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Reaction pathways of ethane oxidative and non-oxidative dehydrogenation on γ-Al_2O_3 studied by temperature-programmed reaction (TP-reaction)

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Abstract

In this work, the reactions of ethane and ethene in an oxidizing and non-oxidizing atmosphere over γ-alumina were investigated under temperature-programmed conditions, in an attempt to estimate the possible contribution and functionality of the support in the reaction pathway of ethane ODH over MoO_3/Al_2O_3 catalysts. The results indicate that alumina contributes to the primary deep oxidation and dehydrogenation routes of ethane to CO_x and coke respectively, which proceed effectively over the acidic OH groups and the Al^{3+}–O^{2-} acidic centers. On the contrary, the formation of ethylene seems to be coupled to the presence of redox sites on the catalytic surface and requires the presence of the molybdena phase. Moreover, the redox sites of the MoO_x species were found to unselectively activate the further overoxidation of the olefin to carbon oxides. Therefore, Al_2O_3 catalyzes the unselective primary oxidation of ethane to carbon oxides, whereas the molybdena phase is involved in the selective oxidative dehydrogenation (ODH) of ethane to ethene and the secondary overoxidation of ethene to CO_x.

Keywords: Ethane; Oxidative dehydrogenation; Molybdena/alumina catalysts; Alumina functionality; Temperature-programmed reaction

1. Introduction

Light olefins are mainly produced by steam cracking of petroleum fractions, a process that operates under severe conditions and is highly energy consuming. The catalytic oxidative dehydrogenation (ODH) of alkanes is an appealing alternative route and the exothermic character may allow developing an energetically well-balanced process. However, the industrial realization of ODH is still hindered by low yields. A wide range of materials have been studied as potential catalysts for the oxidative dehydrogenation of light hydrocarbons, as reviewed in literature [1–3]. However, a significant part of the ongoing research has been focused on catalysts based on early transition metal oxides, i.e., mainly oxides of Mo and V. Our recent study on the selective oxidation of ethane to ethene over molybdena catalysts shows that alumina-supported molybdena catalysts are active and highly selective in the production of ethene [4].

Due to the relatively high temperature at which selective oxidation reactions take place, the occurrence of a homogeneous–heterogeneous reaction scheme has been postulated in literature. In light of this, we undertook a systematic research to elucidate the parallel and consecutive reaction steps in ethane oxidative dehydrogenation over a molybdena/alumina catalyst under transient conditions by the temperature-programmed reaction (TP-reaction) technique [5]. Reactions of ethane in the absence of oxygen were studied in order to investigate the participation of lattice oxygen, while the reactions of the product of interest, ethene, in an oxidizing and non-oxidizing atmosphere were also investigated. Additionally, the pathway of all the above-mentioned reactions was also studied in the gas phase, in the absence of catalyst.

A further step in the study of ethane ODH reaction network over molybdena/alumina catalysts [5] was the evaluation of the possible role of pure alumina in the reaction pathway. Therefore, we report here the investigation of the interaction of ethane and ethene in an oxidizing and non-oxidizing atmosphere with pure alumina under temperature-programmed conditions, monitored by mass spectroscopy. The results presented in this work are also complimentary to in situ IR studies performed on the same support in C_2H_6/O_2 environment

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[6] and confirm the role of the detected surface species in the reaction pathway.

2. Experimental

A commercial γ-Al_2O_3 (Engelhard, S.A. = 183.9 m^2/g) was used as the catalyst. Prior to use, the material was calcined in synthetic air at 650 °C for 6 h. Temperature-programmed reaction experiments were performed under steady flow conditions in a U-shaped quartz reactor, equipped with a coaxial thermocouple for temperature monitoring. For each experiment, a different reactant mixture (2%C_2H_6/He, 2%C_2H_6/2%O_2/He and 2%C_2H_4/2%O_2/He) was introduced in the reactor and the temperature was raised with a constant heating rate of 15 °C/min to 700 °C. The system was maintained isothermally at 700 °C for 20 min under the reactant mixture stream. The exit gas composition was monitored online by a quadrupole mass analyzer (Omnistar, Balzer). The intensity of the signal for each reactant/product was normalized, based on the relative sensitivity factor of each species with respect to helium and corrected for contributions from other components, based on the cracking pattern of each molecule. Further details are given elsewhere [5].

3. Results and discussion

3.1. Oxidative dehydrogenation of ethane

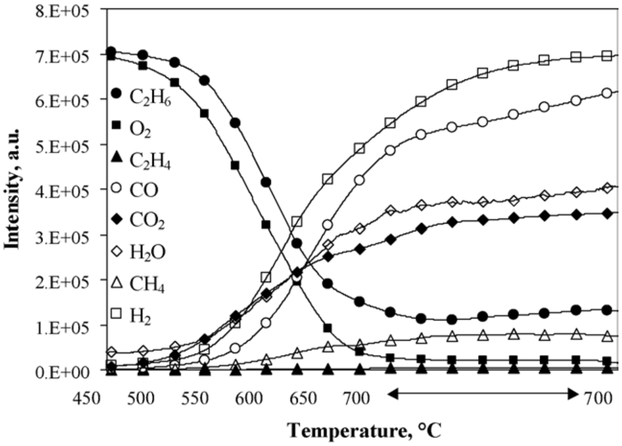

Fig. 1. TP-reaction profile of ethane oxidative dehydrogenation over γ-Al_2O_3 (reaction conditions: $\beta = 15$ °C/min, $W = 0.1$ g, $F = 30$ cm^3/min, 2%C_2H_6/2%O_2/He).

The TP-reaction profile for the reaction of ethane with oxygen (ratio 1/1) diluted in helium over γ-Al_2O_3 is presented in Fig. 1. Al_2O_3 appears certainly not inert, but on the contrary quite reactive, activating ethane at 490 °C. The values of ethane and oxygen conversion and product selectivities in the 500–700 °C range are tabulated in Table 1, with the results for all the experiments performed and presented further down. The first reaction products detected originate from the total oxidation of ethane, CO_2 and H_2O, followed at a slightly higher temperature by the concurrent formation of high amounts of H_2, CO and in low extent CH_4, formed by partial oxidation (POE) and/or reforming reactions of ethane. As temperature and conversion increases, CO is produced in increasing amounts, in expense to CO_2, whose selectivity decreases. Only traces of ethylene were detected, with a selectivity of less than 1% in the whole temperature range studied, in agreement with literature data [7]. Note that at 700 °C, the conversion of ethane calculated based

Table 1
Oxidation and pyrolysis reactions of ethane and ethene over Al_2O_3

Reaction mixture	T (°C)	H/C conv.[a] (%)	H/C conv.[b] (%)	O_2 conv.[c] (%)	Selectivity[d] (%)		
					CO	CO_2	CH_4
C_2H_6/O_2	500	1.87	2.03	6.23	21.26	72.53	6.21
	550	7.40	6.65	18.75	21.83	72.67	5.69
	600	35.79	21.42	48.79	31.99	60.24	7.60
	650	69.94	52.02	78.06	46.16	44.33	8.41
	700	88.98	78.59	93.71	56.65	34.39	8.08
C_2H_4/O_2	500	4.47	3.23	9.68	66.03	31.26	2.72
	550	8.30	5.46	14.24	66.05	31.19	2.76
	600	6.36	12.17	27.11	65.47	31.50	3.04
	650	35.89	30.01	55.10	61.48	34.00	4.52
	700	63.08	58.67	94.30	52.48	39.91	7.61
C_2H_6	500	–	–	–	–	–	–
	550	–	–	–	–	–	–
	600	0.76	0.14	–	67.43	26.69	5.44
	650	5.95	1.62	–	64.77	26.05	8.22
	700	26.90	7.67	–	63.05	25.05	11.73

Hydrocarbon and oxygen conversion values and product selectivities in the 500–700 °C temperature range.

[a] Calculation based on C_2H_6 consumption.

[b] Calculation based on evolution of C-containing gaseous products.

[c] Calculation based on O_2 consumption.

[d] Selectivity to ethylene was negligible in all the TP-reaction experiments performed.

on the gaseous products is 12% lower than the actual conversion (see Table 1), indicating a substantial formation of coke on the alumina surface.

Comparison of the data presented above with previous data acquired at identical conditions using an empty reactor [5] indicates that surface phenomena certainly occur on bare alumina. Homogeneous reactions of ethane oxidation were found to take place at temperature over 650 °C, with main production of primarily ethene and CO originating from secondary side reactions. Over Al_2O_3 activation of ethane proceeds at significantly lower temperature, comparable to that recorded over a 20 wt.% MoO_3/Al_2O_3 catalyst [5], showing that pure alumina is able to convert ethane in the same magnitude as the molybdena catalyst. However, the product distribution significantly differs, since ethylene was produced with high selectivity over the catalyst, indicating the occurrence or dominance of a different reaction pathway in ethane ODH over alumina. In situ IR studies on the same support under C_2H_6/O_2 flow in the temperature range of 50–500 °C showed that ethane interacts with the hydroxyl groups of alumina and forms ethoxide species (reaction (1)), strongly bound to the alumina sites, which with increasing temperature are easily overoxidized to aldehydic intermediates and consequently formates and acetates, precursors for the formation of carbon oxides [6]. The detection of only carbon oxides reported here confirms the above findings for the role of the surface species reported in the IR study. Even though the intermediate species over both the molybdena-on-alumina catalyst and pure alumina are postulated to be ethoxides, the fate of these groups depends on the strength of bonding with the surface. The weak interaction with MoO_x units allows their dehydrogenation to ethylene via β-hydrogen abstraction and the release of ethylene in the gas phase, while the strong bonding with alumina via the OH groups leads to an easy overoxidation to carboxylates and consequently CO_x. Adsorbed ethylene, resulting from the dehydrogenation of the ethoxide groups was also detected. However, the hydroxyl groups of alumina are known to be strong chemisorption sites for olefins [8]. Thus, ethylene does not escape in the gas phase but is overoxidized via the reverse ethoxide route (reaction (2)) to carbon oxides and additionally, polymerizes on the alumina surface to form carbonaceous deposits [9]. Therefore, no gaseous ethylene is detected in the reaction products.

$$C_2H_6 \rightarrow [C_2H_5O]_s \qquad (1)$$

$$CO_x \leftarrow [CH_3COO]_s, [HCOO]_s \leftrightarrow [C_2H_5O]_s \leftrightarrow [C_2H_4]_s \qquad (2)$$

The large amounts of CO and H_2 produced result from the efficient partial oxidation and/or reforming of ethane over Al_2O_3. Alumina has been reported to be catalytically active and favor the formation of syngas via ethane partial oxidation [10]. Adsorption of ethane on the surface of alumina probably leads to C–H and C–C bond cleavage followed by H–H and C–H recombination, producing H_2 and CH_4. Severe dehydrogenation of the adsorbed hydrocarbon fragments leads to formation of carbonaceous deposits, as indicated by our results, while CO is produced by the reaction of gas phase oxygen with the surface deposited carbon.

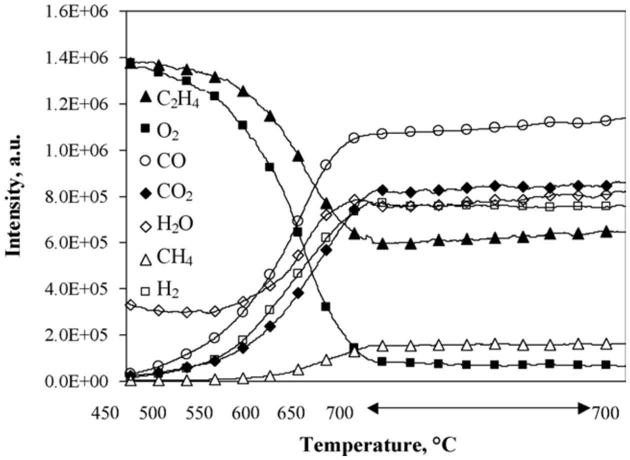

Fig. 2. TP-reaction profile of ethene oxidation over γ-Al_2O_3 (reaction conditions: β = 15 °C/min, W = 0.1 g, F = 30 cm^3/min, 2%C_2H_4/2%O_2/He).

3.2. Oxidation of ethene

As aforementioned, produced ethylene in ethane ODH is strongly absorbed on the surface of alumina, leading to total oxidation products, but also hydrogen and coke formation. In order to investigate the direct interaction of C_2H_4 with alumina, a similar TP-reaction experiment was conducted using ethene with oxygen (ratio 1/1) as feed (Fig. 2). Indeed, ethene reacts with alumina in the same temperature range as ethane, leading to a similar reaction profile with the production of mainly CO, CO_2, H_2 and in higher temperature low amounts of CH_4. Traces of oxygenated products are released in the gas phase at ∼450 °C. The (m/z) fragments 43 and 30, attributed to acetaldehyde and formaldehyde, increase and reach a maximum at 667 °C and 695 °C, respectively. The following decrease accounts for the easy overoxidation of oxygenates to carbon oxides at the high temperatures employed. The production of aldehydes confirms that ethene interacts with the alumina hydroxyls and forms ethoxide species, while carbon oxides are formed from the oxidation of ethoxides to carboxylate species. While CO_2 was the first main product in the case of ethane, CO is the initial dominant oxide in the case of ethene oxidation, with initial carbon-selectivity equal to 65%. The ratio of CO/CO_2 decreases with increasing temperature from 2.3 to 1.3 at 700 °C, due to overoxidation of CO to CO_2, a surface-assisted reaction that becomes important at higher temperatures [5]. Furthermore, even though the activation temperature of both ethane and ethene is the same, the rate of ethene consumption is significantly lower than ethane, indicating that the oxidation and dehydrogenation of ethane occur more readily than that of ethene. Coking observed in the case of ethene oxidation and produced hydrogen was also less, supporting the previous observation. If we compare the results of ethene oxidation over the molybdena/alumina catalyst [5] and the bare alumina support, we observe that both the initial activation and the extent of conversion of ethene are higher for the actual catalyst. This implies that the secondary reactions of ethene overoxidation observed during ethane ODH with increasing conversion cannot be attributed to contributions from the support, but mainly to the action of the molybdena phase.

3.3. Non-oxidative dehydrogenation of ethane

The oxidative dehydrogenation reaction over most transition metal oxide catalysts proceeds via a redox Mars and van Krevelen type mechanism. Thus, a key aspect of selective oxidation catalysts is the presence of redox sites and labile lattice oxygen, as in the case of reducible molybdenum oxide. Indeed, when pure ethane was passed with increasing temperature over the molybdena catalyst, ethylene was produced via the oxidative dehydrogenation route with the participation of the lattice oxygen. Gradually, the catalyst became reduced and catalyzed reforming reactions of ethane leading to syngas production [5]. In the case of bare alumina, Al^{3+} ions should be in principle unreducible. In order to investigate the interaction of alumina with ethane in the absence of oxygen in the gas phase, a 2% C_2H_6/He reaction mixture was passed over the sample and the temperature was raised to 700 °C (Fig. 3). Contrary to the molybdena-containing catalyst, which activated ethane at ~500 °C [5], pure ethane over alumina starts reacting at 600 °C, leading to the production of mainly H_2. The onset of the dehydrogenation reaction over alumina coincides with the initiation temperature of the homogeneous gas phase reactions of ethane dehydrogenation. However, in the homogeneous reactions, dehydrogenation leads to the production of equimolar amounts of ethylene and hydrogen [5], while the conversion of ethane is almost twice the conversion in the presence of alumina at 700 °C. Over alumina, the production of ethylene is minimal, while small amounts of mainly CO and in less extent CO_2 are also produced. This implies the participation of the alumina surface, which alters the reaction pathway. The 70% deviation between the conversion of ethane calculated by the decrease of the ethane signal and the one based on the products shows the formation of a substantial amount of coke on the surface, observed also visually by the black color of alumina after the experiment. The reaction is initiated in the gas phase by the well-known pyrolysis chain mechanism:

$$C_2H_6 \rightarrow CH_3^{\bullet} + CH_3^{\bullet} \tag{3}$$

$$C_2H_6 + CH_3^{\bullet} \rightarrow C_2H_5^{\bullet} + CH_4 \tag{4}$$

However, the decomposition of ethyl radicals to ethene, which takes place in homogeneous pyrolysis, is hindered by alumina. It is probable that the alkyl radicals formed are captured by the alumina surface and are deeply dehydrogenated to hydrogen and carbon deposited on the surface. Ethylene formed during this dehydrogenation procedure, detected by in situ IR during the exposure of alumina in pure ethane flow in the absence of oxygen at 50 °C [6], does not escape in the gas phase, but is further dehydrogenated to coke.

The origin of the oxygen-containing products CO_x is not clear. CO has been reported to appear in TPD spectra of Al_2O_3 after treatment with ethanol in the absence of oxygen and its formation was attributed to partial decomposition of adsorbed fragments via the action of lattice oxygen [9]. However, the participation of the alumina lattice oxygen in the formation of CO_x in our case seems doubtful, since alumina is practically unreducible and the extraction of lattice oxygen is very hard. A temperature-programmed reduction experiment performed in the presence of H_2 over the alumina under study showed no reduction up to temperature of 1000 °C. Hydrogen is a much stronger reductant than ethane, thus the extraction of lattice oxygen from ethane at temperatures up to 700 °C appears highly unlikely. It seems more possible that the oxygen-containing products arise from the interaction of adsorbed hydrocarbon fragments with the alumina hydroxyl groups forming ethoxides (in very small amount), as postulated in the case of ethane/ethene oxidation. These ethoxides decompose and ultimately yield carbon oxides at high temperature.

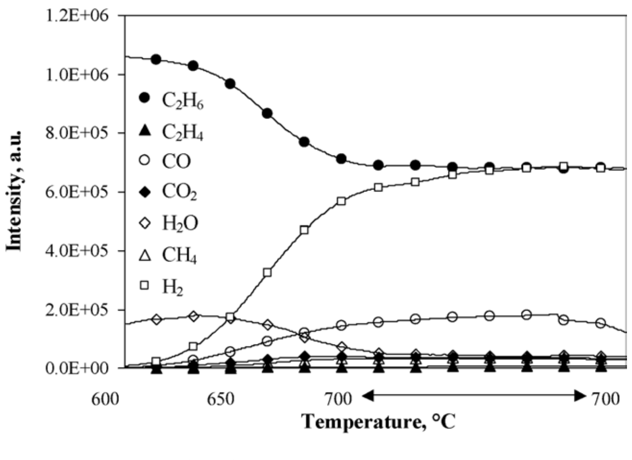

Fig. 3. TP-reaction profile of ethane pyrolysis over γ-Al_2O_3 (reaction conditions: $\beta = 15$ °C/min, $W = 0.1$ g, $F = 30$ cm^3/min, 2%C_2H_6/He).

4. Conclusions

The results of the present work indicate that the formation of ethylene is coupled to the presence of redox sites on the catalytic surface and requires the presence of the reducible molybdena phase. On the contrary, the primary deep oxidation and dehydrogenation routes of ethane to carbon oxides and coke respectively proceed effectively over the acidic OH groups and the Al^{3+}–O^{2-} acidic centers. This is an indication for the participation of different oxygen species in selective and deep oxidation and shows that the formation of carbon oxides does not necessarily follow a redox mechanism. Moreover, according to the present data, the secondary reactions of ethene overoxidation are mainly due to the action of the molybdena phase and cannot be attributed to the alumina support, which predominantly participates only in the primary unselective reactions. The redox sites of the MoO_x species are therefore active for both selectively converting ethane to ethene and unselectively activating the further overoxidation of the olefin to carbon oxides. This last conclusion nicely explains the selectivity–conversion behavior of a series of (0–30 wt.%) MoO_3/Al_2O_3 catalysts, studied in a previous work [4]. Catalysts with Mo loading in the submonolayer regime (<15 wt.%) presented low initial C_2H_4 selectivity, due to primary total oxidation reactions occurring on uncovered Al_2O_3 patches on the surface. Increase of loading, and thus increase of the alumina coverage by the molybdena phase led as expected, based on the present data, to improved initial ethene selectivity, which reached almost 100% with the monolayer and over monolayer coverage catalysts. Another observation that supports the results of the present work is that the trend of the decrease in ethene selectivity with increasing conversion was the same on all catalysts independent of the molybdena loading, indicating again that the MoO_x phase, and not the support, is mainly responsible for the secondary ethene oxidation.

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