Available online at www.sciencedirect.com
SCIENCE DIRECT®

Catalysis Today 106 (2005) 95–98

CATALYSIS TODAY
www.elsevier.com/locate/cattod

Highly effective oxidative cracking of *n*-butane in light olefins on a novel cobalt catalyst

M.L. Kaliya *, S.B. Kogan

Ben Gurion University of the Negev, Beer Sheva 8410, Israel

Available online 22 August 2005

Abstract

A Co-N on alumina catalyst yielded high performance in the oxidative cracking of *n*-butane to ethylene and propylene. A total of 47.7 wt.% yield of olefins including 31% of ethylene and 13% of propylene were obtained at 82% of *n*-butane conversion at 600 °C. Catalyst characterization by SEM, X-ray photoelectron spectroscopy (XPS), XRD and TPR studies suggested that a cobalt oxynitride phase was formed. This resulted in lowering the oxygen binding energy leading to enrichment in mobile, low energy, oxygen species that significantly accelerates the formation of lower olefins.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Ethylene; Propylene; *n*-Butane; Cracking; Oxidation; Cobalt oxynitride

1. Introduction

The demand for light olefins, ethylene and propylene is increasing steadily. Despite intensive development of selective dehydrogenation of paraffins, the high temperature destructive methods like steam cracking and pyrolysis at 800–900 °C still remain, as before, the main methods for production of ethylene and propylene [1]. However, high energy consumption required for the endothermic cracking process and deposition of coke on the reactor walls that hampers heat transfer and leads to an increase of the pressure drop are the chief drawbacks, among many others, in steam cracking.

At first sight the idea of oxygen addition into catalytic steam cracking appears very attractive. Partial oxidation of hydrocarbons may transform the endothermic cracking into exothermic oxidative cracking and remove coke depositions. However, introduction of oxygen significantly decreases olefin selectivity [2–6].

Considerable progress could be made by developing novel catalysts operating at low temperature and providing high and stable yields of light olefins due to accelerated cracking activity. The present work is focused on this subject.

2. Experimental

The testing unit has been described elsewhere [5,6]. γ-Al_2O_3 (Norton 6175, $S = 250\ m^2/g$), SiO_2 (PQ Corp., lot 1030, $S = 300\ m^2/g$), zeolites HY-12 (PQ Corp., $SiO_2/Al_2O_3 = 12$, $S = 720\ m^2/g$) and HZSM-5 (PQ Corp., $SiO_2/Al_2O_3 = 30$, $S = 420\ m^2/g$) were selected for catalyst preparation. θ-Al_2O_3 ($S = 104\ m^2/g$) was prepared by calcination of γ-Al_2O_3 at 1000 °C for 8 h. Most of the supported catalysts were prepared by impregnation using corresponding aqueous solutions of metal nitrates (97–98%, Aldrich), NH_4VO_3 (98%, Aldrich) or H_3PO_4 (85%, Aldrich) followed by drying at 100 °C for 3 h and calcination at 550 °C for 6 h. $CaAlO_2$ and V-MgO ($S = 40\ m^2/g$) catalysts were prepared as mentioned elsewhere [3,7]. Nitrogen containing cobalt catalyst (Co-N) was prepared by deposition of precursor, sodium salt of (4,5-carboxy)-cobalt phthalocyanine, NaCoPc, purity 95% (supplied by Organic Intermediates and Dyes Institute, Moscow, Russia) on

---

* Corresponding author.
E-mail address: mkaliya@bgumail.bgu.ac.il (M.L. Kaliya).

0920-5861/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2005.07.139

γ-Al_2O_3 or SiO_2 followed by thermal decomposition in a stream of He at 700 °C [5,6].

SEM, XRD, XPS, TPR and BET methods were used for catalyst characterization.

The TPR measurements were carried out with AMI-100 Catalyst Characterization System (Zeton-Altamira) equipped with mass-spectrometer (Ametek 1000). The following protocol was adopted. A sample of a catalyst (~0.15 g) was heated in the apparatus cell with gas flow (5% of O_2, 95% of He) up to 550 °C (rate—5 °C/min), calcined for 2 h, cooled to 40 °C in Ar flow and heated up to 520 °C with rate 15 °C/min in Ar flow containing 10% of H_2. Finally, the sample was held under the same conditions for 25 min.

PHI 549 SAM/AES/XPS apparatus with double CMA and Mg Kα X-ray source (1253.6 eV) has been used for X-ray photoelectron spectroscopy (XPS) measurements of the catalyst surface.

X-ray diffractograms were recorded on a Phillips diffractometer PW 1050/70 (Cu K radiation) equipped with a graphite monochromator. Data were obtained at 0.05° step size with 1 s exposition. The peak positions and the instrument peak broadening (β) were determined by fitting each diffraction peak by means of APD computer software.

The content of nitrogen in the calcined catalysts was determined by SEM as 0.6–0.8 wt.%.

3. Results and discussion

Experimental data depicted in Table 1 demonstrate that the yield of light olefins (C_2= + C_3=) in the steam cracking of *n*-butane on heterogeneous catalysts at 750 °C compares well with those obtained in thermal processes. These samples were selected since they exhibit wide range of acidic and basic properties. The high performance of $CaAlO_2$ was reported elsewhere [7].

Obviously, introduction of granulated catalysts in the reactive zone caused inhibition of the radical route due to a decrease of free volume, whereas the activity of the tested catalysts only compensated this negative effect. The overall yield of light olefins 32–36% reached with heterogeneous catalysts was close to 35.2% recorded in the thermal process. Moreover, intense coke formation decreased catalyst performance, thus impeding commercial catalyst's application in steam cracking.

Screening of novel catalytic systems in oxidative dehydrogenation of *n*-butane resulted in the selection of supported Co catalysts, which manifested extended high activity in the production of ethylene and propylene [5,6].

A specific feature of Co catalysts consists in high activity, even at low temperature (400–600 °C) with predominant formation of light olefins. The ratio between light olefins and butenes reached 3.2 at 550 °C while only 0.1–0.4 was recorded on vanadia based samples. Doping with nitrogen enhanced this value to 9.6–11.9 at 550–600 °C and improved catalyst performance significantly, yielding 38.2 and 44% of light olefins at 550 and 600 °C, respectively. Such catalyst performance exceeded the level of *n*-butane steam cracking performance measured at 750 °C and was similar to the 44.3% yield of light olefins recorded at 800 °C (Table 1).

Table 1
Performance of catalysts in oxidation (Comparison of yields with those obtained in steam cracking of n-butane)

Metal (wt.%)	Support	Conversion (wt.%)	Yield of olefins (wt.%)[a]			Ratio (C_2= + C_3=)/C_4=
			C_2	C_3	C_4	
n-Butane oxidation (T = 550 °C, WHSV = 5 h^{-1}, mole ratio O_2/*n*-C_4 = 1.5)						
0.7Co	γ-Al_2O_3	51.2	15.2	7.3	7.1	3.2
0.8Co-N	γ-Al_2O_3	73.7	26.5	11.7	4.0	9.6
0.8Co-N[b]	γ-Al_2O_3	82.0	30.8	13.2	3.7	11.9
2.3Co	SiO_2	23.2	1.9	1.8	13.8	0.3
0.7Co-N	SiO_2	27.6	6.0	5.8	7.8	1.5
0.7V	γ-Al_2O_3	13.5	0.4	0.4	8.6	0.1
30V	MgO	35.6	5.0	2.6	20.1	0.4
n-Butane steam cracking (T = 750 °C, WHSV = 1.2 h^{-1}, mole ratio H_2O/*n*-C_4 = 1.7)						
1.3Co	θ-Al_2O_3	70.6	15.5	18.0	4.8	7.0
2.9P	θ-Al_2O_3	65.7	17.8	19.0	5.6	6.6
5La	θ-Al_2O_3	53.5	15.2	17.0	3.6	8.9
1K	ZSM-5	56.4	17.7	15.4	4.0	8.3
–	HY-12	67.5	20.0	16.2	5.7	6.4
3.3K	HY-12	58.0	17.1	14.8	4.2	7.6
$CaAlO_2$	–	49.3	15.1	16.2	2.1	14
Empty reactor, no catalyst		57.1	18.4	16.8	4.1	8.6
Empty reactor, no catalyst[c]		76.6	32.2	12.1	3.2	13.8

[a] Balance—mainly methane and carbon oxides.
[b] 600 °C.
[c] 800 °C.

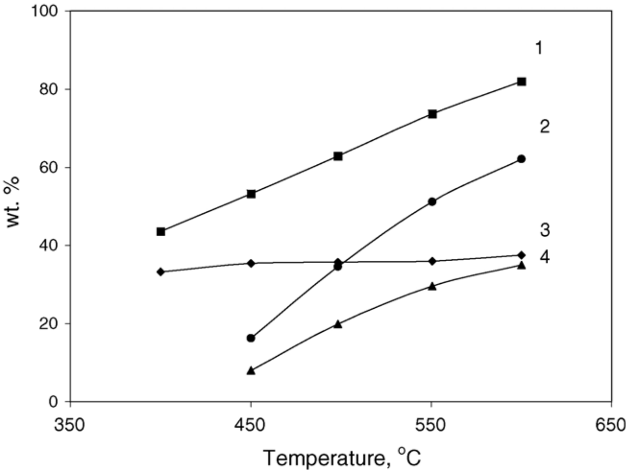

Fig. 1. Performance of cobalt catalysts at WHSV = 5 h^{-1}, mole ratio O_2/*n*-C_4 = 1.5. (1 and 3) 0.8% Co-N/Al_2O_3; (2 and 4) 0.7% Co/Al_2O_3; (1 and 2) *n*-butane conversion; (3 and 4) selectivity to ethylene.

The catalyst was tested for 100 h run with no observed deactivation. Notably, the selectivity to ethylene for 0.8% Co-N/Al_2O_3 catalyst remained constant in the ranges of 400–600 °C in contrast to cobalt catalyst without nitrogen promoter (Fig. 1). A strong effect of temperature on the activity of the modified cobalt catalyst with constant selectivity provided superior olefins yield at 550–600 °C.

Light olefins, ethylene and propylene could be formed from *n*-butane via two different routes. One of them is oxidative cracking of *n*-butane, mentioned in a number of publications [2–6]. The other route for light olefins consists in decomposition of butylenes formed in oxidative dehydrogenation of *n*-butane. In this case preferable formation of light olefins on the Co catalyst has to be explained by a difference in the rate of destruction of butylenes on the Co and V catalysts. However, oxidative conversion of 1-butene on 2.7% V/Al_2O_3 as well as on 2.3% Co/Al_2O_3 carried out at 550 °C and molar ratio $O_2/C_4H_8 = 1$ indicated no difference in 1-butene conversion and distribution of olefins on Co and V catalysts. Hence, predominant ethylene and propylene formation on Co catalyst is caused by direct oxidative cracking of *n*-butane according to the Eqs. (1) and (2).

$$n\text{-}C_4H_{10} + 0.5O_2 = 2C_2H_4 + H_2O \tag{1}$$

$$n\text{-}C_4H_{10} + 2O_2 = C_3H_6 + CO_2 + 2H_2O \tag{2}$$

The overall set of chemical reactions is similar to the network proposed elsewhere [4].

The higher yield of ethylene on Co catalysts indicates preference of route (1).

Such unusual catalytic performance in alumina supported cobalt systems is determined by a combination of three main factors:

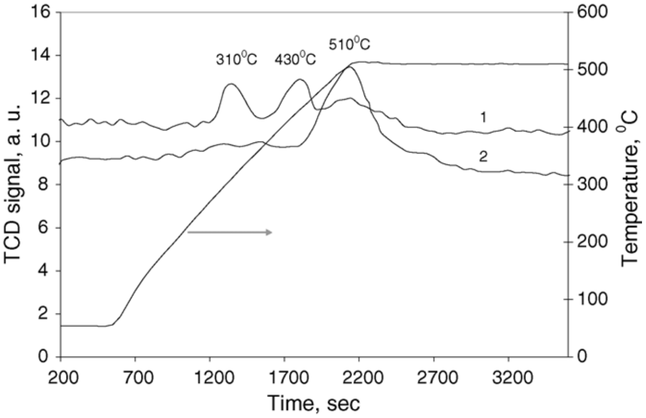

Fig. 2. TPR study on: (1) 2.3% Co-N/Al_2O_3 and (2) 2.5% Co/Al_2O_3.

(i) particular catalytic activity of cobalt oxide manifested enhanced cracking of hydrocarbons;
(ii) selection of γ-alumina as a support that significantly affected catalyst performance;
(iii) specific nitrogen promotion enhanced catalyst activity.[1]

Oxidative cracking of paraffins proceeds through the formation of special activated oxygen species reacting with molecules of gaseous paraffin [5,6,8,9]. Therefore, these points could be integrated in one question: How did these factors provide low temperature oxygen activation?

Detailed catalyst characterization clarified the impact of these points:

(i) The specific behavior of cobalt oxide compared with vanadia is partially explained by a significant lowering of metal–oxygen binding energy that was found from XPS study: O 1s B.E. for Co_3O_4 and V_2O_5 was 529 and 531 eV, respectively. Such a low value of oxygen B.E. on Co_3O_4 indicates higher mobility and reactivity of oxygen. The possibility of different types of oxygen is suggested as being responsible for different routes of hydrocarbon conversion. While high energy oxygen provides mostly oxidative dehydrogenation of paraffins to corresponding olefins, mobile, low energy oxygen species are more active in destruction processes [8,10].
(ii) Introduction of nitrogen in Co/Al_2O_3 promoted formation of mobile oxygen species. Temperature-programmed reduction measurements indicated a considerable decrease of temperature required for catalyst–hydrogen interaction from 510 °C with 2.5% Co/Al_2O_3 to 310–430 °C observed with 2.3% Co-N/Al_2O_3 (Fig. 2).
(iii) Incorporation of nitrogen in the catalyst composition was confirmed by XPS data (peak N 1s). It resulted in

---

[1] Special study indicated that Na_2O also incorporated in catalyst at thermal decomposition of NaCoPc had negligible effect on the catalyst performance [5].

Table 2
XPS data for Co samples

Sample before treatment	Treatment	Sample after treatment	Co 2p B.E. (eV)	Chemical shift (eV)
2.5% Co/Al_2O_3	550 °C in air	2.5% Co/Al_2O_3	780.0	–
NaCoPc	700 °C in He	61% Co-N	779.5	−0.5
$NaCoPc/Al_2O_3$	700 °C in He, 550 °C in air	2.3% $Co-N/Al_2O_3$	779.6	−0.4

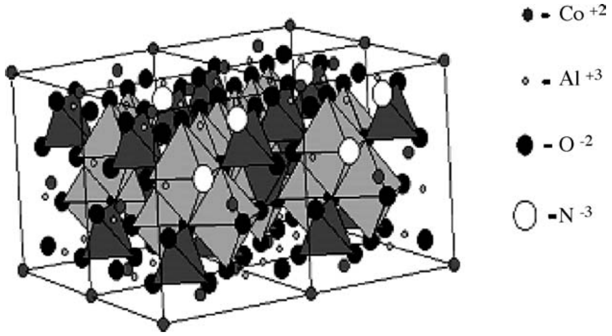

Fig. 3. Computer simulation of alumina supported cobalt oxynitride.

changes in the electronic state of cobalt observed by XPS. A broadening and shift of Co 2p maximum from 780 eV for 2.5% Co/Al_2O_3 to 779.6 eV in 2.3% $Co-N/Al_2O_3$ were recorded (Table 2). Such shift shows decrease of positive Co^{2+}charge and indicates that oxygen is partially replaced by a less electronegative nitrogen [11] forming oxynitride structure [12].

It is important to note that nitrogen promotion of Co/Al_2O_3 resulted in the formation of a stable nitrogen containing structure: XPS, SEM and XRD spectra demonstrated the similar data for the fresh and spent catalysts.

(iv) The essential influence of the support on the activity of supported cobalt catalysts was stressed in our previous studies [5,6]. Alumina supported catalysts demonstrated significantly higher performance compared with Co samples deposited on silica. However, the effect of nitrogen promotion remained considerable on silica supported catalysts. Experimental results indicated that the yield of light olefins on 0.7% $Co-N/SiO_2$ was 11.8% with a ratio between light olefins and butylenes of 1.5 versus 3.7% yield and a ratio of 0.3 measured at 550 °C on a non-promoted sample (Table 1).

A special set of alumina supported cobalt catalysts calcined in the range 500–900 °C was prepared and studied by XRD method. Analysis of XRD plots by Rietveld method [13] showed that samples calcined at $T \geq 700$ °C may be considered as solid solutions of Co and Al oxides or Co spinel in which Co^{2+} occupies tetrahedral vacancies, whereas Al^{3+} cations are located in tetrahedral and octahedral positions. Such structure provides high potential for substitution of anion O^{2-} for anions N^{3-} [14]. A computer simulation of feasible active structure is presented in Fig. 3.

4. Conclusions

Alumina supported cobalt catalysts especially promoted with nitrogen provide superior performance in the production of light olefins. A total ethylene and propylene yield of 44% was observed with 0.8% $Co-N/Al_2O_3$ in the oxidative cracking of *n*-butane at 600 °C. A catalyst study suggested the formation of alumina supported cobalt oxynitride. This results in a lowering of the oxygen binding energy leading to an enrichment of mobile oxygen species that significantly improves the cracking activity and the formation of lower olefins.

Acknowledgement

We would like to thank Professor M. Herskowitz for useful and fruitful discussions.

References

[1] J. Weitkamp, A. Raichle, Y. Traa, M. Rupp, F. Fuder, Chem. Commun. 5 (2000) 403.
[2] F. Cavani, F. Trifiro, Catal. Today 51 (1999) 561.
[3] M.V. Landau, M.L. Kaliya, A. Gutman, L.O. Kogan, M. Herskowitz, P.B. van den Oosterkamp, Stud. Surf. Sci. Catal. 110 (1997) 315.
[4] M.L. Kaliya, O.V. Malinovskaya, M.V. Landau, M. Herskowitz, P. van den Oosterkamp, Stud. Surf. Sci. Catal. 133 (2001) 113.
[5] M.L. Kaliya, S.B. Kogan, N. Froumin, M. Herskowitz, Catal. Commun. 3 (2002) 327.
[6] M.L. Kaliya, S.B. Kogan, N. Froumin, M. Herskowitz, Stud. Surf. Sci. Catal. 143 (2002) 679.
[7] V.A. Kumar, K.K. Pant, D. Kunzru, Appl. Catal. A 162 (1997) 193.
[8] E.A. Mamedov, V.C. Corberan, Appl. Catal. A 127 (1995) 1.
[9] L.M. Madeira, J.M. Herrmann, J. Disdjer, M.F. Portela, F.G. Freire, Appl. Catal. A 235 (2002) 1.
[10] A. Corma, J.M.L. Nieto, N. Paredes, J. Catal. 144 (1993) 425.
[11] M.A. Centero, M. Debois, J. Grange, J. Catal. 192 (2000) 296.
[12] J. Trawczynski, React. Kinet. Catal. Lett. 69 (2000) 286.
[13] R. Young, A. Larson, C. Paiva-Santos, DBWS-9807, Rietveld Analysis of X-Ray and Neutron Powder Diffraction Patterns, 1998.
[14] H. Willems, G. de With, R. Helmholdt, K. Petersen, J. Mater. Sci. Lett. 12 (1993) 1470.