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Oxidative dehydrogenation of ethane to ethylene on Cr_2O_3/Al_2O_3–ZrO_2 catalysts: the influence of oxidizing agent on ethylene selectivity

Y. Ramesh · P. Thirumala Bai · B. Hari Babu ·
N. Lingaiah · K. S. Rama Rao · P. S. Sai Prasad

Abstract Oxidative dehydrogenation of ethane to ethylene was investigated on Al_2O_3, ZrO_2 and Al_2O_3–ZrO_2 mixed oxide supported Cr_2O_3 catalysts taking O_2 and CO_2 as oxidants. The catalysts were characterized by nitrogen adsorption, X-ray diffraction, temperature-programmed reduction, and X-ray photoelectron spectroscopy. The catalytic activity depended on the chromium species formed on the surface. However, the selectivity to ethylene was influenced by the oxidizing agent (O_2 or CO_2). Temperature-programmed desorption of ethylene was employed to confirm the role of oxidant in deciding ethylene selectivity.

Keywords Oxidative dehydrogenation · Ethylene · CO_2 · Chromia catalyst

Introduction

Ethylene is used in the production of various industrially important products such as high and low density polyethylenes, polyvinyl chloride, ethylene glycol, styrene, ethylene oxide, vinyl acetate and ethyl benzene [1, 15]. The current global production of this raw material amounts to 160 million tons per year with an average growth rate of 4 % per year. Ethylene is commercially produced by steam cracking dehydrogenation of hydrocarbon feedstock like natural gas and naphtha [9]. This process has several drawbacks like endothermicity of the reaction, thermodynamic limitation in the paraffin conversion and severe coke formation. Catalytic ODE using molecular oxygen has emerged as a highly attractive alternative in overcoming these difficulties [12]. The reaction becomes exothermic. Elimination of thermodynamic limitation, minimization of coke formation because of the presence of oxygen and decrease in the frequency of catalyst regeneration [1, 2, 12] are the additional advantages. However, the requirement of an air separation unit to generate pure oxygen, thermal runaway of reaction and the difficulty of controlling ethylene selectivity are the major issues associated with this process [2, 12, 14]. Another alternative is the utilization of N_2O as the oxidant, wherein high conversions could be realised due to the formation of O^- radical species, but the limited availability of the oxidant and low ethylene selectivity [19] at high conversions make this methodology of ethylene generation less attractive.

CO_2 is now considered as a mild oxidant in the dehydrogenation of ethane due to its advantages in containing the exothermicity of the reaction, its role as a diluent in offering high equilibrium conversion, improving the selectivity to ethylene, reducing coke formation and maintaining longer catalyst life time [13, 23]. Cr_2O_3/ZSM-5 [13], Cr_2O_3/Al_2O_3, Cr_2O_3/SiO_2, Cr_2O_3/ZrO_2, Cr_2O_3/TiO_2 [21], modified Cr_2O_3/ZrO_2 nano-composites [4], Cr/SBA-15/Al_2O_3/FeCrAl monoliths [17], Cr–O, Cr–V–O oxide [7], Ga incorporated Cr_2O_3 supported on ZSM-5 and silicalite [18] catalysts have been tried for oxidative dehydrogenation of ethane in presence of CO_2. Nevertheless, much work is needed in improving the conversions of ethane and CO_2 and ethylene selectivity, apart from containing catalyst deactivation. Mixed oxides combine good textural and mechanical properties with Cr_2O_3; however, these catalysts have not been studied in detail. The factors

Y. Ramesh · P. Thirumala Bai · B. Hari Babu · N. Lingaiah ·
K. S. Rama Rao · P. S. S. Prasad (✉)
Catalysis Laboratory, Inorganic and Physical Chemistry
Division, CSIR-Indian Institute of Chemical Technology,
Hyderabad 500 007, India
e-mail: saiprasad@iict.res.in

influencing ethylene selectivity also have not been given much attention. The main objective of the present study is to identify the factors influencing ethylene selectivity, while finding the effectiveness of Al_2O_3–ZrO_2 (1:1) mixed oxide as the support for Cr_2O_3, when oxygen or carbon dioxide is used as the oxidant.

Experimental

Catalyst preparation

Commercially available Al_2O_3 (Sud Chemie Ind. Pvt. Ltd) was used as a support. ZrO_2 was prepared by hydrolyzing the aqueous solution of $Zr(O)(NO_3)_2 \cdot 8H_2O$ with ammonium hydroxide at a pH of 10. Co-precipitation method was used to prepare the Al_2O_3–ZrO_2 mixed oxide support (molar ratio 1:1) by adding ammonium hydroxide solution to a mixed aqueous solution of $Zr(O)(NO_3)_2 \cdot 8H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ until the pH reached a value of 10. The precipitate was filtered off, thoroughly washed with deionized water, dried at 120 °C for 12 h in air oven and finally calcined at 650 °C for 6 h. The catalysts with 15 wt% Cr_2O_3 on the above supports were prepared by adopting the impregnation method taking required quantities of $Cr(NO_3)_3 \cdot 9H_2O$. After drying at 120 °C for 12 h, the catalyst masses were calcined at 650 °C for 6 h. As the Cr_2O_3 content was kept uniform (15 wt%) in all the catalysts, the term 15 wt% is omitted in designating the catalysts during the following discussion.

Catalyst characterization

The BET surface areas of the catalysts were determined on QUADRASORB *SI* (Quantachrome Instruments, USA) by nitrogen physisorption at −196 °C. X-ray diffraction patterns of the catalysts were obtained on a Rigaku Miniflex (Rigaku Corporation, Japan) using Ni-filtered Cu Kα radiation. TPR was performed in a flow of 5 % H_2/Ar mixture gas at a flow rate of 30 ml/min with a temperature ramp of 10 °C/min. XPS measurements of the catalysts were performed on a KRATOS AXIS 165 apparatus equipped with a dual anode (Mg and Al) using Mg Kα source. The non-monochromatized Mg Kα X-ray source ($h\upsilon = 1{,}486.6$ eV) was operated at 12.5 kV and 16 mA. For energy calibration, the carbon 1 s photoelectron line was taken with its binding energy as 284.6 eV. A charge neutralization of 2 eV was used to balance the charge up of the sample.

TPDE was performed in the same apparatus used for TPR experiments. The catalyst sample was first pretreated at 500 °C for 1 h in He flow (30 ml/min). Raising the temperature to 650 °C, it was exposed to ethane, O_2 or CO_2 and He at flow rates similar to that of the ODE reaction for 2 h. Then the catalyst was cooled to 100 °C under He flow and pure C_2H_4 was passed for 1 h at 100 °C. After desorbing the physisorbed C_2H_4 under He flow for 50 min at the same temperature, the temperature of the sample was raised to 650 °C at a heating rate of 10 °C/min. The desorbed C_2H_4 was monitored gas chromatographically.

Catalytic evaluation

Catalyst evaluation was carried out in a fixed-bed stainless steel reactor at atmospheric pressure. In each run, about 1 g of catalyst (18/25 mesh size) diluted with equal amount of quartz beads, was suspended between two quartz wool plugs at the centre of the reactor. Prior to reaction, the catalyst was pretreated in He flow (30 ml/min) at 500 °C for 1 h. C_2H_6, CO_2 (or O_2) and He were fed into the reactor at a volumetric ratio of 15/15/30 using mass flow controllers (Alborg, USA). The effluent gas stream was analyzed by an on-line Nucon 5765 GC equipped with TCD using Molecular Sieve 5A and Porapak Q columns. Blank runs (in the absence of catalyst) with quartz wool revealed no conversion of C_2H_6 in the studied temperature range 550–650 °C.

Results and discussion

BET specific surface area

Table 1 shows the specific surface areas of the supports and catalysts. Al_2O_3 has the highest surface area (205 m²/g), ZrO_2 shows the lowest value (57 m²/g) and the mixed oxide support exhibits a value in between. All chromia-supported catalysts show lower values compared to their supports due to blockage of support pores by Cr_2O_3 species [5].

Table 1 BET specific surface areas of all Cr catalysts and their catalytic functionality at 650 °C

Catalyst	SA of support (m²/g)	SA of catalyst (m²/g)	X-C_2H_6 (%)	X-CO_2 (%)	S-C_2H_4 (%)	S-CH_4 (%)
Cr_2O_3/ Al_2O_3	205	154	32.0	21.3	46.2	53.8
Cr_2O_3/ZrO_2	57	33	42.2	37.4	36.0	64.0
Cr_2O_3/ Al_2O_3– ZrO_2 (1:1)	138	97	36.0	29.1	56.2	43.8

X conversion, *S* selectivity
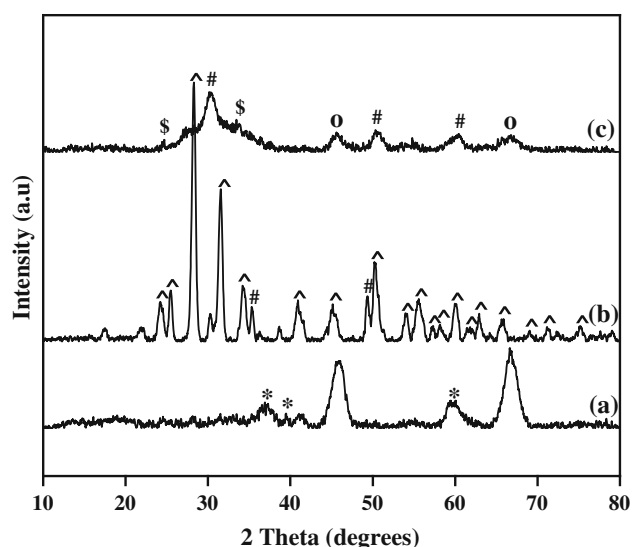
Fig. 1 XRD patterns of catalysts calcined at 650 °C/6 h (*a*) Cr_2O_3/Al_2O_3 (*b*) Cr_2O_3/ZrO_2 (*c*) Cr_2O_3/Al_2O_3-ZrO_2 (1:1); (*O*) Al_2O_3, (*cap*) ZrO_2 monoclinic, (*hash*) ZrO_2 tetragonal, (*asterisk*) CrO_3 and (*dollar*) Cr_2O_3

X-ray diffraction analysis of the catalysts

The XRD patterns of Al_2O_3, ZrO_2 and Al_2O_3–ZrO_2 supported Cr_2O_3 catalysts are shown in Fig. 1. Cr_2O_3/Al_2O_3 exhibits two characteristic peaks at 2θ of 45.8° and 66.8° corresponding to γ-Al_2O_3 (JCPDS 29-0063). Chromia is stabilized on Al_2O_3 with different oxidation states. Cr_2O_3/ZrO_2 shows both the tetragonal and monoclinic phases of ZrO_2. Due to the dominance of the ZrO_2 phases, the crystalline phases of Cr_2O_3 could not be identified clearly. The monoclinic phase of ZrO_2 is not detected in the mixed oxide supported Cr_2O_3 catalysts. This is due to the protective effect of Cr^{+3} which prevents the phase transformation from tetragonal to monoclinic phase [10]. The addition of Al_2O_3 to ZrO_2 also delays this phase transformation as reported previously [8, 11]. The crystalline phases of chromia are not seen in Cr_2O_3/Al_2O_3–ZrO_2 (1:1), probably due to high dispersion on the support.

X-ray photoelectron spectroscopic analysis of the catalysts

Table 2 summarizes the core level binding energies (BE) of Cr 2p, Al 2p and Zr 3d of the catalysts used in this study. Two Cr $2p_{3/2}$ BE values are found for all the supported catalysts. The BE of 576.3 (±0.2) eV can be attributed to the presence of Cr^{+3} species and that at 578.5 (±0.2) eV to Cr^{+6} [4, 21]. The BE of Al $2p_{3/2}$ observed at 75.3 (±0.3) eV indicate that the Al exists in its +3 oxidation state. The BE of Zr $3d_{5/2}$ are obtained as 182.8 (±0.2) eV, which are slightly higher than that obtained for pure ZrO_2

Table 2 Binding energies of Cr based catalysts

Catalyst	Binding energies (eV)			
	Cr $2p_{3/2}$		Al $2p_{3/2}$	Zr $3d_{5/2}$
	Cr^{+3}	Cr^{+6}		
Cr_2O_3/Al_2O_3	576.5	578.6	75.6	–
Cr_2O_3/ZrO_2	576.2	578.3	–	182.6
Cr_2O_3/Al_2O_3–ZrO_2 (1:1)	576.4	578.4	75.3	183.0

(generally observed at 182.1 eV) indicating change in the co-ordination number of Zr by the formation of Zr–O-metal or Zr–O-support bond [16]. Thus, the XPS data establish the existence of chromium in its two favourable oxidation states on the surface of catalysts, which the XRD data could not establish clearly.

TPR profiles of the catalysts

Cr_2O_3/Al_2O_3 catalyst shows (Fig. 2) essentially a single stage reduction of chromia with a peak centered at 379 °C in its TPR profile. The single stage reduction is due to Cr^{+6} to Cr^{+3} transformation [3, 5], as per the following reaction:

$$2CrO_3 + 3H_2 \rightarrow Cr_2O_3 + 3H_2O$$
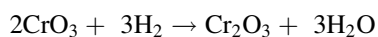
Cr_2O_3/ZrO_2, on the other hand, presents a two-stage reduction with the reduction maxima (T_{max}) appearing between 320 and 470 °C and 480 and 625 °C. The first peak is attributed to the reduction of Cr^{+6} to Cr^{+3} and the second to the reduction of Cr^{+3} to Cr^{+2} [10, 22]. The high temperature peak could also be due to the direct reduction of bulk chromia species to an oxidation state lower than +3 [5], possibly to Cr^{+2}.
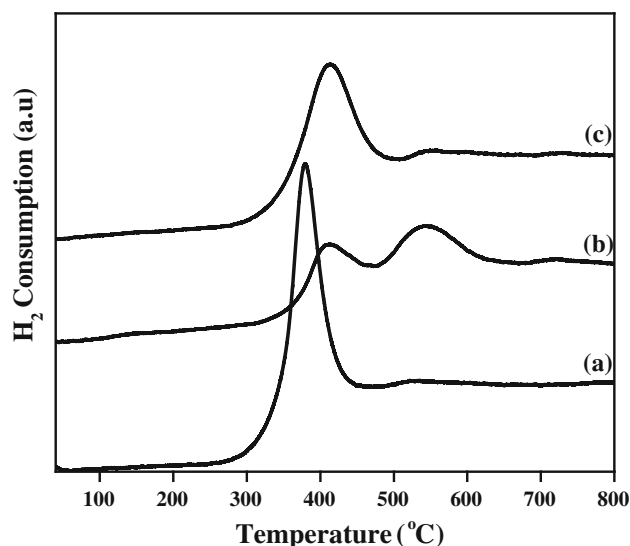

Fig. 2 TPR profiles of catalysts (*a*) Cr_2O_3/Al_2O_3 (*b*) Cr_2O_3/ZrO_2 (*c*) Cr_2O_3/Al_2O_3-ZrO_2 (1:1)

Again, the mixed oxide supported chromia catalyst shows one reduction peak prominently with a small hump corresponding to the second peak indicating the facile reduction up to +3 state and the difficultly in further reduction, even though this catalyst contains ZrO_2.

Oxidative dehydrogenation of ethane

Effect of Cr_2O_3 loading

The effect of chromia loading on the activity and selectivity of catalysts is investigated in the oxidative dehydrogenation of ethane at 650 °C with CO_2 as the oxidant and the results are displayed in Fig. 3. It can be observed that the conversion of ethane and CO_2 increases with rise in chromia content up to 15 wt%. Further increase in loading decreases the conversions of both the reactants. Only slight disparities in ethylene and methane selectivities are observed. Among all the catalysts, 15 wt% Cr_2O_3/Al_2O_3 is seen to exhibit the best performance. Hence, 15 % is fixed as the composition of Cr_2O_3 for further studies.

Effect of support on catalytic activity

The ODE activity of the catalysts with CO_2 as oxidant is presented in Table 1. Cr_2O_3/Al_2O_3 catalyst is seen to exhibit its best catalytic activity with 32 % ethane and 21 % CO_2 conversions and an ethylene selectivity of 46 %. Cr_2O_3/ZrO_2 shows higher activity (42 % ethane conversion) but with a decreased ethylene selectivity (36 %). The formation of methane is high in this catalyst due to facile hydrocracking of ethane to methane catalyzed by the chromium species of lower oxidation state, whose

Fig. 3 Effect of Cr_2O_3 loading in Cr_2O_3/Al_2O_3 catalysts

formation is evidenced by the TPR data. However, the conversion of CO_2 is higher (37 %) than that of Cr_2O_3/Al_2O_3. It is [21] suggested that Cr_2O_3 is more active in the activation of CO_2 at high temperatures. The results on mixed oxide supported catalyst are interesting. $Cr_2O_3/Al_2O_3–ZrO_2$ (1:1) shows 36 % ethane and 29 % CO_2 conversions. These values are higher than for Cr_2O_3/Al_2O_3 but lower than for Cr_2O_3/ZrO_2. Wang et al. [20] reported the ODE with CO_2 over sulfate modified Cr_2O_3/SiO_2 catalysts and obtained 67 % ethane conversion with the ethylene yield of 55 %. The higher catalyst performance could be due to the difference in experimental conditions (ex. 10 vol% of ethane against 25 vol% used in the present investigation).

The variation in the ODE activity of the chromia-based catalysts is due to the difference in their redox property as revealed by Wang et al. [21]. It is also reported that both Cr^{2+} and Cr^{3+} ions have a strong role to play in the catalytic reaction as active sites [6, 21]. The XPS analysis of the present catalysts shows the presence of Cr^{6+} and Cr^{3+} species before reduction. However, the TPR data show more area under the second peak in the case of Cr_2O_3/ZrO_2 indicating the presence of higher amount of Cr^{2+} species, which seems to be responsible for higher activity compared to Cr_2O_3/Al_2O_3 or $Cr_2O_3/Al_2O_3-ZrO_2$ (1:1). Wang et al. [21] have also reported that as Cr_2O_3/ZrO_2 has the strong ability to give oxygen species and hence offers the highest activity and lowest ethylene selectivity compared to the other two catalysts. The activity data obtained on the present catalysts corroborates this observation. The higher basicity of Al_2O_3 than that of ZrO_2 may be the reason for decrease in the activity.

Effect of reaction temperature on catalyst performance in the presence of CO_2 or O_2 as the oxidant

The effect of reaction temperature on catalytic activity and selectivity was studied on $Cr_2O_3/Al_2O_3–ZrO_2$ (1:1) catalyst. The results obtained during the ODE reaction in presence of CO_2 as well as O_2 are presented in Table 3. The conversion of ethane increases with increase in temperature irrespective of the oxidizing agent used in the reaction. The selectivity of ethylene also follows similar trend when O_2 is the oxidant, whereas in the case of CO_2 as the oxidant it increased up to 600 °C and almost remained constant at higher temperature. The conversion of ethane is always higher when the reaction is conducted with O_2 compared to that in CO_2 in the entire temperature region studied. However, the selectivity to ethylene is very low when oxygen is the oxidant, an observation which needs to be understood. It is thought that this discrepancy in ethylene selectivity could be explained due to secondary oxidation of the product ethylene. Oxygen has higher
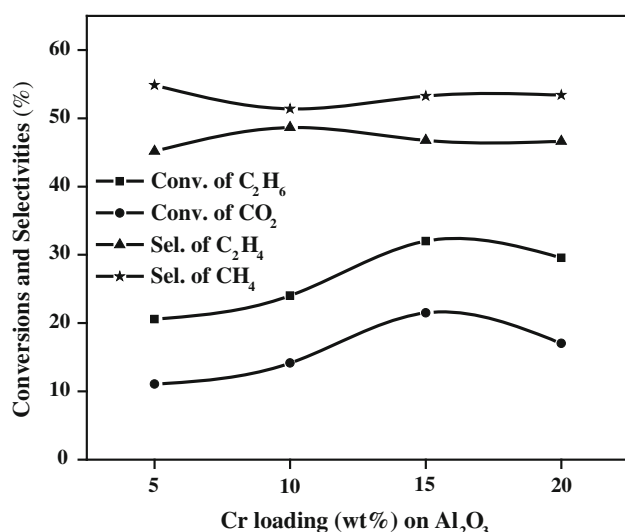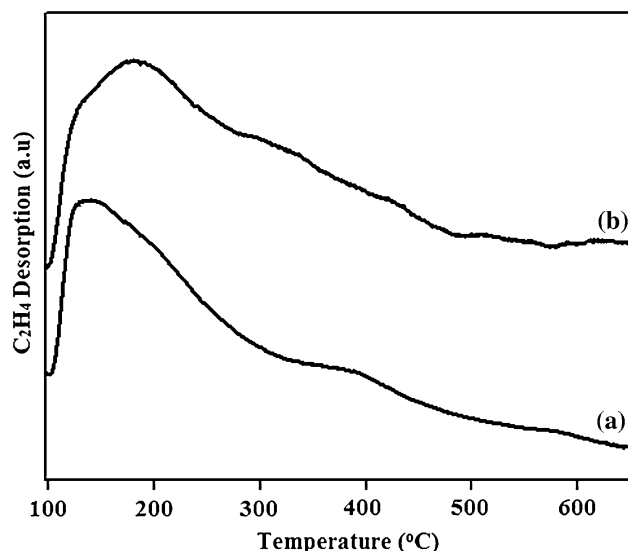
Table 3 Effect of oxidizing agent on catalytic activity of Cr_2O_3/Al_2O_3–ZrO_2 (1:1) in the oxidative dehydrogenation of ethane

Temperature (°C)	CO_2 atmosphere			O_2 atmosphere		
	X-C_2H_6 (%)	S-C_2H_4 (%)	Y-C_2H_4 (%)	X-C_2H_6 (%)	S-C_2H_4 (%)	Y-C_2H_4 (%)
550	15.6	52.9	8.3	33.2	5.8	1.9
600	22.7	57.2	13.0	40.7	9.9	4.0
650	36.0	56.2	20.2	50.3	18.2	9.2

X conversion, *S* selectivity, *Y* yield

Fig. 4 C_2H_4 temperature-programmed desorption profiles of Cr_2O_3/Al_2O_3–ZrO_2 (1:1) catalyst treated at 650 °C for 1 h (*a*) $C_2H_6 + CO_2$ treated (*b*) $C_2H_6 + O_2$ treated

secondary oxidizing ability compared to CO_2. Therefore, in presence of O_2, the selectivity to ethylene decreases as it is subjected to secondary oxidation. On the other hand, the mild oxidizing nature of CO_2 might be responsible for higher ethylene selectivity. This concept has been verified by conducting the TPDE.

TPD of C_2H_4

Figure 4 shows the TPDE profiles observed on Cr_2O_3/Al_2O_3–ZrO_2 catalyst. It may be emphasized here that the ethylene adsorption runs were conducted after carrying out the ODE reactions on the catalyst, such that the nature of surfaces were the same as that of the actual reactions. It is noticed that the amount of ethylene desorbed is higher when O_2 is the oxidant (161 μ mol/g) compared to that when CO_2 is the oxidant (98 μ mol/g). However, the temperature maximum for ethylene desorption is higher in the case of the surface treated with O_2 containing reaction

mixture indicating stronger interaction of ethylene with the surface compared to the other case. From the above results, one can notice that even if the amount of ethylene formed is higher in the case of O_2 as the oxidant, because ethylene stays for a longer time on the surface due to strong interaction, it is subjected to secondary oxidation thus leading to reduced ethylene selectivity. This important observation would help to improve the selectivity of ethylene during ODE with O_2. Better catalysts could be designed by incorporation of efficient promoters so as to decrease the strength of interaction of product ethylene with the surface to prevent secondary oxidation.

Conclusion

Cr_2O_3/Al_2O_3 shows lower catalytic activity in terms of ethane and CO_2 conversions compared to Cr_2O_3/ZrO_2, but offers higher ethylene selectivity. The mixed oxide support is advantageous in terms of attaining higher activity and selectivity towards ethylene compared to Cr_2O_3/Al_2O_3. CO_2 as an oxidant offers higher ethylene selectivity compared to O_2. The reduction in ethylene selectivity during ODE with O_2 could be due to secondary oxidation of ethylene. Stronger interaction of product ethylene with the catalyst surface may be the reason for decreased selectivity.

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