Light alkenes preparation by the gas phase oxidative cracking or catalytic oxidative cracking of high hydrocarbons

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Received 14 November 2003; accepted 21 January 2004

The preparation of light alkenes by the gas phase oxidative cracking (GOC) or catalytic oxidative cracking (COC) of model high hydrocarbons (hexane, cyclohexane, isooctane and decane in the GOC process and hexane in the COC process) was investigated in this paper. The selection for the feed in the GOC process was flexible. Excellent conversion of hydrocarbons (over 85%) and high yield of light alkenes (about 50%) were obtained in the GOC of various hydrocarbons including cyclohexane at 750 °C. In the GOC process, the utilization ratio of the carbon resources was high; CO dominated the produced CO_X (the selectivity to CO_2 was always below 1%); and the total selectivity to light alkenes and CO was near or over 70%. In the COC of hexane over three typical catalysts (HZSM-5, 10% La_2O_3/HZSM-5 and 0.25% Li/MgO), the selectivity to CO_X was hard to decrease and the conversion of hexane and yield of light alkenes could not compete with those in the GOC process. With the addition of H_2 in the feed, the selectivity to CO_X was reduced below 5% over 0.1% Pt/HZSM-5 or 0.1% Pt/$MgAl_2O_4$ catalyst. The latter catalyst was superior to the former catalyst due to its perfect performance at high temperature, and with the latter, excellent selectivity to light alkenes (70%) and the conversion of hexane (92%) were achieved at 850 °C (a yield of light alkenes of 64%, correspondingly).

KEY WORDS: light alkenes; gas phase oxidative cracking; catalytic oxidative cracking; high hydrocarbons; hydrogen addition.

1. Introduction

Although light alkenes are commercially produced by the pyrolysis of hydrocarbons, present pyrolysis confronts some impediments in its further development, which mainly come from its inherent strongly endothermic nature. For example, in order to obtain reaction temperature as high as 850 °C or even higher, the temperature of the cracker wall in the pyrolysis has to be about 1000 °C, which is near the upper temperature limit of the materials for coils (1150 °C) [1].

Efforts have been continuously made to increase alkenes yields and decrease energy consumption as far as possible. Oxidative course emerges as one of the promising alternative methodologies due to its ability to alter the thermodynamics and dynamics of pyrolytic reactions and its internal heating characteristics that could greatly reduce the energy consumption. In 1990's, the homogeneous oxidative dehydrogenation of C_2–C_4 paraffins to parent olefins [2–4] has attracted researchers' attention owing to its high efficiency. Chen *et al.* [5] and Choudhary *et al.* [6] took note of the high ratio (about 10) of CO/CO_2 together with the higher conversion of hydrocarbons and a little decrease of the selectivity to alkenes in the dehydrogenation of ethane and propane, respectively, in the presence of steam and limited oxygen. Choudhary *et al.* also pointed out that the formation of CO instead of CO_2 was favorable because the former was also an important petrochemical feedstock. However, by far, it is yet not clear whether the above superiorities could be retained in the light alkenes preparation from high hydrocarbons because the scissions of much more C–C bonds are involved. Therefore, part of this paper would be focused on it.

Comparing with the work devoted to the catalytic oxidative dehydrogenation of light hydrocarbons, there exists very little work on the catalytic oxidative cracking (COC) of heavy feed. In this paper, three typical catalysts (HZSM-5, 10% La_2O_3/HZSM-5, and 0.25% Li/MgO) have been tested to find out which one is more preferable in the COC of model high hydrocarbon, hexane. There is a challenge for the reduction of selectivity to CO_X in the catalytic oxidative conversion of hydrocarbons, especially for heavy ones. Schmidt and co-workers. [7] had reported the positive effect of the addition of H_2 on the oxidative dehydrogenation of ethane, i.e., the selectivity to ethylene could be as high as 85% and the selectivity to CO_X was below 5% as well. They believed that preferential reactions between O_2 and H_2 with the aid of catalyst reduced the reactions between O_2 and ethane, depressing the formation of CO_X and offering enough heat to pyrolysis of ethane. They also applied the idea in the heavy feed such as cyclohexane, but the aim was to produce oxygenates or higher olefins [8]. In this paper, the effect of the addition of H_2 on the COC of hexane was investigated over the 0.1% Pt/HZSM-5 and 0.1% Pt/$MgAl_2O_4$ catalysts.

2. Experimental

HZSM-5 (SiO_2/Al_2O_3 = 96/3, 300 m^2/g, prepared by Chemistry Department of NanKai University, China)

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1011-372X/04/0400–0031/0 © 2004 Plenum Publishing Corporation

is first calcined in a muffle for 4 h at 540 °C in ambient air before used. 10% La_2O_3/HZSM-5, 0.25% Li/MgO, 0.1% Pt/HZSM5, 0.1% Pt/γ-Al_2O_3 and 0.1% Pt/$MgAl_2O_4$ catalysts were prepared by incipient wetness impregnation of HZSM-5, MgO (70 m^2/g), γ-Al_2O_3 (200 m^2/g) and $MgAl_2O_4$ (0.4 m^2/g) with the corresponding aqueous solutions of stoichiometric lanthanum nitrate, lithium nitrate and chloroplatinic acid. The impregnated samples were digested for 1 h at 55 °C and evaporated at 70 °C with stirring. Further drying was carried out at 110 °C. The dried powder was then calcined for 5 h in air at 600 °C (La_2O_3/HZSM-5), 800 °C (Li/MgO) and 500 °C (all platinum based catalysts). The calcined samples were then grounded and sieved (20–40 mesh). The reactions were carried out with a fixed-bed flow type quartz reactor (i.d. 6 mm × 300 mm) at 1 atm pressure. Empty reactor was used in the gas phase oxidative cracking (GOC) experiments, while quartz grain (20–40 mesh) was filled on both sides of the catalyst bed (10-mm length) to minimize the homogeneous reactions in the COC experiments. A chromel–alumel thermocouple inside a closed quartz thermowell (o.d. 2 mm × 240 mm), located in the center of the reactor was used to record reaction temperature. Another thermocouple was located outside the reactor and within the homothermal zone of a programmable tubular furnace (120-mm length) to show the control temperature. Temperature in this paper, if not specially mentioned, was the reaction temperature. Mass-flow controllers were used to control the flow rate of O_2, H_2 and N_2. Hexane was introduced as vapor with a syringe pump, preheater and superheater in series. Two American Varian 3800 Gas Chromatographs were used to analyze the products on line.

3. Results and discussion

3.1. *GOC of various heavy hydrocarbons*

Hexane, cyclohexane, isooctane and decane were chosen as the model compounds for the straight chain hydrocarbon, cycloalkane, branched chain hydrocarbon and long straight chain hydrocarbon, respectively, in the GOC process. The results for the GOC of above model compounds at 750 °C are summarized in figure 1, in which the data for the pyrolysis of them at comparable reaction conditions are also included for reference.

As shown in figure 1, the conversion of hydrocarbons and the yield of light alkenes (<C_4 olefins, that is ethylene, propylene, butylenes and butadiene) at 750 °C in the GOC process are obviously higher than those in the pyrolysis. For instance, they reach over 85% and about 50% in the GOC process, respectively, while they are below 64% and 44% in the pyrolysis, respectively. This could be attributed to the changes in the thermodynamics and dynamics in the presence of O_2 in the GOC process. Indeed, O_2, as an excellent free radicals initiator, could reduce the activation energy of the initial step of chain reactions and facilitated the whole process. Figure 1 also shows that unlike other model hydrocarbons, the pyrolysis of cyclohexane at 750 °C is negligible. This is reasonable because it is well known that naphthene is inferior to paraffin in the traditional pyrolysis due to its stable structure and tendency to agglomeration. However, unlike in the dynamics-controlled pyrolysis at 750 °C, there existed little differences in the performances of the GOC of various hydrocarbons especially for the feed cyclohexane. Therefore, the selection of feed in the GOC process is flexible and the GOC process appears to be fit for the naphthenes rich heavy feed at moderate temperature.

Although high conversion of hydrocarbons and yield of light alkenes were achieved, the selectivity to light alkenes in the GOC process was lower than that in the pyrolysis due to the formation of CO_X and benzene (for cyclohexane). Just as illustrated in figure 1, the selectivity to light alkenes in the GOC of hexane, isooctane and decane is usually about 13–15% lower than that in the pyrolysis while the selectivity to CO in the GOC process is also about 13–15%. For the GOC of cyclohexane, the selectivity

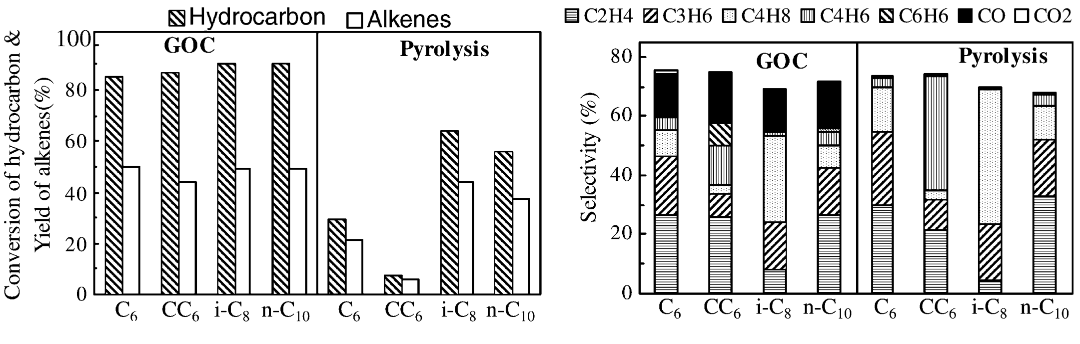

Figure 1. Pyrolysis and GOC of various hydrocarbons at 750 °C, a contact time of 0.7 s. GOC: atom mole ratio of C/O = 2.4, no dilution; Pyrolysis: nitrogen was used to keep the same contact time of corresponding hydrocarbons.

to CO and benzene is about 24%, which could compensate the decreased selectivity to light alkenes in comparison with that in the pyrolysis. Moreover, no matter what feed is chosen, the selectivity to CO_2 is always below 1% in the GOC process. Because CO and benzene are also valuable petrochemical products, the utilization ratio of carbons resources in the GOC process should be equivalent to or even higher than that in the pyrolysis process.

Heat from the CO_X formation reactions is vital for the oxidative course to be an internal heating possess, although the formation of CO_2 is not expected. As indicated above, the CO, but not CO_2, prevailed in the produced CO_X in the GOC process. Based on the industrial running data (the amount of the fuel is equal to 15–18% of the amount of the feed in the pyrolysis [9]) and the assumption (in the GOC process, part of feed was partially oxidized to CO and water offering heat to the pyrolysis of the remained feed), some important parameters for the GOC process in an autothermal mode were calculated and summarized in table 1, i.e., the hydrocarbon/O_2 ratio, the ratio of CO_2 from the pyrolysis and CO_2 from the GOC process and the proportion of CO in the total carbon resources in the GOC process. Table 1 shows that a proper hydrocarbon/O_2 ratio of 0.4–0.6 (atom mole ratio of C/O is about 2.4) can be chosen to run the GOC of various hydrocarbons in an autothermal mode. The autothermal mode minimizes the emission of CO_2 from the external burning of fuel. Just as shown in table 1, the emission of CO_2 in the pyrolysis is about 13–19 times larger than that in the GOC process. Therefore, about 90% of CO_2 emission in the pyrolysis would be saved in the GOC process.

The utilization ratio of total carbon resources in both processes is illustrated in figure 2 on the premises that fuel is also the carbon resources and the formation of CO is the effective utilization of carbon resources. About 13–15% of total carbon resources is wasted in the form of CO_2 in the pyrolysis while about 20–24% of total carbon resources is converted to CO in the GOC process. Therefore, the utilization ratio of total carbon resources in the GOC process is greater than that in the pyrolysis. However, it should be noted that in the pyrolysis, the wasted carbon resource mainly comes from the cheaper fuel oil, natural gas etc. while the CO comes from the valuable feed in the GOC process. So the GOC process seems fit for the cheaper heavy feed such as heavy oil and residual etc. Due to the considerable CO in the products, the GOC process is not suitable for the preparation of pure light alkenes but suitable to offer raw materials to some process such as hydroformylation, which demands for the mixture of alkenes and CO.

Table 1
Calculated parameters in the GOC of various hydrocarbons in an autothermal mode

	Hexane	Cyclohexane	Isooctane	Decane
Hydrocarbon/O_2 (Autothermal mode)[a]	0.7–0.8	0.7–0.8	0.5–0.6	0.4–0.5
Ratio of CO_2 (Pyro.)/CO_2(GOC)[b]	16–19	16–19	13–16	14–16
CO/total carbon source (%)[c]	20–23	21–24	20–24	21–24

[a] Ratio of hydrocarbon and oxygen; for the GOC process in an autothermal mode.

[b] Ratio of CO_2 from the pyrolysis and CO_2 from the GOC in an autothermal mode.

[c] Proportion of carbon resource in the produced CO in the total carbon resource.

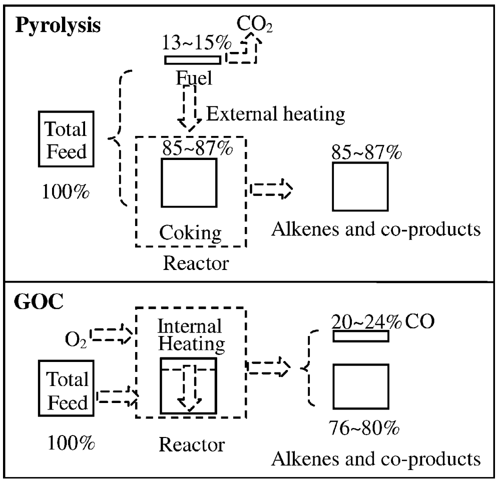

Figure 2. Illustration for the utilization ratio of carbon resources in the pyrolysis or GOC process.

3.2. COC of hexane

It is well known that the catalysts, which are successfully applied in the catalytic oxidative dehydrogenation of C_2–C_4 hydrocarbons, could not be simply extrapolated to the COC of heavy hydrocarbons due to the involvement of the cracking of more C–C bonds. Therefore, three typical catalysts (HZSM-5, 10% La_2O_3, 0.25% Li/MgO) were selected to find out which is preferable for the COC of model compound, hexane. A solid acid catalyst, HZSM-5, is famous for its ability to crack the heavy hydrocarbons to light ones; a basic catalyst, Li/MgO, is good at its dehydrogenation ability [10]; a rare earth metal modified solid acid catalyst, La_2O_3/HZSM-5, was selected because excellent catalytic performance was reported in the catalytic pyrolysis of naphtha with the similar catalyst [11].

Experiments for the effect of quartz grain on the GOC reaction indicated that under certain reaction conditions, the quartz grain could hinder the GOC reactions to an extent enough for the separate study on

Table 2
COC of hexane (C6) with three typical catalysts at 700 °C, $C6/O_2/N_2$ = 12/15/93 (mL/min, STP), GHSV = 30,000 h^{-1}

Entry		Conv. (%)		Selectivities (%)			
		C6	Alkenes	Alkanes	BTX	CO	CO_2
1	Blank[a]	89.56	63.58	16.27	0.22	12.62	0.08
2	Quartz grain	10.42	79.69	8.77	0	1.39	0
3	HZSM-5[b]	53.30	47.77	22.33	5.48	18.95	4.31
4	La/HZSM-5[b]	43.22	52.23	14.84	3.79	19.61	7.88
5	Li/MgO[b]	64.44	67.51	6.61	0.53	3.79	10.46

[a] Empty tube.

[b] Both sides of the catalysts were filled with quartz grain.

the catalytic reactions (see, table 2, entry 1 and 2). The experiments of COC of hexane with various catalysts were performed just under these conditions. As shown in table 2, the Li/MgO catalyst is superior to the other two catalysts. With the Li/MgO catalyst, the conversion of hexane and the selectivity to light alkenes were 64.4% and 67.5%, respectively, however the selectivity to CO_2 was as high as 10.5%. For the solid acid catalysts, the conversion of hexane was relatively low and the selectivity to light alkanes and aromatics were high (although lanthanum addition could reduce them to a certain extent). Furthermore, with the solid acid catalysts, the selectivity to CO was over 18% indicating that active sites on the catalysts preferred to catalyze the partial oxidation reactions rather than the cracking reactions. The Li/MgO catalyst was the most promising one among the catalysts tested here, but the conversion of hexane and the yield of light alkenes over it still cannot compete with those in the GOC process. No matter what catalyst was chosen, the selectivity to CO_X could not be reduced enough. Therefore, in the presence of catalysts, it was hard to prevent the partial or total oxidation reactions between O_2 and hexane. Thus we performed the following experiments of the COC of hexane with the addition of H_2 in the feed and expected to reduce the selectivity to CO_X effectively.

3.3. *COC of hexane with the addition of H_2*

Pt/HZSM-5 catalyst (0.1%) was first chosen to catalyze the COC of hexane with the addition of H_2. Platinum, as the active component, is well known for its catalytic performance for a combustion reaction, while HZSM-5, as the support, is widely used in the catalytic cracking of heavy hydrocarbons to light ones. As shown in figure 3, the conversion of hexane and O_2 was high (70% and 99%, respectively) and the selectivity to CO_X was below 5% over the 0.1% Pt/HZSM-5 catalyst. When only the HZSM-5 was used, not only the conversion of O_2 was low, but also the cracking ability of the HZSM-5 at low temperature was inhibited. It was believed that without platinum, instead of reacting with H_2 in the feed, O_2 reacted with the activated C atoms and H atoms in the hexanes absorbed on the surface of the HZSM-5, forming CO and CO_2 and leaving carbon precursors on the active sites. These carbon precursors could not be easily eliminated by O_2 at low temperature, therefore the cracking activity of the HZSM-5 was sharply decreased. When the platinum was supported on γ-Al_2O_3, the conversion of O_2 was complete, however, the conversion of hexane was low and the selectivity to CO_2 was as high as 63%. This indicated that 0.1% Pt/γ-Al_2O_3 catalyst could not catalyze the cracking of hexane but the total oxidation of hexane. Based on the experiments with three catalysts, it was evident that with the aid of platinum, most of O_2 reacted with H_2 releasing heat to the cracking of hexane on the HZSM-5. Therefore, 0.1% Pt/HZSM-5 was an excellent bifunctional catalyst.

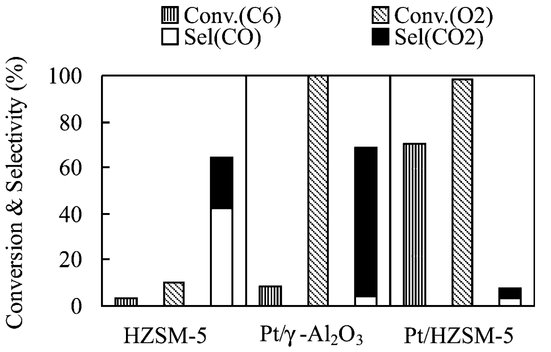

Figure 3. Effect of the addition of hydrogen on the COC of hexane at a control temperature 500 °C, hexane/O_2/H_2/ N_2 = 12/15/15/78 (mL/min STP), GHSV = 30,000 h^{-1}.

The effect of mole ratio of H_2/O_2 on the COC of hexane with H_2 addition was studied over the 0.1% Pt/HZSM-5 catalyst and illustrated in table 3. With the increase of the concentration of H_2, the conversion of hexane increased to 78% and the selectivity to CO_X decreased to 2%. It was obvious that with the increase of the ratio of H_2/O_2, the reactions between O_2 and hexane were further depressed and more active sites were ready for the cracking of hexane. Table 3 also shows that without the participation of O_2 (a H_2/O_2 mole ratio of ∞), the conversion of hexane is decreases by 30%, which can be attributed to the lower temperature around the catalyst in an endothermic process. The temperature profile along the reactor showed that at the same control temperature (500 °C), the reaction temperature of the COC process with H_2 addition could reach 630 °C while it was only 480 °C due to the endothermic nature of the non-oxidative catalytic process. With the increase of the ratio of H_2/O_2, the selectivity to light alkenes also increased a little, but not over 55% due to the high selectivity to C_2–C_4 alkanes (as high as 32%) in the products. High reaction temperature favored the increase of the selectivity to light alkenes and the decrease of the selectivity to C2–C4 alkanes. As shown in table 4, the selectivity to light alkenes increases to over 60% while the selectivity to C_2–C_4 alkanes decreases to 21% and the selectivity to CO_X is still below 5% at a reaction temperature of 717 °C. The results at higher reaction temperature had not been achieved because of the poor thermostability of the support HZSM-5.

In order to obtain the results at high temperature, the second platinum based catalyst, 0.1% Pt/$MgAl_2O_4$, was chosen. The effect of the temperature on the COC of hexane with the addition of hydrogen ($H_2/O_2 = 1$) over the 0.1% Pt/$MgAl_2O_4$ catalyst was investigated and listed in table 5. It shows that the

Table 3
Effect of mole ratio of H_2/O_2 on the COC of hexane (C_6) with the addition of hydrogen over a 0.1% Pt/HZSM-5 catalyst at a control temperature 500 °C, $C_6/O_2 = 12/15$ (mL/ min STP), nitrogen was used to balance the GHSV (30,000 h^{-1})

$n(H_2)/n(O_2)$[a]	Conv. (%)				Selectivity (%)				
	C_6	O_2	C_2H_4	C_3H_6	C_4H_8	BTX	CH_4	C_2–C_4[b]	CO_X
0	68.72	98.05	14.04	26.26	9.80	4.62	1.81	26.49	15.32
1	69.92	98.62	15.72	27.42	10.60	5.08	2.02	29.70	7.36
2	72.85	97.48	16.80	27.06	10.40	6.84	2.47	30.94	3.25
3	77.77	98.54	17.43	26.02	10.04	7.19	2.86	31.95	2.19
∞	48.16	–	13.93	28.83	12.81	2.89	1.40	35.97	0

[a] Mole ratio of hydrogen and oxygen.
[b] C_2–C_4 alkanes.

Table 4
Effect of temperature on the COC of hexane (C_6) with the addition of hydrogen over a 0.1% Pt/HZSM-5 catalyst, $C_6/O_2/H_2/N_2 = 12/15/45/48$ (mL/min STP), GHSV = 30,000 h^{-1}

T(°C)[a]	Conv. (%)				Selectivity (%)				
	C_6	O_2	C_2H_4	C_3H_6	C_4H_8	BTX	CH_4	C_2–C_4[b]	CO_X
531 (350)	64.37	99.22	10.68	18.75	12.32	6.03	2.13	42.87	1.35
580 (450)	76.85	98.32	15.33	23.23	10.63	7.45	2.54	36.22	1.21
650 (540)	78.24	98.60	18.91	28.64	9.82	6.68	3.23	28.41	2.69
717 (640)	84.98	100.00	23.17	30.63	8.35	7.49	4.58	21.49	3.15

[a] Temperature in the brackets are the control temperatures.
[b] C_2–C_4 alkanes.

Table 5
Effect of temperature on the COC of hexane (C_6) with the addition of hydrogen over a 0.1% Pt/$MgAl_2O_4$ catalyst, $C_6/O_2/H_2/N_2 = 12/15/15/78$ (mL/min, STP), GHSV = 30,000 h^{-1}

T(°C)[a]	Conv. (%)				Selectivity (%)				
	C_6	O_2	C_2H_4	C_3H_6	C_4H_8	C_4H_6[b]	CH_4	C_2–C_4[c]	CO_X
747 (650)	17.34	99.02	14.74	10.88	7.80	1.01	4.52	1.22	43.80
786 (700)	33.76	96.63	26.86	18.73	12.43	2.25	7.35	1.98	20.36
821 (750)	67.94	96.14	34.49	21.29	10.86	3.88	9.71	2.38	11.02
855 (800)	91.78	96.26	39.63	19.22	6.07	5.12	12.15	2.46	10.19

[a] Temperature in the brackets are the control temperatures.
[b] Butadiene.
[c] C_2–C_4 alkanes.

Table 6
Effect of mole ratio of H_2/O_2 on the COC of hexane (C_6) with the addition of hydrogen over a 0.1% Pt/$MgAl_2O_4$ catalyst at 820 °C, C_6/O_2 = 12/15 (mL/min STP), nitrogen was used to balance the GHSV (30,000 h^{-1})

$n(H_2)/n\ (O_2)$[a]	Conv. (%)				Selectivity (%)				
	C_6	O_2	C_2H_4	C_3H_6	C_4H_8	C_4H_6[b]	CH_4	C_2–C_4[c]	CO_X
0	61.96	97.09	29.34	18.84	10.30	3.02	8.17	1.94	22.44
1	67.49	96.14	34.49	21.29	10.86	3.88	9.71	2.38	11.02
2	70.65	95.80	36.31	22.53	10.63	4.15	10.90	2.51	6.15
3	72.76	93.37	37.00	22.91	9.96	3.96	12.16	3.00	4.31

[a] Mole ratio of hydrogen and oxygen.
[b] Butadiene.
[c] C_2–C_4 alkanes.

excellent catalytic performance of the 0.1% Pt/$MgAl_2O_4$ catalyst is achieved only at high temperature. For example, at 850 °C, the selectivity to light alkenes and the conversion of hexane reached 70% and 92%, respectively, (a yield of light alkenes of 64% correspondingly) while they were too low (34% and 17%, respectively) and the selectivity to CO_X was too high (44%) at 750 °C. The selectivity to CO_X decreased with the increase of the temperature and reached about 10% at 850 °C. Unlike with the 0.1% Pt/HZSM-5 catalyst (see table 3 and table 4), ethylene but not propylene was the dominated light alkene with the 0.1% Pt/$MgAl_2O_4$ catalyst. It is reasonable because the reaction mechanisms over these two catalysts are totally different. It is well known that the mechanism for the HZSM-5 catalyst at moderate temperature is a carbonium mechanism while a free radical mechanism should be for the 0.1% Pt/$MgAl_2O_4$ catalyst at high temperature.

With the increase of the ratio of H_2/O_2 at 820 °C, the selectivity to CO_X was further decreased and below 5% at a H_2/O_2 ratio of three (see, table 6) in the COC of hexane with H_2 addition over the 0.1% Pt/$MgAl_2O_4$ catalyst. The conversion of hexane and the selectivity to light alkenes also increased with the increase of the H_2/O_2 ratio and reached to 73% and 74%, respectively, (a yield of light alkenes of 54% correspondingly) at a H_2/O_2 ratio of three. Therefore, with the 0.1% Pt/$MgAl_2O_4$ catalyst, high selectivity to alkenes and low selectivity to CO_X could be obtained at high temperature in the COC of hexane with H_2 addition. It should be noted that unlike pyrolysis, the high reaction temperature was easily obtained due to the exothermic nature of the reactions. In fact, as shown in table 5, the control temperature is far below the reaction temperature.

4. Conclusions

The GOC of heavy hydrocarbons is an efficient process with the traits of a high conversion of the flexible feeds (especially for the naphthene rich feed), a high yield of light alkenes, a high utilization ratio of carbon sources and a low emission of CO_2 in an autothermal mode. Due to the high selectivity to CO_X, high selectivity to alkenes was hard to obtain in the COC of hexane in the presence of only oxygen. With the addition of H_2 in the feed, the selectivity to CO_X could be sharply decreased and the selectivity to alkenes was enhanced. With the 0.1% Pt/$MgAl_2O_4$ catalyst, 92% conversion of hexane, 70% selectivity to alkenes (a yield of alkenes of 64%, correspondingly) and 10% selectivity to CO_X could be obtained with a ratio of H_2/O_2 of 1 at 850 °C.

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