LBL-32858
UC Code 108

QUARTERLY REPORT

July 1, 1992 - September 30, 1992

CONVERSION OF ETHANE AND OF PROPANE TO HIGHER OLEFIN HYDROCARBONS

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This work was supported by the Assistant Secretary for Fossil Energy, Office of Technical Coordination, U.S. Department of Energy under Contract DE-AC03-76SF00098, through the Pittsburgh Energy Technology Center, Pittsburgh, Pennsylvania.

INDEX

I. Task Description for FY 1992

Initial work on this project has shown that it is possible to convert ethane and propane in the presence of steam and oxygen over a catalyst comprising calcium-nickel-potassium oxide to both lower and higher hydrocarbons at temperatures in the range of 300-600° C. Major amounts of CO_2 are formed at the higher temperatures and conversions are relatively low at the lower temperatures. However, there are indications that the objective of preparing C_6 to C_{12} olefins may be achieved by operating at intermediate temperatures and much higher space velocities than have thus far been used. It is proposed to do a systematic investigation making blank runs to distinguish between thermal and catalytic reactions and investigating modified catalysts such as calcium cobalt potassium oxide, calcium nickel sodium oxide, magnesium nickel potassium oxide, and others. A wide variety of operating conditions will be investigated. The catalytic reaction mechanism and the role of carbon on the catalyst will be investigated by experiments with carbon and oxygen isotopes.

II. Introduction

It has become apparent during the past few months that results obtained in the oxidative coupling of methane cannot be extended to ethane and propane. Good selectivities and yields for the oxydehydrogenation to olefins can be obtained but production of higher hydrocarbons is small. The present report summarizes results of experiments using zeolite based catalysts and compares these with basic oxide catalysts.

III. Highlights

- The oxydehydrogenation of ethane over zeolite based catalysts (H^+-, Na^+-, Ni^{2+}-, Pt^{2+}-, Ga^{3+}-, and [V]-ZSM-5) and oxide catalysts (Li/MgO, Ca-Ni-K) was studied in the temperature range 450-600°C.

- Selectivity to olefins close to 80% was achieved at 550 °C.

- Basic (Na-ZSM-5) and neutral (V-ZSM-5) zeolite catalysts were shown to be more active and selective for the oxydehydrogenation of ethane than oxide catalysts.

- Small, but significant amounts of higher C_{3+} hydrocarbons were produced when using ZSM-5 containing Ga- Pt- or Ni- cations. Na-, V-, and H-exchanged ZSM-5 are less effective in producing C_{3+} hydrocarbons.

- Steam has a profound effect on the performance of both zeolite based and oxide catalysts. For zeolite catalysts, the addition of steam can enhance their selectivity to hydrocarbons and reduce their tendency to form methane. In contrast, the presence of steam causes a decline in the activity and selectivity to hydrocarbons of oxide catalysts during the oxydehydrogenation of ethane.

- High conversion (~42%) and high selectivity (~78%) to hydrocarbons were achieved at temperatures around 550°C. Higher reaction temperature results in the formation of methane and lower reaction temperature causes lower selectivity to hydrocarbons.

IV. Progress of Studies

Using SnO_2 or Dy_2O_3 promoted Li^+-MgO-Cl^- catalysts for the oxydehydrogenation of ethane, Lunsford et al [1] were able to achieve ethylene yields of up to 55% with selectivity to ethylene of >70% at temperatures ~600°C. Among the oxidized products, carbon dioxide is predominant. No hydrocarbon products other than C_2's and C_3's were reported. The formation of methane was negligible.

In the present study, the performance of ZSM-5 zeolite exchanged with different metal cations was explored for the oxydehydrogenation of ethane. For comparison, some catalysts which have shown activity for the oxidative coupling of methane were also studied, e.g. Ca-Ni-K oxide [3], and Li-Mg oxide [4]. In light of a previous discovery [3] that steam can greatly increase the selectivity to hydrocarbons in the oxidative coupling of methane over Ca-Ni-K oxides [3] and Li-Mg oxide [4], the effect of adding steam into the reaction mixture of ethane and oxygen has also been investigated.

Most of the data were obtained at 550°C. Although, in terms of selectivity to hydrocarbons, these catalysts were not greatly superior to those reported in the literature [1] (e.g., Li/MgO, containing small amounts of promoters, such as Cl^- or other oxides, i.e. Dy_2O_3, or SnO_2), they offer alternatives to develop catalysts which are active at lower temperatures and are of greater thermal stability. Therefore, zeolite-based materials hold promise for developing catalysts of high selectivity to hydrocarbons for the oxydehydrogenation of ethane.

One of reasons to choose zeolite based catalysts is their ability to convert light hydrocarbons to higher hydrocarbons. Due to their ion exchangeability and structure diversity, zeolite materials offer a variety of choices of possessing either acidic or basic, or neutral properties, and having more than one type of active sites. A combination of the right features may give good catalytic performance.

Acid-form ZSM-5 zeolites have been studied for the oxydehydrogenation of ethane [2] by using oxygen or nitric oxide as oxidants. Selectivities to ethylene of up to 60% were obtained at low reaction temperature (~400°C) and very low conversion. Carbon dioxide was the only oxidation product and no carbon monoxide formation was mentioned.

Ca-Ni-K oxide [3] and Li-Mg oxide [4] have been shown to be moderately selective for the oxidative coupling of methane at relatively low temperature and long contact time and in the presence of steam. In addition to the dominant C_2 products, those catalysts were also able to generate small amounts of higher hydrocarbons (C_3's and C_4's). Thus, it is interesting to see if these catalysts can facilitate the oxydehydrogenation and oxidative coupling of ethane.

A. EXPERIMENTAL

a) Materials:

High purity grade (99.8+%) ethane and oxygen were obtained from Matheson and were used without further purification. Ga_2O_3 (99.99%) was from Aldrich.

$Ca_3NiK_{0.1}$ oxide was prepared following the procedure described previously [3].

Li/MgO was prepared from their corresponding nitrates and calcined at 680°C. Before calcination, the homogenized mixture was heated on a hot plate to near dryness. The presence of a small amount of water in the material before calcined seemed to be essential for better performance.

Zeolite H-ZSM5 was prepared and characterized by the standard method [5], giving a sample having a SiO_2/Al_2O_3 molar ratio of 59/1. The ZSM-5 consisted of hexagonally terminated lath-like crystal (average size ca. 2 μm) associated into aggregates as shown by scanning electron microscopy.

Na^+–, Ga^{3+}–, and Ni^{2+}– exchanged ZSM-5 samples were prepared by exhaustive ion-exchange of H-ZSM-5 zeolite with the corresponding 1.0 M nitrate solutions. The concentration of metal cations of the exchange zeolites samples were determined by atomic absorption spectroscopy and is given in Table 1a.

Pt-ZSM-5 was prepared by exchanging of 5 g of H-ZSM-5 with 20 cm^3 of 0.5wt.% $Pt(NH_3)_4Cl_2$ aqueous solution.

V-ZSM-5 was prepared by treatment of H-ZSM-5 zeolite with $VOCl_3$ via gas-solid state reaction. Treatment with $VOCl_3$ was carried out in a quartz reactor (I.D. 35 mm) with the zeolite (5.0 g) supported on a quartz frit. The zeolite was first dehydrated at 520°C for 2h in a stream of dry nitrogen (120 $cm^3 \cdot min^{-1}$), following which the zeolite was treated for 1h at 520°C with a nitrogen stream saturated with $VOCl_3$ vapor at 20°C (p_{VOCl_3} ca. 2.1 kPa). At the end of this treatment, the sample was purged with dry nitrogen for 1h at room temperature after initial rapid quenching from 520°C. The treated zeolite sample was used after shaking the zeolite overnight in 1.0 M HCl solution (35 cm^3) at room temperature. This treatment resulted in the total removal of the acidic sites. XRD examination gave no evidence of structural change in the H-ZSM-5 as a result of these treatments. XPS examination of V-ZSM-5 showed that most of the introduced vanadium remains as V^{5+} (~93%) with a small fraction of V^{4+} species (~ 7%) which was believed formed by the reduction of V^{5+} by HCl suggested by Whittington and Anderson [6].

b) Reactions and Product Analysis

Reactions were carried out in a tubular quartz reactor (I.D., 10 mm). The reactor was half-filled with quartz chips to reduce post-reaction dead volume. Catalyst samples (0.5 g) were first pretreated in oxygen (20 $cm^3 \cdot min^{-1}$) at 450- 550°C for more than 4 h, then cooled or heated to the required reaction temperature before pe-mixed reactants (ethane: 3 $cm^3 \cdot min^{-1}$; oxygen: 1 $cm^3 \cdot min^{-1}$) were introduced. Reactions in the presence of steam were also conducted. In this case, the ratio of ethane to steam was 5:6 while the ratio of ethane to oxygen was kept the same as in the absence of steam. The steam was introduced in the manner previously reported [3].

The composition of reaction effluent gas was analyzed by on-line gas chromatography (Hewlet-Packard 5890, packed columns: Carbon Sieves IIS column/TCD; Porapak-Q column/FID). A cold trap (ice-bath) was used at the outlet of the reactor in order to remove water and other liquid products. No attempts were made to obtain quantitative data for the liquid product collected in the cold trap.

B. RESULTS AND DISCUSSION

A number of zeolite and oxide catalysts were tested for the oxydehydrogenation of ethane. Experiments in the presence and in the absence of steam were conducted in order to investigate the effect of steam on the reaction between ethane and oxygen. The results obtained are summarized in Table 1b. To check the potential contribution made by the reactor materials, blank experiments were carried out at different temperatures. Under identical experimental conditions, the contribution of reactor materials was insignificant until the reaction temperature reached 600°C. At this and higher temperature, the reactions were dominated by the formation of carbon dioxide. At lower temperatures (≤ 550°C), ethylene was the predominant constituent among the hydrocarbon products, indicating that in the absence of catalysts cracking was not important. It appeared that addition of steam increased the production of carbon monoxide, suggesting that steam reforming might take place.

a) Zeolite Based Catalysts

1) In the Absence of Steam

The data of Table 1 show that the activity of catalysts in facilitating the conversion of in the presence of oxygen decreases in the order of: Na-ZSM-5 > V-ZSM-5 > Ni-ZSM-5 ~ H-ZSM-5 ~ Ga-ZSM-5 > Pt-ZSM-5. Except for Pt-ZSM-5, most of these catalysts gave high selectivity to hydrocarbons. However, the relatively high activity of Ga-ZSM-5 and Ni-ZSM-5 in promoting cracking, leading to the formation of methane and carbonaceous materials makes them unsuitable for the oxydehydrogenation of ethane to produce ethylene. The high conversion and selectivity to hydrocarbons of Na-ZSM-5 compared to H-ZSM-5 suggests that basic sites (created by replacing H^+ by Na^+) are more effective in catalyzing the oxydehydrogenation of ethane than the Brönsted acid sites present in H-ZSM-5. Nevertheless, H-ZSM-5 is also able to facilitate the reaction and gives quite high selectivity to hydrocarbons (>50% at 550°C). This is in agreement with previous work [2]. However, in contrast to that work where CO_2 was reported as the only oxidation product, CO was the predominant oxidation product over H-ZSM-5 in the present work. Actually, except for transition metal containing V-ZSM-5, Pt-ZSM-5 and Ni-ZSM-5 zeolites, all the other zeolite catalysts produced much greater amount of CO than of CO_2. Obviously, this is associated with the oxidation ability of the metal cations. The high activity and selectivity to hydrocarbons of V-ZSM-5 are the result of incorporation of V^{5+} into the framework of ZSM-5 and the total removal of the acidic sites. XRD examination of the V-ZSM-5 gave no evidence of structural change in the ZSM-5 and XPS measurement of V-ZSM-5 revealed that most of the introduced vanadium species remain as V^{5+} (93%) with only a small fraction of V^{4+} species (~7%) which was probably formed by the reduction of V^{5+} by HCl during the post-reaction treatment in a diluting HCl aqueous solution in order to remove those non-framework species generated during the treatment with $VOCl_3$. Vanadium oxides are known to be good catalysts for the oxidation or partial oxidation of light alkanes [8]. Introduction of V^{5+} species into the zeolite framework greatly increased the CO_2 to CO ratio (from 0.1 of H-ZSM-5 to 1 of V-ZSM-5). This is the result of oxidation of CO to CO_2 which most probably occurs on V^{5+} sites because the total amount of CO_x remained the same. Over most zeolite based catalysts, an appreciable amount of higher hydrocarbons (C_{3+}) was formed in addition to the dehydrogenation product ethylene and the oxidation products CO_x. This means that either oxidative coupling of ethane or ethylene oligomerization also occurred. In some cases, a small but significant amount of liquid condensate was obtained, suggesting oligomerization reactions might have taken place leading to the formation of higher hydrocarbons.

2) In the Presence of Steam

The addition of steam had little or no effect on the activity of these catalysts, except for H-ZSM-5, in which case, steam greatly reduced its activity (from 29% to 18%). Apart from this decline in activity, the effect on the product distribution was only marginal. Generally, it appears that adding steam increases the selectivity to hydrocarbons. Ni-ZSM-5 is an exception. In the case of Ga-ZSM-5, steam significantly reduced the formation of methane (from 31% to 8%). This can not be explained by the interaction between water molecules and Ga species because for an unsupported Ga_2O_3 catalyst steam addition caused a great increase in cracking activity (*vide infra*). A possible explanation is a potential synergistic effect between Ga^{3+} sites and Brönsted acid sites. This may have implications for the CYCLAR Process developed by British Petroleum Co. to make aromatics from light alkanes (e.g. propane) using Ga-ZSM-5 zeolite as catalyst where cracking represents a major side reaction.

Results in Table 1b also show that except for Pt-ZSM-5 and Ni-ZSM-5, the addition of steam did not change the amount of C_{3+} hydrocarbon products. For Pt-ZSM-5, steam greatly increased the production of C_{3+} hydrocarbons, whereas for Ni-ZSM-5, steam significantly reduced the amount of C_{3+} hydrocarbons formed. Among the zeolite catalysts, Ga^{3+}-, Pt^{2+}-, and Ni^{2+}- containing ZSM-5 catalysts gave higher selectivity to C_{3+} hydrocarbons than those exchanged with Na^{+}-, V^{5+}-, and H^{+}. This may be attributed to the high activity of Ga^{3+}, Pt^{2+}, and Ni^{2+} in catalyzing dehydrogenation and aromatization of hydrocarbons. Na^{+}, V^{5+} and H^{+} are much less effective in facilitating such reactions and thus produce less amount of higher hydrocarbons.

b) Oxide Catalysts

1) In the Absence of Steam

The activity of oxides decreases in the order of: Li/MgO > $Ca_3NiK_{0.1}O_x$ ~ Ga_2O_3 while the selectivity to hydrocarbons follows the order of : Li/MgO > Ga_2O_3 >> $Ca_3NiK_{0.1}O_x$. The high selectivity to hydrocarbons of Li/MgO is in agreement with previous work [1]. Ca-Ni-K oxide catalyst is the least active and selective in catalyzing the oxydehydrogenation of ethane. Thus, despite its similarity to Li/MgO in the oxidative coupling of methane, Ca-Ni-K oxide is not effective in facilitating the reaction of ethane with oxygen. Judging from the amount of C_{3+} hydrocarbons formed relative to the amount of dehydrogenation product, both Ca-Ni-K oxide and Li/MgO oxide catalyst are not effective in catalyzing reactions leading to the formation of higher hydrocarbons (C_{3+}). Therefore, catalysts good at oxidative coupling of methane may not be effective in the oxidative coupling of ethane.

2) In the Presence ot Steam

For Li/MgO catalyst, addition of steam dramatically decreased the activity and selectivity to hydrocarbons. The presence of steam also had negative effect on the activity and selectivity to hydrocarbons of Ga_2O_3 catalyst. For Ca-Ni-K oxide catalyst, steam seems to have little effect on its activity, but significantly increases its selectivity to hydrocarbons. Generally, it appears clear that steam does not have a positive effect on the oxide catalysts, two of which are shown to be quite active and moderately selective in the oxidative coupling of methane in the presence of steam at temperatures around 600 °C.

In addition to the differences described above between zeolite catalysts and oxide catalysts, the former generate a greater amount of higher hydrocarbons (C_{3+}) than the latter. In particular, the production of C_{3+} hydrocarbons over Ga-ZSM-5 catalyst was quite significant. This is in agreement with the high aromatization activity observed over a similar Ga-ZSM-5 catalyst [7].

In summary, in the absence of steam, V-ZSM-5 and Na-ZSM-5 catalysts perform better at our conditions than Li/MgO catalyst (one of the best catalysts reported in literature), and in the presence of steam the former are much better than the latter. Therefore, zeolite based catalyst are superior to oxide catalysts.

c) Effect of Temperature

1) H-ZSM-5 catalyst

Results obtained using H-ZSM-5 catalyst at different temperatures are reported in Table 2. Under the present experimental conditions, much lower selectivity to hydrocarbons and more dominant CO formation were obtained compared to previous results obtained by others [2]. This may be due to the lower ethane/oxygen ratio (3/1) used compared to that of previous work (ethane/oxygen= 10/1) [2]. It appears that conversion and selectivity to hydrocarbons increase with the increase of temperature. Below 600°C, cracking is not significant. The presence of steam significantly lowered the conversion of ethane and at the same time enhanced the selectivity to hydrocarbons and lowered the formation of methane.

In summary, higher selectivity to hydrocarbon was achieved on H-ZSM-5 by addition of steam into the reactant mixture. However, the addition of steam lowers the conversion of ethane and the ethylene yield is about the same. Steam definitely inhibits cracking to methane. This may imply that presence of steam alters the reaction course of ethane with oxygen. This effect will be addressed in the future work.

2) Ga-ZSM-5:

Tables 3 and 4 present the results obtained over Ga_2O_3 and Ga-ZSM-5 catalysts. The later was a physical mixture of Ga_2O_3 and H-ZSM-5 * . Data in Tables 3 to 4 show that Ga-ZSM-5 is more active than both H-ZSM-5 and Ga_2O_3 alone. This indicates that Ga_2O_3 has a promoting effect on H-ZSM-5 for the reaction of ethane with oxygen. Ga_2O_3 gave a lower

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* Previous work [7] showed that a physical mixture of H-ZSM-5 zeolite and Ga_2O_3 behaved very similarly to a GaH-ZMS-5 obtained by ion exchange of H-ZSM-5 with Ga^{3+} in activating light alkanes.

ethylene/methane ratio and higher cracking activity than H-ZSM-5. This is also reflected in Ga-ZSM-5. Thus, in terms of making ethylene from ethane, introduction of Ga into zeolite failed to increase the selectivity to hydrocarbons other than methane. The purpose of investigating Ga-containing zeolite was the demonstrated activity of gallium in enhancing the aromatization of small alkanes, for instance propane [7]. The enhancement of cracking activity by introducing gallium may imply that its role in activating a carbon-carbon bond which leads predominantly to cracking product is greater than that in activating a carbon-hydrogen bond resulting in dehydrogenation and or new carbon-carbon bond formation. With each of these catalysts, a significant effect of steam was observed. Addition of steam slightly reduced the activity of the catalyst but greatly increased the selectivity to hydrocarbons. Presence of steam significantly reduced the formation of methane.

In addition to the effects of steam mentioned above, the presence of steam increased the CO/CO_2 ratio, suggesting that the water-gas shift reaction was not significant . Data of Tables 2-4 imply that the lower the reaction temperature the greater the effect of steam. Reactions at lower temperatures greatly reduce the formation of cracking product. Thus, lower reaction temperatures are desirable to avoid the formation of methane. However, reactions at temperatures below 550°C tend to give lower selectivity to hydrocarbons. Therefore, a reaction temperature around 550°C seems to be optimal for achieving high selectivity to hydrocarbons while maintaining a low level of cracking.

3) V-ZSM-5 catalyst

Table 5 gives results obtained with a V-ZSM-5 catalyst. Higher reaction temperatures favor the formation of hydrocarbon products over that of carbon oxides. Steam plays a very significant role at lower reaction temperatures. The presence of steam lowers the activity of the catalyst and significantly enhances the selectivity to hydrocarbons. However, in this case, the presence of steam did not change the cracking activity of the catalyst presumably due to the fact that V-ZSM-5 catalyst has a very much lower cracking activity than H-ZSM-5, Ga_2O_3, and Ga_2O_3/H-ZSM-5 catalysts. Another effect of adding steam was to lower the CO/CO_2 ratio which is contrary to what was found on H-ZSM-5 and Ga_2O_3 catalysts. The effect of steam at higher temperatures ($\geq$ 600°C) is negligible.

4) Na-ZSM-5 catalyst

Data of Table 6 show that there is no noticeable effect of steam on the activity of the catalyst. However, steam had a significant effect on product distribution. At temperatures ≤450°C, steam greatly enhances the selectivity to hydrocarbons and lowers the cracking activity. This is evidenced by a much greater ethylene to methane ratio in the presence of steam (22 vs. 4). Steam also increases the CO to CO_2 ratio. This enhancement suggests that the water gas shift reaction does not play an important role at temperatures ≤450°C. An increase in CO to CO_2 ratio (from 0.1 to 0.9) and a decrease in ethylene to methane ratio (from 35 to 15) at 500°C indicates that the role of steam is to decrease the oxidation of CO to CO_2 and to increase cracking activity. At 550°C, adding steam increases the selectivity to hydrocarbons and in suppresses the formation of cracking product methane.

5) Ni-ZSM-5

Results presented in Table 7 show that Ni-ZSM-5 catalyst is already quite active at 400°C in facilitating the reaction between ethane and oxygen. The most striking feature of this catalyst is its high activity in catalyzing the cracking reaction which leads to the formation of methane. This is a reflection of the capability of Ni^{2+} to activate the carbon-carbon bond. The effect of steam was not significant at temperatures ≤500°C. At 550°C, adding steam lowered the overall conversion of ethane and greatly reduced the selectivity to hydrocarbons . The very low ethylene to methane ratio (0.2) suggests that the formation of cracking product was predominant. Thus, although Ni-ZSM-5 has greater activity than most of the other zeolite catalysts tested, its extremely high activity to generate methane excludes it from being a good oxydehydrogenation catalyst.

6) Pt-ZSM-5 catalyst

Results obtained over Pt-ZSM-5 catalyst are given in Table 8. It shows that at low temperatures (≤550°C), formation of CO_2 was dominant. At higher temperatures (≤600°C), in addition to CO_2, CO, ethylene and methane were major products. The selectivity to hydrocarbons did not exceed 50%. Methane was a major component except at 550°C. The addition of steam had little on the catalyst activity. However, its presence greatly enhanced the selectivity to hydrocarbons and somewhat lowered the cracking tendency of the catalyst (giving a higher ethylene/methane ratio). Despite the improvement of the selectivity to hydrocarbons by adding steam, the relative high cracking activity of this catalyst strongly indicates that Pt-ZSM-5 is not a good candidate as catalysts for the oxydehydrogenation of ethane.

7) Li/MgO catalyst

Table 9 gives the results obtained over a Li/MgO catalyst. Apart from the very low activity at temperatures ≤500°C in the absence of steam, Li/MgO was very selective in facilitating the oxydehydrogenation of ethane. Even at 550°C, this catalyst could still give a selectivity to hydrocarbons greater than 60%. In addition to its high selectivity to hydrocarbons, its cracking activity is very low which is highly desirable in order to increase the selectivity to ethylene. The data of Table 9 strongly suggest that steam plays a very significant role. At low temperatures (≤500°C), adding steam increased the activity of the catalyst. However, at higher temperatures ≥550°C, steam appears to lower the activity. More importantly, at temperatures ≥500°C, adding steam resulted in a decline in selectivity to hydrocarbons. Thus, adding steam has negative effects on oxydehydrogenation of ethane at high temperatures.

8) $Ca_3NiK_{0.1}O_x$ catalyst

Results given in Table 10 show that reaction of ethane with oxygen over Ca-Ni-K oxide catalyst leads mainly to oxidation products, almost exclusively carbon dioxide. In the absence of steam, higher reaction temperatures results in lower selectivity to hydrocarbons. In the presence of steam, high reaction temperature benefits the production of hydrocarbons but the highest selectivity was only 30%. Thus, Ca-Ni-K oxide seems not be a good candidate for the oxydehydrogenation of ethane.

C) CONCLUSION

Basic Na-ZSM-5 and neutral V-ZSM-5 zeolites have been shown to be more active and selective in the oxydehydrogenation of ethane than oxide catalysts, e.g. Li/MgO. In addition to the oxydehydrogenation product, a significant amount of higher hydrocarbons (C_{3+}) was produced by using zeolites containing Ga^{3+}, Pt^{2+}, or Ni^{2+} cations. Na^{+}-, V^{5+}-, and H^{+}- exchanged ZSM-5 catalysts are less effective in facilitating the production of higher hydrocarbons (C_{3+}). For zeolite based catalysts, the addition of steam can enhance their selectivity to hydrocarbons and reduce their tendency to form methane. On the other hand, the presence of steam causes a decline in the activity and selectivity to hydrocarbons of oxide catalysts for the oxydehydrogenation of ethane. To achieve high conversion and high selectivity to hydrocarbons while keeping the cracking reaction to a minimal level, the oxydehydrogenation of ethane should be carried out at temperatures around 500-550°C. Above 550°C, the formation of methane becomes important which is undesirable. Reactions at low temperatures (<500°C) result in lower selectivity to hydrocarbons.

The exact role played by steam in the reaction of ethane with oxygen occurred on those two type of catalysts is not clear at present. This issue will be addressed in our future work.

ACKNOWLEDGEMENT

This work was supported by the Assistant Secretary for Fossil Energy, Office of Technical Coordination, U.S. Department of Energy under contract No. DE-AC03-76SF00098, through the Pittsburgh Energy Technology Center, Pittsburgh, PA 15236.

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Table 1a Composition of Catalysts

Catalyst	[H+] m.mol/g	Metal Cation m.mol/g	Surface Area m^2/g
H-ZSM-5	0.52	0	170 [a]
Na-ZSM-5	0.02	0.50	165 [a]
Ni-ZSM-5	0.36	0.08	172 [a]
Pt-ZSM-5	0.16	0.16	–
V-ZSM-5	0	0.50	–
Li/MgO	–	b	0.8
Ca-Ni-K	–	c	0.7

a, external surface area obatined by t-plot method;
b, nominal composition: Mg_2LiO_x;
c, nominal composition: $Ca_3Ni_{0.1}O_x$;

Table 1b Results of Reaction of Ethane with Oxygen over Different Catalysts at 550°C *

Catalyst	Steam	Conversion of Ethane (mol. %)	Selectivity to Hydrocarbons (mol. %)	Selectivity to CO (mol. %)	Selectivity to CO_2 (mol. %)	Selectivity to Ethylene (mol. %)	Selectivity to Methane (mol. %)	Selectivity to C_{3+} (mol. %)	Selectivity to Hydrogen (mol. %)
V-ZSM-5	No	36	56	21	23	53	3	3	0
	Yes	37	59	20	21	55	2	2	0
Na-ZSM-5	No	42	62	30	8	54	4	4	0
	Yes	43	78	17	5	65	7	5	†
Li/MgO	No	31	62	8	30	58	2	2	0
	Yes	18	18	12	69	17	1	1	0
Ca-Ni-K-O	No	21	11	0	89	10	0	1	0
	Yes	22	30	8	62	26	1	3	0
Ga_2O_3	No	20	54	2	44	44	8	2	7
	Yes	15	38	2	60	3	34	1	7
H-ZSM-5	No	29	50	45	5	45	3	2	1
	Yes	18	55	41	4	49	4	2	2
Ga-ZSM-5	No	28	54	36	10	13	31	10	14
	Yes	25	52	32	16	37	8	7	6
Pt-ZSM-5	No	16	13	9	78	11	2	0	0
	Yes	16	40	8	35	30	4	7	4
Ni-ZSM-5	No	30	52	19	30	28	9	15	0
	Yes	25	11	25	64	2	9	0	†

*, Catalyst: 1.0 g; ethane: 3 $cm^3 \cdot min^{-1}$; oxygen: 1 $cm^3 \cdot min^{-1}$; steam: 3.3 $cm^3 \cdot min^{-1}$; †, detection of hydrogen not allowed due to the use of helium as carrier gas.

Table 2 Reaction of Ethane with Oxygen over H-ZSM-5 Catalyst

Temperature °C	Presence of Steam	Conversion Ethane %	Selectivity HC [a] %	Selectivity CO%	Selectivity CO_2 %	Ethylene/ Methane
400	No	5	8	62	30	9.0
400	Yes	2	30	50	20	13.0
500	No	14	27	44	29	9.6
500	Yes	7	32	53	15	19.3
600	No	26	32	44	24	4.1
600	Yes	23	45	40	15	6.7

a, hydrocarbons excluding reactant ethane;

Table 3 Reaction of Ethane with Oxygen over Ga_2O_3 Catalyst

Temperature °C	Presence of Steam	Conversion Ethane %	Selectivity HC [a] %	Selectivity CO%	Selectivity CO_2 %	Ethylene/ Methane
500	No	9	11	15	74	0.36
500	Yes	9	14	26	60	1.1
550	No	21	54	2	44	2.4
550	Yes	15	38	2	60	0.03

a, HC: hydrocarbons excluding ethane;

Table 4 Effect of Steam on the Performance of Ga-ZSM-5 Catalyst

Temperature ℃	Presence of Steam	Conversion Ethane %	Selectivity HC [a] %	Selectivity CO%	Selectivity CO_2 %	Ethylene/ Methane
500	No	11	14	49	37	1.7
500	Yes	14	20	43	37	5.3
550	No	28	54	36	10	0.4
550	Yes	25	52	32	16	2.3
600	No	35	62	31	6	0.7
600	Yes	36	59	32	9	1.7

a, HC: hydrocarbons excluding ethane;

Table 5 Reaction of Ethane with Oxygen over V-ZSM-5 Catalyst

Temperature °C	Presence of Steam	Conversion Ethane %	Selectivity HC [a] %	Selectivity CO%	Selectivity CO_2 %	Ethylene/ Methane
400	No	5	11	17	72	25.5
450	Yes	1	16	7	77	5.9
500	No	18	19	23	58	29.8
500	Yes	5	31	14	55	29.5
550	No	36	56	21	23	7.6
550	Yes	37	59	21	20	13.3

a, HC: hydrocarbons excluding ethane;

Table 6 Reaction of Ethane with Oxygen over Na-ZSM5 Catalyst

Temperature °C	Presence of Steam	Conversion Ethane %	Selectivity HC [a] %	Selectivity CO%	Selectivity CO_2 %	Ethylene/ Methane
400	No	2	7	16	77	3.5
450	Yes	3	24	42	34	22.2
500	No	7	29	7	64	34.7
500	Yes	8	30	35	35	15.2
550	No	42	62	30	8	6.7
550	Yes	43	78	17	5	8.7

a, HC: hydrocarbons excluding ethane;

Table 7 Reaction of Ethane with Oxygen over Ni-ZSM-5 Catalyst

Temperature °C	Presence of Steam	Conversion Ethane %	Selectivity HC [a] %	Selectivity CO%	Selectivity CO_2 %	Ethylene/ Methane
400	No	17	11	34	55	0.5
450	Yes	21	24	12	64	0.3
450	No	22	28	21	51	0.1
500	Yes	22	28	27	45	1.8
550	No	30	52	18	30	1.3
550	Yes	25	12	26	62	0.2

a, HC: hydrocarbons excluding ethane;

Table 8 Reaction of Ethane with Oxygen over Pt-ZSM-5 Catalyst

Temperature °C	Presence of Steam	Conversion Ethane %	Selectivity HC [a] %	Selectivity CO%	Selectivity CO_2 %	Ethylene/ Methane
450	No	15	7	7	89	0.3
450	Yes	8	8	4	91	0.5
550	No	17	8	6	88	3.3
550	Yes	16	40	9	51	4.0
600	No	36	20	12	68	1.2
600	Yes	32	48	17	35	1.6

a, HC: hydrocarbons excluding ethane;

Table 9 Reaction of Ethane with Oxygen over Li/MgO Catalyst

Temperature °C	Presence of Steam	Conversion Ethane %	Selectivity HC [a] %	Selectivity CO%	Selectivity CO_2 %	Ethylene/ Methane
450	No	0.2	99	0	0	3.0
450	Yes	1	100	0	0	24
500	No	3.5	88	0	12	42.5
500	Yes	6	40	5	55	21.0
550	No	31	62	8	30	14.0
550	Yes	18	18	12	70	17.2

a, HC: hydrocarbons excluding ethane;

Table 10 Reaction of Ethane with Oxygen over $Ca_3NiK_{0.1}$ Oxide Catalyst

Temperature ℃	Presence of Steam	Conversion Ethane %	Selectivity HC [a] %	Selectivity CO%	Selectivity CO_2 %	Ethylene/ Methane
450	No	8.4	27	0	73	15.6
450	Yes	9.0	4	0	96	16.5
500	No	13.7	11	0	89	7.4
500	Yes	14.8	15	0	85	7.4
550	No	20.6	11	0	89	16.5
550	Yes	21.5	30	8	62	9.6

a, HC: hydrocarbons excluding ethane;

END

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