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Selective oxidehydrogenation of ethane with CO_2 over CeO_2-based catalysts

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Abstract

Ceria catalysts were found active and selective to the oxidehydrogenation of ethane (ODE) with CO_2 and the actual contribution for C_2H_4 formation from heterogeneous catalysis was 75–55% in the range 953–993 K. The presence of calcium ions in solid solution in the ceria crystalline network increased significatively the selectivity to ethene and the efficiency of CO_2 as oxidant in the heterogeneous reaction. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

To reach higher selectivities to desired products is a main challenge in development of the catalytic process of oxidative dehydrogenation of light alkanes. This is because various oxygen species are in dynamic equilibrium together with oxygen in gas phase and different oxidation reactions are taking place simultaneously. In order to avoid such complicated reaction patterns, there are several reports which propose using inert CO_2 as an oxidant for the selective conversion of alkanes C_1–C_3 in olefins and syngas [1–6]. CO_2 can dissociate on the catalyst surface to produce active oxygen species as expressed in Eq. (1)

$$CO_2 \Rightarrow CO + O \quad (1)$$

Krylov et al. [3] showed that manganese oxide catalysts were active for these reactions. The properties of these catalysts can be modified by addition of other oxides (Cr, Ca, K) and their use was studied in the transformation of different organic compounds (olefins, alcohols) [1]. Other catalytic systems like PbO–MgO [2] or La_2O_3–ZnO [5] have been studied in OCM with CO_2, producing high selectivities to C_2 products. Nevertheless, the mechanisms of reaction of organic compounds with CO_2 are not clear.

However, it is noteworthy that most data presented in literature were obtained under high temperature (around 1000 K), and certainly, under such a reaction temperature, dehydrogenation of light alkane in gas phase is seriously involved. For example, the thermodynamic equilibrium of ethane dehydrogenation at 1023 K is about 80%, whereas the equilibrium of the reaction

$$C_2H_6 + CO_2 \Rightarrow C_2H_4 + CO + H_2O \quad (2)$$

is about 57% at the same temperature. Therefore, it is necessary and of significance to identify the real contribution from heterogeneous catalysis.

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In our initial study [7], we analysed the contribution of the homogeneous and heterogeneous processes in oxidative dehydrogenation of ethane (ODE) with CO_2 on pure ceria. It was found that this is a real heterogeneous catalytic reaction over CeO_2 catalysts. It was concluded that CeO_2 is active and selective for the ODE with CO_2. The redox Ce^{+4}/Ce^{+3} of CeO_2 can be used for the activation of CO_2 and to produce active oxygen species for the reaction.

In this communication, we study the ODE over CeO_2 and CaO–CeO_2 solid solution catalysts to identify the contribution from heterogeneous catalysis and to analyse the role of the catalyst composition on the heterogeneous reaction. We first studied the reaction in the gas phase and analysed the role of CO_2 in this homogenous reaction. Based on these results, we will study the contribution and the nature of the net heterogeneous reaction on both catalysts and the role of calcium in the heterogeneous reaction selectivity will be analysed.

2. Experimental

The ceria catalyst was prepared by precipitation from a solution of cerium nitrate (C.P. grade) using an oxalic acid solution (A.R. grade) as the precipitant. The precipitate was filtrated, dried at 393 K for 4 h and calcined in air at 1123 K for 6 h. The mixed CaO–CeO_2 catalyst with a calcium oxide content of 10 mol% (hereafter denoted 10CaCe) was prepared by coprecipitation following the same procedure, but calcining at 1373 K for 6 h. Surface areas, determined by the BET method using Ar as adsorbate, were 2.3 and 1.1 m^2/g, respectively. The calcined samples were pressed, crushed and sieved into granules of 20–40 mesh for further use.

X-ray diffractograms were obtained with a Rigaku D/maxRB instrument at room temperature using the Cu Kα radiation (40 kV and 100 mA, scanning rate 8°/min). Raman spectra were obtained with an FT-Raman Bruker RFS100 spectrometer using Nd-YAG laser as excitation source. Spectra were obtained at room temperature with a resolution of 4 cm^{-1} by averaging 100 scans.

The catalytic tests of ODE with CO_2 were carried out in a fixed-bed tubular, down flow reactor at 973–1023 K, using a mixture $C_2H_6/CO_2/He=10/20/170$ ml/min, and a catalyst load of 1 g. Prior to the test, the catalyst was pretreated at 1023 K in a flow of mixture He/CO_2 for 2 h. Then the reactor was cooled down to the desired reaction temperature and the feeding of reacting mixture was started. Blank tests were conducted under the same conditions, by substituting the catalyst for SiC particles of the same size. Pre- and post-catalytic zones of the reactor were filled with SiC bits to reduce the extent of gas-phase reactions. The reactor effluent was analysed on line by gas chromatography. In all cases, mass and carbon balances were within 100±3%. In the initial stage, conversions of ethane and CO_2 were calculated assuming that all hydrocarbons in the exit gas (C_2H_4 and CH_4) came from the conversion of C_2H_6 while CO came from CO_2. Selectivities and differential rates were calculated in the conventional way. The reaction tests were carried out at short residence-time to maintain the ethane conversion relatively low, in such a way that the contribution from heterogeneous catalysis to the title reaction may be estimated on the basis of addition principle of the contributions from homogeneous and heterogeneous catalysis.

3. Results and discussion

3.1. Homogeneous reaction

The reaction in the gas phase between ethane and CO_2 was studied in detail in a previous work [8]. It was shown that conversion depended linearly with residence times for total gas flows lower than 200 ml/min. At higher flows, this linearity disappears indicating that the reaction goes on proceeding at the post-catalytic volume, probably by dragging of radical intermediates by the gas flow. Accordingly, our experiments here were conducted with a total gas flow of 200 ml/min. The homogeneous reaction of ethane and CO_2 is mainly an ethane dehydrogenation, as the products were ethene (selectivity about 95.2%), hydrogen, and minor amounts of methane at the higher temperatures. The evolution of the yield of the products with the residence time allows to establish that ethene and H_2 are primary products while methane is a secondary product formed by hydrocracking of ethane according to the reaction

$$C_2H_6 + H_2 \Rightarrow 2CH_4 \tag{3}$$

Table 1
Homogeneous reaction of ethane in presence and the absence of CO_2

Temperature (K)	With CO_2					Without CO_2		
	Conversion (%)		Yield (%)			Conversion (%)	Yield (%)	
	C_2H_6	CO_2	C_2H_4	CH_4	CO	C_2H_6	C_2H_4	CH_4
953	0.78	0	0.76	0.02	Trace	1.54	1.49	0.05
963	1.19	0	1.17	0.02	Trace	2.33	2.26	0.07
973	1.89	0	1.85	0.04	Trace	3.58	3.47	0.12
993	4.26	0.04	4.17	0.09	0.03	7.59	7.36	0.24
1003	6.52	0.06	6.37	0.15	0.05	11.17	10.79	0.38
1013	9.51	0.08	9.30	0.21	0.08	15.71	15.17	0.54
1023	13.44	0.09	13.14	0.30	0.09	21.63	20.91	0.71

However, under all experimental conditions used in this work, the highest conversion of CO_2 observed in the homogeneous reaction in the gas phase between C_2H_6 and CO_2 was only about 0.1%. This is indicative that the homogeneous reaction between C_2H_6 and CO_2 was negligible, CO being formed at the higher temperatures, probably by a reverse-water gas shift reaction:

$$H_2 + CO_2 \Rightarrow CO + H_2O \tag{4}$$

Thus, CO_2 is not activated in this gas-phase reaction. To clarify its role in the reaction, we repeated the same experiments but substituting the CO_2 by inert (i.e. C_2H_6+He mixture, 10:190 ml/min). The results (Table 1) show clearly that CO_2 acts as an inhibitor in the gas-phase reaction.

3.2. Reaction in the presence of catalysts: heterogeneous ODE

The results of the tests in the presence of each catalyst are compared with those obtained in their absence in Fig. 1. As it can be seen there, in the presence of both catalysts, the conversion of ethene increases, but the most relevant feature is that the dissociation reaction of CO_2 proceeds following the reaction equation (1), its conversion being equal or higher than that of ethane. The reaction products are the same in the three cases, but their distribution varies: in the presence of catalysts, the yield of ethene increases while that of methane shows practically no change. This reveals that the cracking reaction proceeds only in the gas phase and not on the catalyst surface.

Noteworthily, the catalytic activity was stable for at least 80 h on stream. The catalytic results were also reproducible after treatment with a mixture of He and CO_2 at 1023 K for 1 h. It was observed that after catalytic tests, the catalyst samples remained white, which points to the absence of carbon formation on their surface during the reaction.

As CO_2 does not participate in the homogeneous reaction, we may assume that the homogeneous and heterogeneous reactions are independent, and the contribution of the net heterogeneous reaction may be estimated by calculating the rates of product formation by difference between the values for the overall and the homogenous reactions. The results of this calculation are shown in Fig. 2.

It is clear from the figure that ceria-based catalysts show a fairly good catalytic performance for the ODE with CO_2. The reaction may be expressed as Eq. (2). However, the ratio between the rates of formation of the main products and the product distribution from the heterogeneous reaction is different on each catalyst. On pure ceria, the rate of CO formation exceeds that of ethene formation. Taking into account the stoichiometry of reaction (2), this result involves the simultaneous presence of a heterogeneous unselective oxidation of ethane to CO. Since no carbon deposit was found on the ceria surface, according to Ref. [9], we may suggest a non-selective catalytic reaction as follows:

$$C_2H_6 + 5CO_2 \Rightarrow 7CO + 3H_2O \tag{5}$$

Heterogeneous reactions (2) and (5) separate the heterogeneous depletion rates of C_2H_6 and CO_2 and the

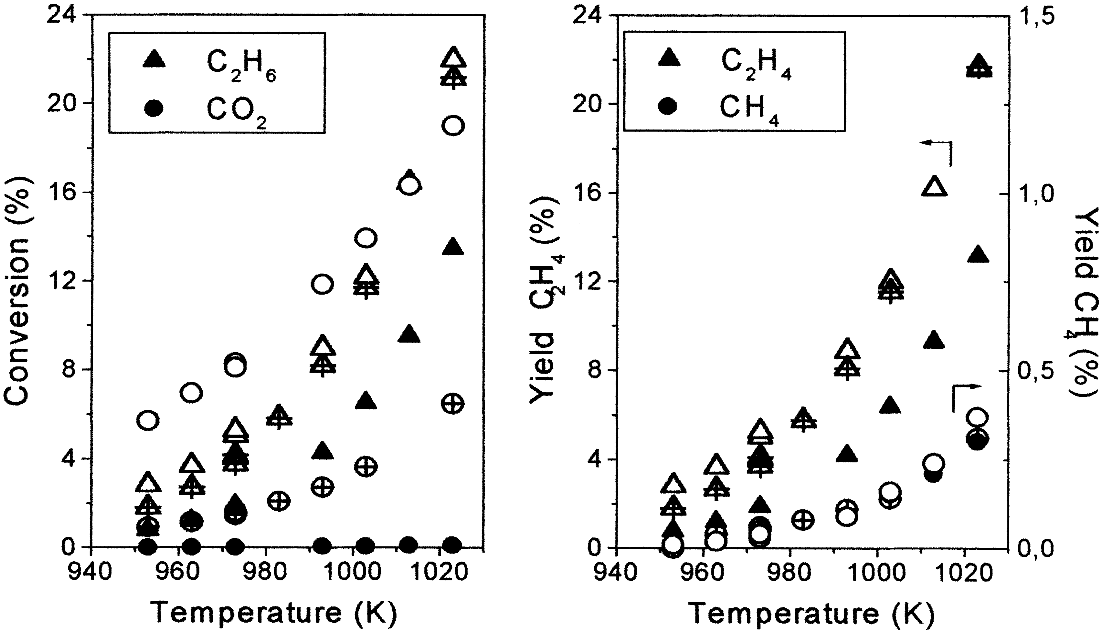


Fig. 1. Conversion of ethane and CO_2 (left) and yields of ethene and methane (right) in ODE with CO_2 in the presence of CeO_2 (empty symbols), of 10CaCe (crossed-empty symbols) or in the absence of catalysts (full symbols).

formation rate of CO into two parts: one is selective and responsible for the formation of C_2H_4, and the other is non-selective and leads to the production of CO. The corresponding apparent activation energies and the reaction order with respect to C_2H_6 are listed in Table 2. The apparent activation energy for reaction (2) is in the range of the ODE with gaseous O_2 over various catalysts [10]. The reaction order with respect to C_2H_6 is 0.95±0.05, which is reasonable. All these confirm that the analysis for the reaction is correct.

Taking into account the different stoichiometry between ethane and CO_2 in the two heterogeneous reactions (2) and (5) and their formation rates, it is possible to calculate the effectiveness of CO_2 for selective oxidation (i.e. the percentage of CO_2 taking part in the selective ODE reaction (2)) and the actual contribution from heterogeneous ODE with CO_2 to the formation

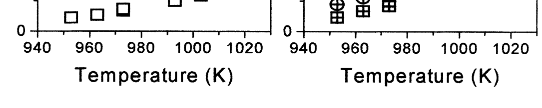


Fig. 2. Specific rates of formation of ethene (squares) and CO (circles) by heterogeneous reaction of ODE with CO_2 over ceria (left) and 10CaCe (right) catalysts. Experimental conditions in text.

Table 2
Apparent activation energies and the reaction order with respect to C_2H_6 in heterogeneous reactions on CeO_2 at a total flow rate of 200 ml/min[a]

Depletion rate of C_2H_6	Activation energy (kcal/mol)		Reaction order to C_2H_6	
	Ea[a]	r^b	n	r^b
rC_2H_6-ht	34.5±2.3	0.998	0.83±0.05	0.999
rC_2H_6-ht (2)	35.6±3.4	0.995	0.95±0.05	0.999
rC_2H_6-ht (5)	32.0±1.9	0.998	0.55±0.06	0.996

[a] Confidence interval for 95% of cases.
[b] Correlation coefficient of the fitting.

of C_2H_4 over CeO_2. In the range 953–1023 K, the CO_2 is of 22–27% and the selectivity to ethene of 58–65%.

3.3. *Influence of calcium in the catalytic activity*

At a variance of ceria, over CaO–CeO_2, the rate of heterogeneous formation of ethene is rather close to that of CO (Fig. 2), and similar to that observed on pure ceria. This implies that the main effect of the presence of calcium in the catalyst is to inhibit the non-selective oxidation (5). In fact, the calculated effectiveness of CO_2 increases to 60–75% and the heterogeneous selectivity to ethene to 88–94%. On the other hand, taking into account their different specific surface areas, the areal activity of 10CaCe is almost twofold than that of pure ceria.

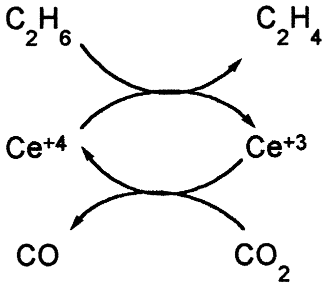
X-ray diffractograms of both the pure ceria and the mixed catalyst were practically identical, showing only the reflections corresponding to a cubic CeO_2 phase (JCPDS file 34-394, cerianite). This result agrees well with those of Zhang and Baerns [11] who reported that for mixed calcium–cerium oxides, a fluorite-type CaO–CeO_2 solid solution was formed for low Ca content. They also reported that over the entire range of CaO contents (0–100%), the XPS surface composition was approximately the same as the bulk. The formation of a solid solution in the ceria network is further evidenced by the Raman spectra: the spectrum of 10CaCe sample shows only the very strong peak at 465 cm^{-1} characteristic of CeO_2, but broader than in the pure-ceria spectrum, and the minor, very weak peak at 609 cm^{-1} of ceria appears as a small shoulder to the main peak. This supports the interpretation of a uniformly distributed Ca in the catalyst.

Zhang and Baerns [11] found that the selectivity to C_2 hydrocarbons in the oxidative coupling of methane (OCM) over these catalysts varied with CaO contents in parallel to the variation of oxygen-ion conductivity. This parameter increased linearly with CaO content up to a maximum for 20 mol% of CaO. Very recently, Wang et al. [6] reported that CO_2 increased the selectivity to C_2 products in the OCM with CO_2 over a CaO–CeO_2 (atomic ratio Ca/Ce=0.5) catalyst. Although the contribution of the homogeneous reactions, and therefore, the effect of CO_2 on them were not analysed, the authors showed by CO_2-TPD studies that the desorption peak of CO_2 shifted to higher temperatures when the CO_2 partial pressure in the gas phase increased. They interpreted this as being indicative of the existence of a pool of chemisorbed-CO_2 on the catalysts' surface.

In our case, we may assume that the presence of Ca in the solid solution of catalyst 10CaCe causes an increase of oxygen-ion mobility which leads to a change in the nature of the main oxygen species in the surface during the reaction. Besides, the surface basicity must be increased by the presence of Ca. The combination of these two factors could be responsible for a quicker desorption of the formed olefin, thus favouring the selectivity to ethene.

4. Conclusions

Our present study shows evidence that the ODE with CO_2 over ceria-based catalysts is a heterogeneous catalytic reaction. The reaction is rather complicated because of the coexistence of homogeneous dehydrogenation in the gas phase and heterogeneous catalysis on the catalyst surface. In the ODE with CO_2 over CeO_2 catalyst, CeO_2 plays the role of a redox catalyst. Therefore, we suggest that the catalytic reaction is carried out via the reduction of the catalyst by C_2H_6 and its oxidation by CO_2, expressed as follows:



or expressed in the following equations:

$$2CeO_2 + C_2H_6 \Rightarrow Ce_2O_3 + C_2H_4 + H_2O \qquad (6)$$

$$Ce_2O_3 + CO_2 \Rightarrow 2CeO_2 + CO \qquad (7)$$

The overall reaction, i.e. (6)+(7), is reaction (2). Therefore, the redox properties and the ability to store and release oxygen of CeO_2 are also seen when CO_2 is used as an oxygen source and/or oxidant in the ODE. The selectivity to olefin is highly increased by the solid solution of calcium ions in the cubic framework of CeO_2.

The features for this reaction are that the selectivity to C_2H_4 of the heterogeneous reaction can be higher than 90% under a proper catalyst composition and reaction condition, and that in addition to H_2O, CO is the only non-selective product. As presently available technologies may use CO as raw material, the practical application of this type of reaction could lead to processes that could make use of the 100% of the carbon-containing products.

Summarizing, ceria-based catalysts are able to activate CO_2 and to use it as a selective oxidant for the oxidehydrogenation of ethane. A more detailed study on the oxidehydrogenation of other light alkanes with CO_2 on CeO_2 and CeO_2-based catalysts is now underway.

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References

[1] T. Nishiyama, K. Aika, J. Catal. 122 (1990) 346.
[2] V.R. Choudhary, V.H. Rane, J. Catal. 135 (1992) 310.
[3] O.V. Krylov, A.Kh. Mamedov, S.R. Mirzabekova, in: V. Cortés Corberán, S. Vic Bellón (Eds.), New Developments in Selective Oxidation II, Stud. Surf. Sci. Catal. 82 (1994) 159.
[4] O.V. Krylov, A.Kh. Mamedov, S.R. Mirzabekova, Catal. Today 24 (1995) 371.
[5] G. Li, X. Guo, Catal. Lett. 42 (1996) 149.
[6] Y. Wang, Y. Takahashi, Y. Ohtsuka, Appl. Catal. A 172 (1998) L203.
[7] R.X. Valenzuela, G. Bueno, V. Cortés Corberán, Y. Xu, C. Chen, Proceedings of the 215th ACS National Meeting (Abstracts), Dallas 1998, COLL-085.
[8] C. Chen, Y. Xu, R.X. Valenzuela, G. Bueno Sobrino, V. Cortés Corberán, in: A. Centeno, S.A. Giraldo, E.A. Paez (Eds.), Actas XVI Simposio Iberoamericano de Catalisis, Cartagena de Indias, Colombia, Vol. 2, 1998, p. 1465.
[9] S.P. Mirzabekova, A.Kh. Mamedov, O.V. Krylov, Kinet. Catal. 38 (1997) 651.
[10] R.J. López, N.S. Godjayeva, V. Cortés Corberán, J.L.G. Fierro, E.A. Mamedov, Appl. Catal. A 124 (1995) 281.
[11] Z.-L. Zhang, M. Baerns, J. Catal. 135 (1992) 317.