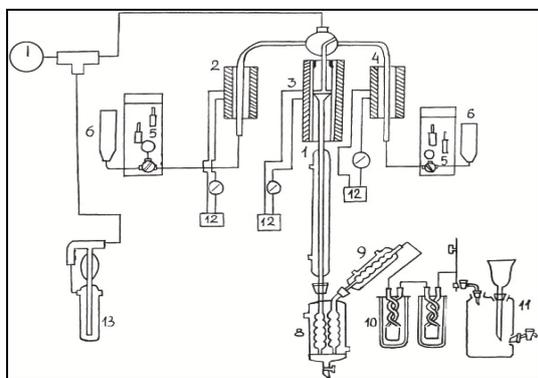

Fig. 1. The experimental arrangement used for the naphtha catalytic pyrolysis measurements: (1) quartz reactor; (2)(4) electric furnaces for preheating of water and naphtha; (3) reactor furnace; (5)(6) dispensers for row materials; (7) condenser; (8) condenser support (9) recirculation condenser; (10) receptacle; (11) gas reservoir; (12)ammeter; (13) manometer.

Some properties of the raw naphtha feed used in this study and the proportion of C4-C10 hydrocarbons contained in each of its constituent,

are shown in Table 1. The total average molecular weight of naphtha was 80-85.

Table 1
Properties of the Naphtha feed constituents

	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
C8	4-6	5-6		1.2-2.0
C9	0.5-1.5	1-15		0.2-1.0
C10	0.2-0.5	0.5-0.7		0.1
Final boiling point (C°)	140-160			
total sulphur (wt ppm)	200-500			
density (kg/m3)	660-680			
viscosity (cP)	0.33			

Results and Discussion

Table 2 shows the SHS process parameters as well as the physical properties of the synthesized spinel materials. The SHS materials display good compressive strength (3.0 MPa – 7.5MPa) and low surface area (0.05 – 1.2m^2/g) due to the high combustion temperatures achieved by SHS. The low surface area is beneficial in the case of pyrolysis catalysts as it reduces the production of coke on the surface of the catalyst.

Table 2
Weight percent of coke relative to total naphtha fed after pyrolysis at 880°C for 5 hours

Composition of SHS charge of the catalyst	Compressive strength MPa	Total Porosity %	Density g/cm^3	Surface area m^2/g
MgAl$_2$O$_4$, Co, 3Al$_2$O$_3$·2SiO$_2$,SiO$_2$, CoAl$_2$O$_4$	7.5	50	2.4	0.1
MgAl$_2$O$_4$, CoAl$_2$O$_4$, Al$_2$O$_3$	6.0	70	1.4	0.05
MgAl$_2$O$_4$, CoAl$_2$O$_4$, KVO$_3$, AlVO$_4$	4.7	80	0.9	1.2

The basis of the catalyst tested is a mixture of $MgAl_2O_4$ and $CoAl_2O_4$. This catalyst has been shown to be active in the process of diesel pyrolysis [9-10]. Four ranges of materials were produced: one with the addition of H_3BO_3 in the initial powder mixture between 0 and 20wt%, a second one with 5wt% K_2SO_4 or K_2CO_3, a third one with 5wt% V_2O_5 and the forth one with a combination of additives.

The SHS combustion product consisted mainly of $MgAl_2O_4$ with some of the Mg ions substituted by Co ions. Previous investigations have shown that SHS produces materials containing a large concentration of lattice defects which are known to be active centres in catalysis. The substitution of Mg by Co in the Mg-Al-O spinel system deforms the structure changing slightly the crystal lattice parameters, depending on the amount of Co in the lattice, which can result in a significant number of lattice defects. Pure Mg-Al spinel displays catalytic activity for pyrolysis of hydrocarbons. However, the catalyst is quickly covered by coke and its activity is suppressed. The substitution of Mg by Co though, increases significantly the catalytic activity of the spinel while at the same time suppressing the production of coke [9]. A small percentage of Co-Al spinel (0.22wt% in the initial batch) in the catalyst resulted in catalytic activity and the catalyst coke content was reduced 10 times in comparison with the catalyst without Co. This effect is particularly important as far as the active life time of such catalysts is concerned, especially at high temperatures. Coke accumulation leads to blocking of micropores, crushing and pulverisation of material and finally cessation of catalytic activity.

An SHS catalyst 99.3%$MgAl_2O_4$ and 0.7%$CoAl_2O_4$ displays good catalytic activity for naphtha pyrolysis at 880^oC, the yield of $C_2H_4+C_3H_6$ is 55.5% (Fig.2), but the coke/naphtha formation is 0.065%.

We measured the amount of coke deposition on the SHS catalysts with various additives at the outlet zone of the reactor after 5 hours run, where the coke deposition is the most severe (Fig. 3, 4). The thickness of external coke film on catalyst surface is found to be 1-5 μm. For example for Co spinel catalyst it is 3.9 μm (Fig.4). The table 2 shows the effect of additives on the coke deposition at 880^oC.
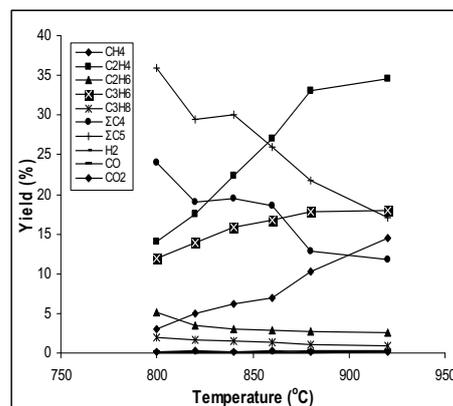

Fig 2. Influence of temperature on gas products yields in the catalytic naphtha pyrolysis. Catalyst: $MgAl_2O_4$, $CoAl_2O_4$, Al_2O_3.
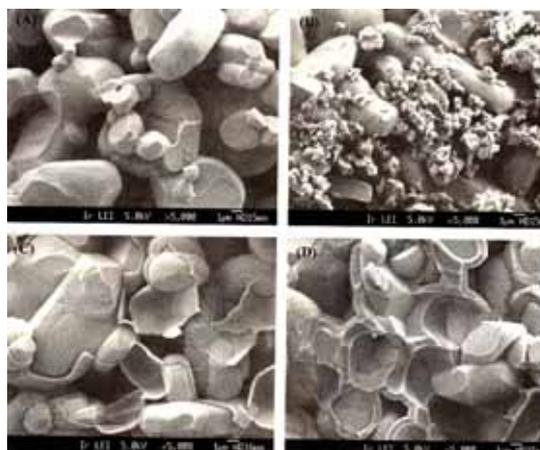

Fig 3. SEM photographs of the catalyst at different bed locations after naphtha pyrolysis for 4 hr; (A) fresh catalyst, (B) inlet, (C) middle and (D) outlet points
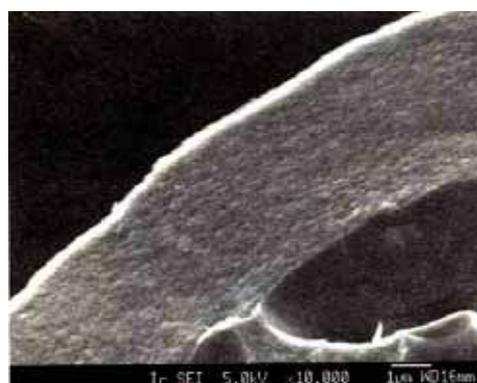

Fig 4. SEM photograph for the external surface of coked catalyst

SHS catalyst (MgAl$_2$O$_4$, CoAl$_2$O$_4$, Al$_2$O$_3$) With additives	Weight percent of coke relative to naphtha fed (%)
none	0.065
2% H$_3$BO$_3$	0.042
5% H$_3$BO$_3$	0.052
10% H$_3$BO$_3$	0.065
20% H$_3$BO$_3$	0.085
5%K$_2$SO$_4$	0.048
5%K$_2$CO$_3$	0.055
5%V2O5, 5% H$_3$BO$_3$	0.13
5% H$_3$BO$_3$, 5%V$_2$O$_5$, 5%K$_2$SO$_4$	0.01
5% H$_3$BO$_3$, 5%V$_2$O$_5$, 5%K$_2$CO$_3$	0.005
5%V$_2$O$_5$, 5%K$_2$CO$_3$	0.008

The coke deposition decreases in catalysts with small amounts of H$_3$BO$_3$ (2-5%) but further addition of H$_3$BO$_3$ (10-20%) has opposite effect. These results can be explained by the fact that during SHS, 2-5% of H$_3$BO$_3$ decreases specific surface area from 0.15m^2/g to 0.09 m^2/g which leads to decreased coke formation Further increasing of H$_3$BO$_3$ (10-20%) bring changes in the SHS reactions and as a consequence increases the surface area up to 0.17 m^2/g. Addition of alkali metal compounds K$_2$SO$_4$, K$_2$CO$_3$ which are known as catalysts for the steam gasification of carbon [11] tend to solve this problem. Addition of V$_2$O$_5$ has the opposite effect but combination of additives: 5%H$_3$BO$_3$, 5% V$_2$O$_5$ and 5% K$_2$CO$_3$ gave the best result. This is connected with KVO$_3$ origination (of about 7%) during SHS process. The decrease in the coke deposition on SHS catalyst comes from coke gasification by KVO$_3$ which leads to an increase of the CO$_x$ concentration in the gas product [6] due to reactions:
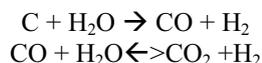
$$C + H_2O \rightarrow CO + H_2$$
$$CO + H_2O \Longleftrightarrow CO_2 + H_2$$

Fig. 5 shows the effect of H$_3$BO$_3$ and 5%H$_3$BO$_3$, 5% V$_2$O$_5$, 5% K$_2$SO$_4$ additives to initial batch of the Co-spinel based catalyst (99.3%MgAl$_2$O$_4$ and 0.7%CoAl$_2$O$_4$) on the ethylene and propylene yields.

The best results were received on Co-spinel catalysts (fig.5). The same catalyst with additives of V$_2$O$_5$, H$_3$BO$_3$ and K$_2$SO$_4$ (or K$_2$CO$_3$) offered yield of olefins 2% less, but coke formation is 5 -13 times less (table 2). During SHS reaction those additives to initial batch react with origination

KVO$_3$, which acts as reducer of coke formation [6], which also explains the increas of CO$_2$ in the gas products. CO$_2$ formation from naphtha thermal cracking was negligible. From Co-spinel catalyst formation of CO$_2$ is much lower than from Co spinel catalyst with KVO$_3$ (fig.6). In a catalyst produced by SHS pass temperatures 1700-1900°C (table 2), KVO$_3$ is produced during SHS and is in much more stable form, than during impregnation, H$_3$BO$_3$ which also helps stabilization of KVO$_3$.
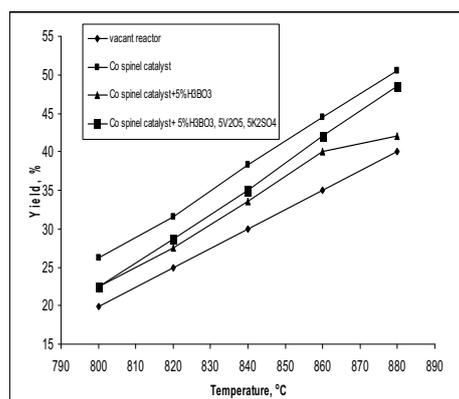

Fig. 5. Influence of temperature and additives to catalyst on the olefins (C$_2$H$_4$+C$_3$H$_6$) yield.
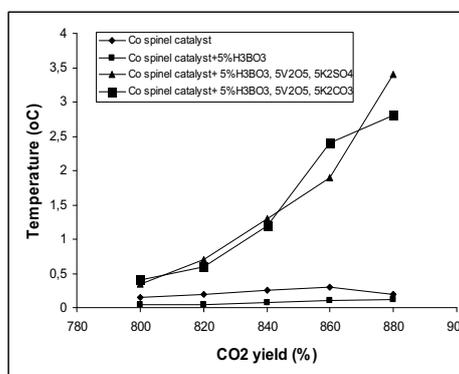

Fig. 6. Influence of temperature and additives to catalyst on the CO$_2$ yield.

Conclusions

The catalytic pyrolysis of naphtha has been carried out on KVO$_3$-Co-spinel catalysts to produce light olefin at high yields. The yields of ethylene and propylene reach 50.5% and it is 10% higher values compared to those of the thermal pyrolysis in vacant tube at the same operational conditions.

Best results for the weight percent of coke relative to naphtha feed is 0.008%. The reduction of coke formation was due to the KVO_3 presence. In a catalyst produced by SHS pass temperatures 1700-1900°C, KVO_3 originates and is in much more stable form, than after impregnation. H_3BO_3 also helps stabilization of KVO_3. Thus, SHS catalysts are stable and active catalysts for pyrolysis of naphtha.

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