Catalytic pyrolysis of *n*-heptane on unpromoted and potassium promoted calcium aluminates

K.K. Pant [a,*], D. Kunzru [b]

[a] *Department of Chemical Engineering, Indian Institute of Technology, Hauz Khas, New Delhi 110016, India*
[b] *Department of Chemical Engineering, Indian Institute of Technology, Kanpur 16, India*

Abstract

Steam pyrolysis of *n*-heptane has been studied over different calcium aluminates and potassium impregnated calcium aluminate in a fixed bed reactor at atmospheric pressure. Various calcium aluminate catalysts were prepared by changing the precursor salt for obtaining CaO, which was subsequently used with Al_2O_3 for catalyst preparation. Depending on the source of CaO, the catalytic properties such as X-ray diffraction patterns, surface area, weight loss during reduction and the amount of CO_2 chemisorbed (basicity) were different. Compared to the unpromoted catalysts, K_2CO_3 impregnated catalyst significantly reduced the coke deposited on the catalyst, but only had marginal effect on the products selectivities. The activation energy for the coke gasification reaction was 140 kJ/mol. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Steam pyrolysis of hydrocarbons is an important process for the production of light olefins such as ethylene, propylene and butenes. Considerable efforts have been made on developing catalysts for the pyrolysis and limited data available on catalytic pyrolysis has been summarized by Pant and Kunzru [1] and Taralas [2]. The main aim of catalyst development is to either increase the yield of olefins or to lower the coke deposition on the reactor wall and on the catalyst so as to maintain its activity for the reaction. Calcium aluminates with $12CaO–7Al_2O_3$ as the major crystalline phase and mixed oxides proved to be very stable and active catalysts for hydrocarbon cracking and reforming [3–6]. The catalytic effect of cheap materials like clay, quartz, calcined limestone or dolomite and others have also been studied with various model compounds with beneficial effects in the kinetics, yields and selectivity [7,8]. One of the problem which need to be overcome before catalyst can be developed for commercial use is to reduce the coke deposition on the catalyst. Coke deposition results in loss of activity and selectivity and catalyst regeneration by burning off the deposited coke is necessary. This additional step reduces the overall productivity of the process. Although it has been reported by various investigators that the addition of alkali or

alkaline earth oxides to the catalyst is effective in preventing coke formation in various reactions [9–11] there is very limited information available in published literature regarding the effect of potassium on product yields and coke gasification activities of the catalyst during hydrocarbon pyrolysis.

The objective of this study was to investigate the effectiveness of unpromoted calcium aluminates prepared from various source materials and to study the effect of potassium carbonate impregnation to the catalyst on the conversion, product yields and coke gasification activity of the catalysts during the pyrolysis of *n*-heptane.

2. Experimental

2.1. Catalyst preparation

The calcium aluminate catalyst was prepared by mixing the required amounts of CaO and Al_2O_3 in the presence of a binder. CaO was obtained from the decomposition of either calcium hydroxide, calcium carbonate, calcium acetate or calcium oxalate. CaO and Al_2O_3 in the mass ratio of 1.06:1 were mixed in the presence of a binder, dried, crushed and then molded into cylindrical pellets. The calcium aluminate catalyst made from calcium acetate, calcium hydroxide, calcium oxalate and calcium carbonate have been designated as CA1, CA2, CA3 and CA4, respectively. The pellets

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* Corresponding author.
E-mail address: kkpant@chemical.iitd.ernet.in (K.K. Pant).

were aged at 353 K for 24 h and then sintered for 18 h. The sintering temperature of CA1, CA2, CA3 and CA4 catalysts were 1643, 1643, 1699 and 1653 K, respectively. For CA1 and CA2, a sintering temperature lower than 1643 K resulted in catalysts which crumbled in few days during storage. CA3 and CA4 could not be properly sintered even at 1643 K. The calcium aluminate prepared using the above procedure showed good crystallinity as measured by X-ray diffraction and were stable in air as well as water.

Potassium promoted catalyst was prepared from calcium aluminate catalyst (CA2) by incipient wetness technique and the impregnated catalyst was then heat treated at 1023 K for 6 h. The initial potassium carbonate loading on the catalyst was made using 5, 10 and 15% of K_2CO_3. However, due to heat treatment process there was a loss of potassium from the catalyst as measured by atomic absorption spectroscopy. The final potassium content on these catalysts was 2.2, 4.8 or 6.4 wt.%, respectively. These catalysts were designated as IKx, where x is the potassium content on the catalyst. The unpromoted and potassium promoted catalysts were characterized by X-ray diffraction, surface area measurements, CO_2 chemisorption, weight loss during reduction and atomic absorption spectroscopy (for potassium promoted catalysts). The X-ray diffraction spectra were obtained on an Inel X-ray analyzer using monochromatized Cu-Kα radiation with a wavelength of 1.5406 Å.

2.2. Experimental procedure

For pyrolysis runs, the catalyst samples were crushed and sieved and the fraction containing 2.5 ± 0.2 mm were retained for use. Preliminary runs with these catalyst using a size fraction of 1.2 ± 0.2 mm confirmed that there was no effect of catalyst size on conversion and product yields. Details of the experimental set-up has been discussed earlier [12] and are only briefly discussed here. n-Heptane and water were pumped to a vaporizer maintained at 573 K and this heated stream was then entered to the reactor. To passivate

the reactor walls 200 ppm of carbon disulfide was added to the n-heptane feed. The tubular reactor (19 mm i.d., 600 mm length) was constructed of stainless steel and heated in a three-zone furnace. The axial temperature profile in the reactor was measured with type K thermocouples using two thermowells (o.d. 6 mm) attached to the inlet and outlet of the reactor. A circular plate containing ten 1 mm holes was fixed to the upper thermowell and served as the catalyst retaining support. During the course of a run the total condensed liquid, together with the volume and composition of the product gases was measured at regular intervals. At the completion of the run the reactor was flushed with steam for 1 h and then either the reactor was decoked with air or the coked catalyst was removed from the reactor for subsequent analysis. The non-condensable gases, which mainly consisted of C1–C4 hydrocarbons were analyzed by gas chromatography using three columns, viz. Duropak, Porapak-Q and Carbosphere. The liquid products were analyzed on a capillary column (Petrocol DH; i.d: 0.25 mm; length: 100 m).

3. Results and discussion

3.1. Catalyst characterization

The X-ray diffraction spectra show that for all the catalysts, the major phase was $12CaO–7Al_2O_3$ together with some minor phase $3CaO–Al_2O_3$ (Table 1). In addition, traces of $CaO–Al_2O_3$ and $CaO–2Al_2O_3$ were present in CA1 and CA4 catalysts, and traces of CaO and CaO_2 were present in CA3 catalyst. The diffraction pattern of K_2CO_3 impregnated catalyst was similar to unpromoted catalysts, indicating that no new crystalline phase was formed due to K_2CO_3 impregnation.

The total surface area of the catalysts was measured with an accuracy of $\pm 3\%$ using the dynamic pulsing technique on a Micromeritics Pulse Chemisorb 2700 unit. Due to high sintering temperature the surface area of all the catalysts

Table 1
Physicochemical properties of calcium aluminates

S. No.	Properties	Catalyst				
		CA1	CA2	CA3	CA4	K_2CO_3 impregnated CA2 (IK4.8)
1	Major phase	$12CaO–7Al_2O_3$	$12CaO–7Al_2O_3$	$12CaO–7Al_2O_3$	$12CaO–7Al_2O_3$	$12CaO–7Al_2O_3$
2	Minor phases	$CaO–Al_2O_3$, $CaO–2Al_2O_3$, $3CaO–Al_2O_3$	$3CaO–Al_2O_3$	CaO_2, CaO, $3CaO–Al_2O_3$	$CaO–Al_2O_3$, $CaO–2Al_2O_3$, $3CaO–Al_2O_3$	$3CaO–Al_2O_3$
3	Surface area (m^2/g)	0.88	0.92	0.72	1.07	0.75
4	Weight loss during reduction (%)	0.83	1.10	3.60	0.94	8.6
5	CO_2 chemisorbed at 323 K (cm^3/g)	0.068	0.144	0.216	0.256	a
6	Potassium content of fresh catalyst (wt.%)	–	–	–	–	4.8

a Not measured.

were low and for unpromoted catalysts ranged between 0.72 and 1.07 m^2/g. This relatively low surface area is considered beneficial for these type of pyrolysis catalysis as it results in low formation of coke, thereby increasing their useful life. As can be seen from Table 1 that the catalyst made from CaCO$_3$ (CA4) showed the largest surface area. There was a slight decrease in the surface area due to potassium impregnation and surface area decreased with an increase in the potassium content of the catalyst. The surface areas were 0.82, 0.75 and 0.65 m^2/g for IK2.2, IK4.8 and IK6.4 catalyst, respectively. The relative surface basicity of each unpromoted catalyst was determined using chemisorption of CO$_2$ at 323 K. As shown in Table 1, the catalyst made from calcium carbonate (CA4) had the highest basicity whereas the catalyst made from calcium acetate (CA1) had the lowest basicity. Although the nature of the basic sites on calcium aluminates is not precisely known, it is most likely due to the presence of oxygen ions on the surface. Iizuka et al. [13] studied the nature of basic sites of CaO and reported that the basic sites are predominantly O^{2-} sites. In this context, it should be noted that the basicity of MgO has also been reported to be strongly affected by the precursor used, due to creation and annihilation of surface defects resulting in changes in the coordination of the surface ions, consequently affecting basicity [14].

The catalyst weight loss during reduction till 1073 K was determined using a thermogravimetric analyzer (Model TG 722, Harrop Industries). As can be seen from Table 1, among all the unpromoted calcium aluminates, the weight loss for catalysts CA3 was significantly higher. A probable reason for this may be the decomposition of CaO$_2$ phase, which was present in this catalyst only. Most of the weight loss occurred between 633 and 703 K. The weight loss recorded for these catalysts was in good agreement with the weight loss of 1.45% reported for unpromoted calcium aluminate

[3]. The weight loss on reduction for the K$_2$CO$_3$ impregnated calcium aluminate (CA2) was significantly higher. The most probable reason for this high weight loss is the formation of potassium hydride, which is volatile. If all the potassium in the catalyst was in the form of K$_2$CO$_3$ then the maximum weight loss for the catalyst containing 4.8 wt.% potassium would be 8.5% due to the formation of potassium hydride.

3.2. Effect of source of calcium oxide on conversion and product yields for unpromoted calcium aluminates

To study the effectiveness of the catalysts on *n*-heptane pyrolysis, runs without catalyst and with different calcium aluminate catalysts were conducted at atmospheric pressure and 1023 K using steam as the inert diluent. For these set of runs 3.0 g of catalyst was placed in the reactor and mass flow rate of *n*-heptane and steam were kept at 1.0 and 2.5 g/min, respectively. Isothermal conditions were maintained in the central portion of the reactor where the catalyst was placed and the temperature mentioned refers to the isothermal zone temperature.

The conversion and product yields obtained with different catalysts as well as non-catalytic runs are shown in Table 2. The conversion of *n*-heptane increased significantly in the presence of catalysts. The main products during *n*-heptane pyrolysis were methane, ethane, ethylene, propylene and 1-butene, whereas 1,3-butadiene, propane, *n*-butane, 3-methyl butene, 1-pentene, 1-hexene and benzene were obtained as minor products. In addition, small amounts of coke and carbon oxides were also produced. Compared to non-catalytic pyrolysis, cracked gas yields as well as the yield of carbon oxides were affected due to the presence of the catalyst. The cracked gas yield varied from 70.9 wt.% feed for catalyst CA1 to 75.1 wt.% feed for catalyst CA4. In comparison, for non-catalytic pyrolysis the total cracked

Table 2
Conversion and product yields obtained with different unpromoted catalysts (*n*-heptane flow rate: 1.0 g/min; steam flow rate: 2.5 g/min; catalyst weight: 3.0 g; catalyst zone temperature: 1023 K)

Product yields (wt.% feed)	Non-catalytic	Catalyst			
		CA1	CA2	CA3	CA4
Methane	6.5	8.2	8.7	8.8	9.2
Ethane	2.3	3.6	3.4	1.8	2.6
Ethylene	32.1	35.0	38.5	39.1	39.7
Propane	0.3	0.4	0.3	0.3	0.3
Propylene	15.8	16.0	18.2	16.5	13.0
1-Butene	3.0	2.6	4.9	3.5	1.8
1,3-Butadiene	1.5	1.5	1.0	1.8	2.0
Total cracked gas yield (wt.% feed)	62.7	70.9	71.7	72.2	75.1
C4+	7.3	8.5	7.3	6.8	6.5
Carbon monoxide	tr[a]	8.1	tr	6.4	6.1
Carbon dioxide	tr	1.8	tr	0.85	1.3
Conversion (%)	69.0	88.7	81.0	78.8	86.7
Coke deposited after 3 h run (wt.% of catalyst)	–	4.81	3.80	4.29	3.84

[a] Trace.

gas yield was only 62.7 wt.% feed. The trend of ethylene yields were similar to that of the total cracked gas yield, i.e. higher the conversion, higher was the ethylene yield. Compared to ethylene, the propylene yield was highest for CA2 catalyst and lowest for CA4 catalyst. The yields of carbon oxides and coke deposited for the various catalysts were also different. Significant yield of carbon oxides were formed with CA1, CA3 and CA4 catalysts whereas negligible yields of carbon oxides were formed with CA2 catalyst. Coke on these catalysts after a 3 h run were 4.81, 3.80, 4.29 and 3.84 wt.% for CA1, CA2, CA3 and CA4, respectively. The results of calcium aluminate catalyst (CA2) and non-catalytic pyrolysis show that the effect on hydrocarbon steam reaction with this catalyst was negligible. The effect of CA1, CA3 and CA4 catalysts on the hydrocarbon steam reforming and the coke gasification reaction was estimated in terms of carbon oxide yields by assuming the coke gasification activity of CA2 catalyst to be zero. The contribution of the carbon oxide yields from coke gasification was calculated from the difference in the coke deposited between CA2 and the respective catalyst. These calculations showed that major contribution of carbon oxide yields was due to the hydrocarbon steam reforming reaction. The results also show that the conversion and product yields obtained with different catalysts did not correlate either with the surface area or the weight loss during reduction. Lemonidou and Vasalos [3] postulated that the active component in calcium aluminate is some form of oxygen that reacts with hydrogen at higher temperature. Results from these study show that not all the oxygen that reacts with hydrogen contributes to the cracking activity. Even though in comparison to the other catalyst, the CA3 catalyst had much higher weight loss during reduction, it only had an intermediate cracking activity.

The results show that cracking activity increased with increasing basicity although the increase was not linear. The nature of the basic sites on the calcium aluminates is most likely due to the presence of oxygen ions on the surface. Different types of oxygen ions (O^-, O^{2-}) can be formed on the surface and these can increase the initiation reaction by abstracting hydrogen from the parent hydrocarbon. In another study Mallens et al. [15] also reported that on MgO based catalyst there were two types of surface lattice oxygen present out of which one was active in radical formation

and subsequently in the formation of ethane and ethylene whereas other lattice oxygen present was responsible for the direct conversion of methane to carbon oxides. The non-linear variation of cracking activity with basicity suggests that not all the basic sites are contributing equally to the increase in activity most likely due to the difference in the strength of the sites. In an earlier study [16], using benzoic acid titration, the basicity of the CA2 catalyst was determined at two pK_{BH} values ($pK_{BH} = 9.3$ and 7.2). The concentrations of stronger basic sites was approximately 30% of the concentration of the weaker basic sites.

3.3. Conversion and product yields for potassium promoted catalysts

To study the effect of K_2CO_3 impregnation, runs were conducted in the presence of steam at atmospheric pressure for various temperatures and inlet flow rates. The experiments covered the following range of variables: temperature, 953–1023 K; *n*-heptane flow rate, 0.4–2.4 g/min; steam flow rate, 1.0–6.0 g/min; inlet steam to *n*-heptane ratio, 1.0–3.0 kg/kg. For the purpose of comparison all runs were made at identical conditions with unpromoted calcium aluminate catalyst CA2 and IK2.2, IK4.8 and IK6.4 catalysts. As can be seen from Table 3 compared to unpromoted catalyst, CA2, the conversion with potassium promoted catalysts were marginally reduced.

With the increasing potassium content of the catalyst, the conversion and the yields of CH_4, C_2H_4 and C_3H_6 progressively decreased. The amount of coke deposited on the catalyst also decreased whereas the yields of carbon dioxide increased with an increase in potassium content of the catalyst. To compare the potassium loss from the different catalysts, the potassium content of each of the used catalyst was determined after a 3 h run and results are also shown in Table 3. As can be seen, potassium loss was higher for higher initial potassium content. To be effective as a coke gasification catalyst, the alkali needs to be mobile on the surface. This alkali mobility, which is necessary for catalytic action, also results in alkali loss from the catalyst. The potassium compounds react with steam during pyrolysis to form potassium hydroxide, which has been postulated as the precursor for the active species during carbon steam

Table 3
Conversion and product yields for the various catalyst, run time: 3 h ($T = 1023$ K, steam/*n*-heptane: 2.5 kg/kg, catalyst weight: 3.0 g)

Catalyst	Conversion (%)	Product yields (wt.% feed)					Coke on catalyst (wt.% catalyst)	Potassium loss during reaction (%)	Surface area of regenerated catalyst (m²/g)
		CH_4	C_2H_4	C_3H_6	CO	CO_2			
Non-catalyst	69.0	6.5	32.1	15.8	tr[a]	tr	–	–	–
12CaO–7Al₂O₃ (CA2)	81.0	8.2	37.5	18.5	tr	tr	3.8	–	0.98
IK2.2	79.7	8.0	36.7	18.2	0.2	0.8	3.4	22.7	0.85
IK4.8	78.4	7.9	36.0	18.1	0.2	2.5	0.8	47.9	0.82
IK6.4	77.7	7.8	34.6	18.0	0.4	3.4	0.6	53.1	0.72

[a] Trace.

reaction [10]. During reaction with carbon these active species are reduced which can be re-oxidized by steam. The loss of potassium is due to the vaporization of the reduced form of the catalyst. Thus, the gasification activity as well as the potassium loss from the catalyst would depend on the rate of reaction between active species and carbon. The results show that, both the gasification activity and potassium loss were highest for the IK6.4 catalyst, implying that the mobility of the alkali is higher for this catalyst. The surface area of potassium promoted catalyst increased due to loss of potassium in the regenerated catalyst. The activity of unpromoted catalysts decreased with time due to significant coke deposition. To study the reduction of activity and the effectiveness of potassium as a gasifying agent 12 h runs were conducted at 1023 K. For this set of runs the conversion and yields of CH_4, C_2H_4 and C_3H_6 decreased with run time from 8.3, 37.8, 18.5 to 7.5, 36.0, 18.1, respectively, for unpromoted calcium aluminate (CA2) catalyst. On the other hand, these were nearly constant for the potassium promoted catalyst. This is due to the significantly low coke deposited on this catalyst (Fig. 1). The amount of coke deposited on the catalyst was compared with the difference between the coke formed and coke gasified during the reaction. The detailed products selectivity obtained with IK4.8 catalyst at various temperature is shown in Table 4. Depending on the stability of the hydrocarbon and secondary reactions the selectivities of CH_4, C_2H_4, 1,3-C_4H_6 and C_3H_6 were increased with temperature and space-time. Determination of kinetics of catalytic pyrolysis of *n*-heptane has been discussed elsewhere [1]. The selectivities of the hydrocarbon product at the same conversion level were
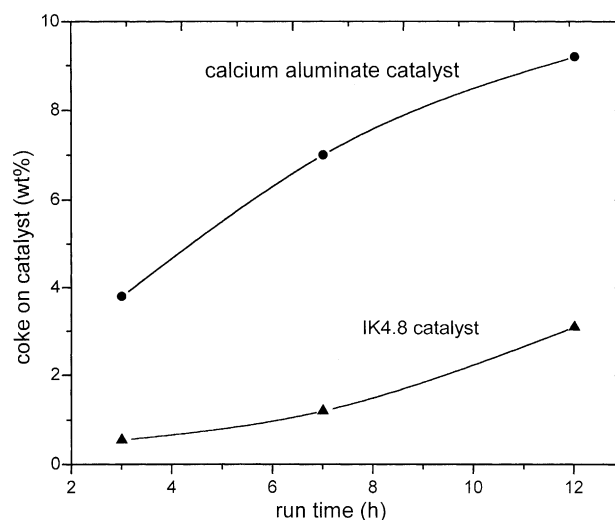

Fig. 1. Comparison of coke deposited on unpromoted and potassium promoted catalyst with run time.

nearly the same for these catalysts which shows that lower coke deposition in the potassium promoted catalyst was due to more coke removal due to gasification. The yields of carbon oxides with potassium impregnated catalyst were significantly higher confirming the higher gasification activity of these catalysts compared to unpromoted catalyst. Various mechanisms have been proposed to explain the effect of potassium carbonate during carbon gasification. Most of these mechanism are based on oxidation–reduction cycles at the potassium carbonate interphase. Huttinger

Table 4
Product selectivities during catalytic pyrolysis of *n*-heptane (moles product/100 moles *n*-heptane decomposed)

	Run number									
	1	2	3	4	5	6	7	8	9	10[a]
Temperature (K)	923	953	953	973	973	993	993	1023	1023	1023
Feed flow rate (g/min)	2.38	2.38	0.40	0.60	0.40	2.38	0.60	1.50	1.00	1.00
Water flow rate (g/min)	5.95	5.95	1.02	1.50	1.02	5.95	1.02	3.74	2.50	2.50
Catalyst weight (g)	6.0	6.0	3.0	3.0	3.0	6.0	3.0	4.0	3.0	3.0
Conversion (%)	6.7	18.0	65.5	68.5	76.0	35.0	76.5	67.0	80.0	81.0
Methane	42.0	38.7	61.2	61.9	65.8	54.9	66.2	61.3	64.5	64.8
Ethane	12.6	16.2	20.2	21.3	20.5	14.8	18.0	19.5	18.9	18.7
Ethylene	121.3	126.0	160.5	166.0	173.1	147.5	178.5	158.5	176.7	178.8
Propane	0.3	0.6	1.0	1.0	1.3	0.9	1.1	1.0	1.0	0.9
Propylene	30.4	38.7	47.2	38.8	42.1	35.8	45.5	41.5	53.6	52.8
n-Butane	tr	0.5	0.3	0.3	0.3	0.4	0.3	0.3	0.2	0.2
1-Butene	18.3	16.7	13.3	8.8	6.8	14.7	7.4	12.9	9.3	8.8
1,3-Butadiene	0.5	1.9	4.5	4.2	4.3	2.6	4.5	4.7	5.6	5.8
3-Methyl butene	1.0	0.8	0.6	0.1	0.2	0.5	0.1	0.7	0.2	0.2
1-Pentene	14.6	9.7	3.6	3.5	3.3	6.2	3.2	2.9	1.5	1.7
1-Hexene	7.5	5.1	0.8	0.7	0.5	5.8	0.4	0.8	0.4	0.8
Benzene	0.4	0.7	0.8	0.8	1.0	0.4	0.9	1.1	1.5	1.6
Carbon monoxide	tr[b]	tr	0.8	0.6	0.9	0.2	1.0	0.6	1.5	tr
Carbon dioxide	tr	0.5	4.9	4.8	5.1	1.4	5.3	4.8	6.0	tr
Others	1.6	2.2	0.5	0.5	0.5	1.5	0.6	0.8	0.8	0.9
Coke content (wt.% catalyst) after a run time of 3 h	0.0	tr	tr	tr	0.3	0.1	0.4	0.1	0.8	3.8

[a] Unpromoted calcium aluminate catalyst (CA2).
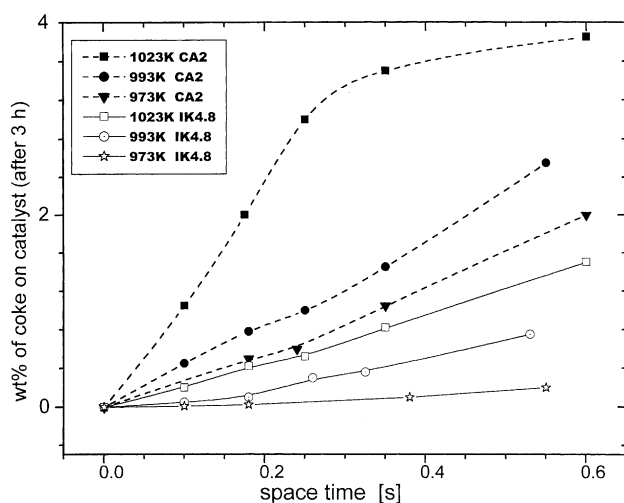
[b] Trace.

Fig. 2. Effect of space-time on coke deposited on catalyst for unpromoted and potassium carbonate impregnated calcium aluminate (run time: 3 h).

and Minges [17] postulated that in the presence of steam, potassium carbonate is converted to potassium hydroxide, which reacts with the carbon and form carbon dioxide. As discussed before for a 12 h run at 1023 K, the conversion and yields of CH_4, C_2H_4 and C_3H_6 decreased with run time for unpromoted calcium aluminate catalysts. On the other hand, for impregnated catalyst the conversion and yields of these products were nearly constant due to lower amount of coke deposited on these catalysts (Fig. 1). As can be seen from Fig. 1, after a 12 h run the coke deposited on IK4.8 was 3.1 wt.% compared to 9.1 wt.% on the unpromoted catalyst. Also the yields of CO_2 decreased with run time indicating a decrease in gasification activity of the catalysts.

3.4. Kinetics of coke gasification

To develop a coke gasification model, runs were taken at various temperatures for unpromoted and potassium promoted catalyst (IK4.8). The coke deposited on the catalyst after a run time of 3 h at different space-time and temperature for the two catalysts is shown in Fig. 2. The decrease in the amount of coke deposited on the K_2CO_3 impregnated calcium aluminate catalyst was due to the increased rate of coke–steam reaction because the yields of carbon oxides were negligible with $12CaO–7Al_2O_3$ catalyst. The rate of coke gasification was calculated as the difference in the rates of coke deposition on the unpromoted and promoted IK4.8 catalyst. The kinetics of coke gasification was evaluated by using a power law form

$$r_g = A_g \exp\left(-\frac{E_g}{RT}\right) \bar{C}_c^a P_w^b$$

where r_g is the rate of coke gasification (kg coke gasified/kg cat h), $\bar{C}_c$ the average coke content of the unpromoted catalyst (kg coke/kg cat) during a run, E_g the activation energy for the coke gasification reaction, A_g the pre-exponential

factor and P_w the partial pressure of steam (atm). Using non-linear regression, the rate parameters were evaluated. The values obtained for E_g, a, A_g and b were 140 kJ/mol, 0.3, 5.79×10^5 (kg coke/kg cat)$^{0.7}$ (h atm)$^{-1}$ and 1, respectively, with a correlation coefficient of 0.96. The activation energy of 140 kJ/mol as obtained in this result is in good agreement with the value of 146 kJ/mol reported by Mims et al. [18] for the K_2CO_3 catalyzed graphite steam reaction.

4. Conclusions

The results of this study show that the source of calcium oxide has a significant effect on the catalyst properties as well as on the activity of the catalyst for the cracking and gasification reactions. Compared to non-catalytic pyrolysis, the conversion and product yields are significantly increased in the presence of these catalysts. Incorporation of potassium carbonate to the calcium aluminate significantly reduces the coke deposition on the catalyst by enhancing the coke–steam reaction but does not have any significant effect on the product selectivities. The coke gasification activity of potassium impregnated catalyst could satisfactorily be modeled as a function of coke on the catalyst and steam partial pressure. The estimated activation energy of coke gasification reaction was 140 kJ/mol.

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