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Catalysis Today 112 (2006) 148–152

CATALYSIS TODAY

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Determination of kinetic parameters of the oxidehydrogenation of ethane with CO_2 on nanosized calcium-doped ceria under fast deactivation processes

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Abstract

Kinetic parameters of the oxidehydrogenation of ethane with CO_2 on nanosized Ca-doped CeO_2 have been investigated. During reaction, interaction of the reactants with the oxide catalyst causes a fast deactivation process. Overlapping of this fast deactivation with catalytic reaction makes quite difficult the reliable determination of kinetic parameters. This handicap can be overcome by getting sufficient data in a short testing time, thus reducing the degree of deactivation. The kinetics of catalytic reaction and of catalyst deactivation have been studied by conducting a series of consecutive tests at increasing temperatures in steps of 20 °C and monitoring the evolution of the reaction for periods of 30 min on stream at each temperature, with full product analysis every 3 min. At temperatures above 680 °C, catalytic rates decreased linearly with run time at isothermal operation, while deactivation rates increased with increasing temperature. Analysis of the results allows to uncouple catalyst deactivation and catalytic reaction and to obtain the kinetic parameters of both processes (i.e., steady-state and deactivation rates, and their apparent activation energies). Deactivation rate of CO formation is one order of magnitude faster than of ethene formation but both processes show the same apparent activation energy, ca. 47 kcal/mol. The apparent activation energy values for the catalytic reaction are 32 ± 4 and 26 ± 2 kcal/mol for the rates of formation of ethene and CO, respectively.

Keywords: Ceria catalysts; CO_2 as oxidant; Oxidehydrogenation; Ethane; Deactivation kinetics

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1. Introduction

Oxide catalysts act as one active component of the reaction network in the oxidation reactions they catalyse. As a consequence, their interaction with the reactants modify their nature and surface properties, producing a transient behaviour in working conditions. This evolves leading either to reach a dynamic equilibrium with the reaction media, or to deactivation processes simultaneous to the catalysed reaction. The latter was the case of the oxidehydrogenation (ODH) of ethane with CO_2 on nanosized ceria-based catalysts: in a previous study in a continuous flow reactor [1], it was found that the catalytic performance of nanosized CaO-doped CeO_2 evolved with run time during the reaction. When reaction temperature exceeded 680 °C a very fast decrease in the formation of CO occurred, in such a way that an increase of reaction temperature could not increase the observed rate of formation [1].

When fast deactivation occurs, its overlapping with the catalysed reaction makes quite difficult, or even inhibits, the reliable determination of kinetic parameters for each of these two processes (reaction and deactivation), as the observed kinetic data depend not only on the catalytic reaction kinetics (i.e., steady-state kinetics) but also on the time on stream (or run time) of the catalyst sample, which determines the deactivation degree at the time of measurement. Probably because of this there are very few studies of deactivation during oxidation reactions in the literature [2,3]. This experimental problem is specially serious when operating in a continuous regime, and using gas chromatography to follow the evolution of the reaction under transient conditions. The relatively long analysis time needed impedes a close monitoring of the catalytic performance evolution and brings along a bigger deactivation during the tests.

To overcome these difficulties, we have used experimental strategies that yield the sufficient number of data in a short time.

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doi:10.1016/j.cattod.2005.11.018

This allows, on one hand, to reduce the degree of deactivation (by reducing the reaction time) and, on the other, to study the deactivation kinetics in a short experimentation time. Once the deactivation parameters are determined, the kinetic data (product formation rates) of the catalytic reaction without deactivation can be estimated, and the kinetics of the very catalytic reaction can be analysed.

In this paper we report the investigation of the kinetics and the deactivation of nanosized CaO-doped CeO_2 catalysts in the ODH of ethane with CO_2 applying this approach, analysing the catalytic behaviour evolution in a relatively short testing time by means of a testing unit with very fast response to operational changes, equipped with fast on-line GC analysis. Such a combination allows to change and stabilize the reaction conditions in very short times (typically, 6 min for a 20 °C temperature jump and almost instantaneous for a reactants flow change), and to analyse all the gaseous reaction products in 90 s, thus providing a practically continuous monitoring of the reaction products. The procedure to separate the steady-state kinetics and the time-dependent term is described in detail, and the kinetic results are compared with those previously obtained by conventional methods.

2. Experimental

2.1. Catalyst

Preparation of 10 mol% CaO-doped CeO_2 (denoted 10CaCe-FD) catalyst by the freeze drying method is described in [1]. In short, they were obtained by calcining (300 °C, 12 h) amorphous acetate precursors obtained by freeze drying. As prepared, the BET areas and average particle size were: 91 m^2/g and 6.7 nm for the Ca-doped catalyst. XRD, EDX and Raman spectra showed only a single crystalline phase (cubic CeO_2) and a homogeneous distribution of Ca in the doped sample [1]. The samples were pressed, crushed and sieved into granules of 20–40 mesh for further use.

2.2. Catalytic tests

The catalytic tests were conducted in an automatized unit Microactivity-Reference (hereinafter denoted μAc-R) [4], from PID Eng. and Tech. It consists of a down flow tubular fixed-bed reactor (305 mm long, 9 mm i.d.) made of stainless steel, located inside an electrical furnace with low thermal inertia, built without isolation. Reactor, furnace and in and out piping are placed inside a hot box, kept at 160 °C to avoid condensations. Reaction temperature is controlled through an axial K-type thermocouple inserted in the reactor, in direct contact with catalyst bed without thermowell. This allows temperature readings with a response time of milliseconds. Reactant flows are controlled by mass flow controllers (Hi-Tec Bronkhorst). The μAc-R unit has local control (by programmable automats) and remote control via Ethernet by means of the Process@ software (PID Eng. and Tech.) for data acquisition and control. This tool allows to create and configure an experiment as a series of several 'sessions' (or process states), which are later executed sequentially in a fully automatic way, with continuous data acquisition.

Catalytic tests of ODH of ethane with CO_2 were done using a mixture $C_2H_6/CO_2/He = 10/20/170$ ml/min and 1 g of catalyst, conditions selected in previous works [5] to minimize the extent of the homogeneous reaction, at reaction temperatures (T_R) between 500 and 720 °C. Reactor pre- and post-catalytic zones were filled with SiC bits to reduce the extent of gas phase reactions. To determine the extent of homogeneous reaction contribution, blank tests were conducted under the same conditions, by substituting the catalyst for SiC particles of the same size. Conversion, yield and selectivity are expressed in mol% and calculated on a C-atom basis. All C balances were within 100 ± 3%.

2.3. Product analysis

After condensing the liquid products at the exit of the reactor, gaseous reactants and products are analyzed on line in a Varian MicroGC instrument. It is equipped with a capillary PPQH (Pora Plot Q) column (10 m) and a micro-TCD. Operated isothermally, it brings very short analysis times (usually below 90 s), thus allowing a very continuous and precise monitoring of the reaction.

3. Results and discussion

3.1. Preliminary tests

Prior to the catalytic study, the system stability and results reproducibility of the μAc-R unit were tested at 680–750 °C, using the reactor filled with SiC (0.42–0.84 mm) and the same reacting mixture later used for the catalytic tests. The experiment was configured by a series of successive sessions, starting from the secure stop of the system, heating the system in a CO_2/He flow (5/35 ml/min) in order to reproduce the operating protocol previously used in the conventional reactor system, followed by introduction of the reactant mixture at the first reaction temperature tested and sessions at progressively higher T_R, with on line analysis of products, and a final session of secure stop of the system. The results, shown in Fig. 1,

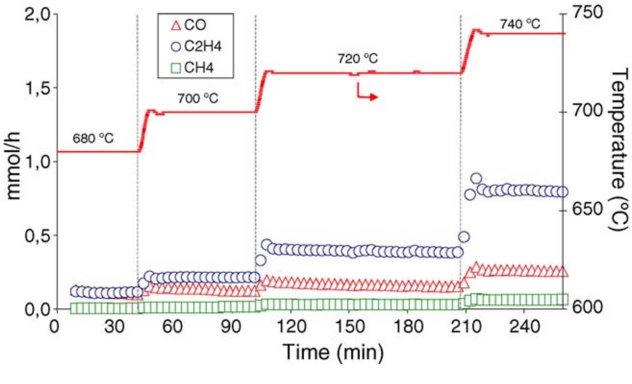

Fig. 1. ODH of ethane with CO_2 without catalyst: product formation rates as a function of temperature and run time. Feed: $C_2H_6/CO_2/He = 10/20/170$ ml/min. Vertical lines show the time of changing the temperature setting.

allowed to conclude that even operating at demanding conditions, such as 700–750 °C, the system response to the temperature increase is very fast, with a control precision of ±1 °C, without overshoot; the system is very stable, reaching the ‘‘stationary’’ state in around 10 min, which allows studying the deactivation (or its absence) by measuring the kinetic parameters after this short period. The analysis is highly reproducible and fast. All this makes feasible to get a very detailed monitoring of the reaction evolution in real time (time delay of just 3 min between consecutive analyses), providing a high number of data in a short period, which allows to follow the time dependence of catalytic performance.

3.2. Homogeneous reaction

The effect of reaction temperature (T_R) and residence time on the homogeneous reaction was studied using a constant reactant molar ratio C_2H_6:CO_2:He = 1:2:17, and varying the total flow of reactants. The tests (sessions) were conducted in increasing temperature steps, varying the total flow at each temperature in a decreasing order, and maintaining each set of conditions for 30 min. Comparison of the results with those previously reported in a quartz reactor [5,6] shows that, for identical reaction conditions, ethane conversion was much lower with the μAc-R unit, reaching only 0.5% conversion at 720 °C, although CO formation is higher (Table 1). Ethane conversion depended linearly of residence time at each temperature (Fig. 2) but, at a variance of the result with the quartz reactor, the extrapolation of the straight lines did not pass through the origin, showing ordinate intercepts that increase with reaction temperature. This fact, together with the CO formation observed, seems to indicate that the steel reactor wall has some catalytic effect on CO_2 decomposition. Nevertheless, this secondary reaction did not affect the apparent activation energy of the homogeneous reaction, which calculated value (77 ± 2 kcal/mol) reproduced well that measured in the conventional quartz reactor (79 ± 2 kcal/mol).

3.3. Catalytic tests

To study the kinetics of the catalytic reaction and that of the deactivation, two temperature ranges were selected, one without deactivation (500–600 °C) and the other with fast deactivation (680–720 °C), with a big temperature gap in between to clearly distinguish both types of behaviour. The kinetics of the deactivation of 10CaCe-FD was studied by conducting a series of tests at increasing T_R, in steps of 20 °C, all above 650 °C. The fresh catalyst sample was heated up to 300 °C (its calcination temperature) in a CO_2/He flow (5/35 ml/min), and kept 30 min at this temperature. Then reactant feed was started and the tests were consecutively conducted at increasing temperatures, measuring the evolution of catalytic performance for 30 min. This period was chosen as a compromise between the need to obtain enough data for consistency of the further statistical analysis and the need to shorten the testing time to limit the degree of deactivation. Fig. 3 shows the evolution of products formation rates of the heterogeneous ODH of ethane with CO_2 (i.e., after subtracting the homogeneous contribution) with run time and T_R. After setting the increase of temperature, marked by the vertical lines, there is period of increasing activity as temperature increases to its new set point, with a maximum due to a slight overshoot (typically 1–2 °C); this is more acute for the sharp change between 600 and 680 °C, due to the bigger temperature jump.

It may be seen that, as expected, at $T_R < 650$ °C, all rates stabilize after the initial 10 min period (for the system to stabilize), while at $T_R > 650$ °C the rates decrease linearly with run time after such a period, with a slope of the decrease increasing with increasing temperature. This corroborates that (fast) deactivation occurs at this temperature range, and its rate increases with temperature.

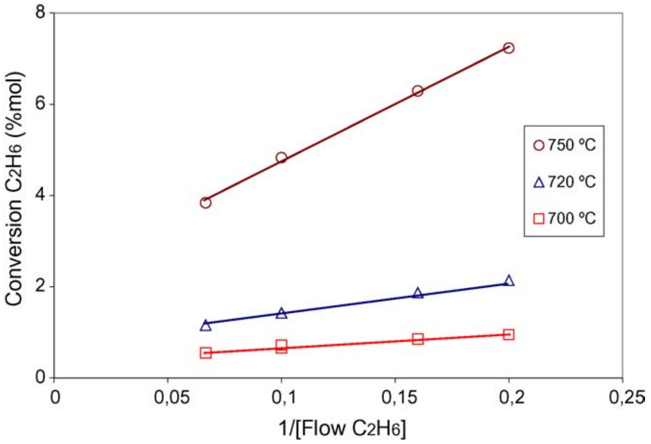

Fig. 2. Effect of the residence time in the ethane conversion in the ODH of ethane with CO_2 without catalyst in the μAc-R unit. Feed as in Fig. 1.

Table 1
Comparison of homogeneous ODH of ethane with CO_2 in the μAc-R unit and conventional quartz reactor [4]

T (°C)	μAc-R unit					Conventional quartz reactor				
	Conversion (mol%)		Yield (mol%)			Conversion (mol%)		Yield (mol%)		
	C_2H_6	CO_2	C_2H_4	CH_4	CO	C_2H_6	CO_2	C_2H_4	CH_4	CO
680	0.33	0.15	0.32	0.01	0.16	0.78	0	0.76	0.02	0
700	0.72	0.19	0.68	0.04	0.20	1.89	0	1.85	0.04	0
720	1.59	0.30	1.52	0.07	0.30	4.26	0.04	4.17	0.09	0.03
740	3.52	0.54	3.38	0.14	0.54	9.51	0.08	9.30	0.21	0.08
750	5.14	0.75	4.94	0.2	0.75	13.44	0.09	13.14	0.30	0.09

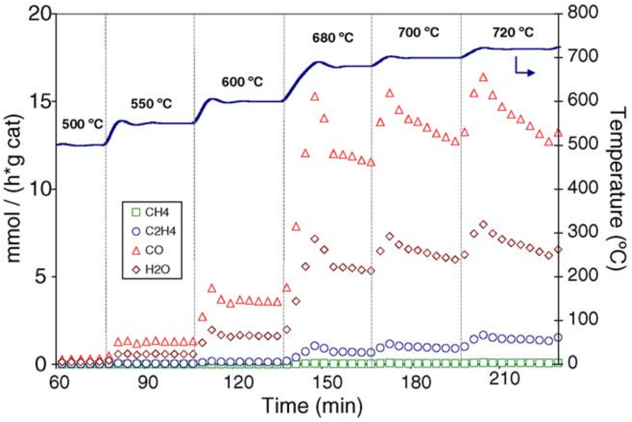

Fig. 3. Heterogeneous ODH of ethane with CO_2 over 10CaCe-FD catalyst: product formation rates vs. temperature and run time. Vertical lines show the time of changing the temperature setting. Conditions: feed $C_2H_6/CO_2/He = 10/20/170$ ml/min, 1 g catalyst.

3.4. Catalytic activity and deactivation kinetics

Under fast deactivation conditions, the rate equation is the result of two terms: a term describing the steady-state kinetics of the catalytic reaction at time zero, hence being independent of time, and an activity term, which is by its definition the time-dependent function. If reaction and deactivation kinetics are separable, the term describing deactivation is merely a function of changing catalyst properties over the time which is, of course, being influenced by reaction conditions [7]. That is, only the number of active sites might decrease throughout the experiment [8]. The criterion for separability is the independence of the activity term on temperature and concentration [9].

Thus, by keeping the reactant concentration and the temperature constant, the variation in the rate of reaction is due solely to the deactivation process and can be studied directly [2]. In our tests at each temperature step, conversion levels were low enough to consider reactant concentrations practically constant; therefore, the kinetic terms of reaction and deactivation are separable and the observed variation is due to catalyst deactivation solely.

The rate of deactivation of CO and ethene formation at each temperature was calculated by linear regression of formation rates versus run time in the linear part (usually after the stabilization time) observed in each T_R step, and the thermal coefficient (apparent activation energy) of the deactivation process by adjusting these deactivation rates versus T_R to an Arrhenius-type expression.

At each temperature, the minimum squares fitting of the formation rates versus run time at this 'linear' section gives a meaningful fit to a straight line, which slope is the rate of deactivation. The calculated values, expressed in (mmol/h g_{cat})/(h on stream), for the three temperatures in increasing order are 0.245, 0,41 and 0.67 for ethene formation and 2.71, 4.86 and 7.40 for CO formation. As previously observed [1], CO formation decay is roughly one order of magnitude faster than that of ethene formation; however, the apparent activation energy for the decay rate is similar for both processes, 47.0 ± 0.3 and 47.1 ± 8.8 kcal/mol for ethene and CO formation, respectively.

3.5. Catalytic reaction kinetics

With these deactivation rate parameters the intrinsic kinetics of the catalytic ODH may be also estimated by analysing separately each 'session' or 'temperature step' in the experimentation. As the decay of the product formation rates is linearly dependent on run time of its temperature step (t), one may calculate the rate without deactivation at this temperature (T) step, $(r_0)_T$, by extrapolating to the run time when the temperature setting was changed, $t = 0$ of the step (i.e., the vertical lines in Fig. 2). This value corresponds to the state of the catalyst (the degree of deactivation) at the same run time at the previous temperature step. Thus, the ratio of rates between this estimated initial value at the higher $T_R = T1$, $(r_0)_{T1}$, and the rate measured at the lower $T_R = T2$ at the same runtime, the 'final' measured rate at this lower temperature, $(r_f)_{T2}$, is independent of run time and, hence, of deactivation; it depends only on the intrinsic (steady-state) kinetics of the catalytic reaction, i.e., its activation energy, which in turn could be calculated from these values.

On the other hand, for each temperature step (T) where deactivation occurs, we have two values of rate: the measured one at the final run time of the step $(r_f)_T$ and the calculated one at the initial run time of the step $(r_0)_T$. Therefore, by using these two ratios, $(r_0)_T$ and $(r_f)_T$, (for correction inside each step) and the ratio $(r_0)_{T1}/(r_f)_{T2}$ (for the changes between consecutive steps), one may estimate stepwise the "intrinsic" catalytic rate values for each temperature, splitting up the overlapping of the deactivation.

Thus, as no deactivation is observed at the step $T_R = 600$ °C, we may assume that the extrapolated value (r_0) at step $T_R = 680$ °C corresponds to the catalyst state prior to the start of deactivation. Then, for example, the intrinsic rate at 700 °C can be calculated by multiplying this (r_0) at 680 °C by the $(r_0)_{700}/(r_f)_{680}$ ratio, and with this value for 700 °C we may calculate the intrinsic rate at 720 °C by multiplying it by the $(r_0)_{720}/(r_f)_{700}$ ratio. When the rate values calculated in this way are fitted together with those measured in the temperature range (500–600 °C) where no deactivation was observed into an Arrhenius-type plot, a statistically quite meaningful fit results (correlation coefficient: 0.9965, Exner's ψ [10] = 0.102 for six fitting points). This seems to support the validity of the proposed methodology.

In this way, we have calculated that the apparent activation energy values are 32 ± 4 and 26 ± 2 kcal/mol for the rates of formation of ethene and CO, respectively. The first value agrees reasonably with the value calculated in the conventional reactor (37 ± 3 kcal/mol [1]). It should be noted that the value for the CO formation rate could not be calculated in the conventional set up, due to its overlapping with the fast deactivation.

3.6. General discussion

Our previous studies [1,5,6] have shown that during the ODH of ethane with CO_2 over ceria-based catalysts, both homogeneous and heterogeneous processes take place. The homogeneous one consists in a thermal dehydrogenation, and some hydrocracking to methane at very high temperatures, with practically no CO_2 transformation. This allows studying the pure catalytic reaction by subtracting the yields of products of the homogeneous reaction obtained in the same reaction conditions. On the catalyst surface two heterogeneous reactions proceed, say, the selective ODH:

$$C_2H_6 + CO_2 \Rightarrow C_2H_4 + CO + H_2O \tag{1}$$

and the unselective oxidation of ethene to CO:

$$C_2H_6 + 5\,CO_2 \Rightarrow 7\,CO + 3\,H_2O \tag{2}$$

The incorporation of Ca into a solid solution in the ceria framework reduces the activity but improves markedly the selectivity to ethene and the efficiency of CO_2 [6], and the use of the freeze drying method for preparing the 10CaCe-FD catalyst produces an improvement of the catalyst performance [1], but this catalyst, at a variance of the undoped CeO_2-FD catalyst prepared by the same method, deactivates markedly under reaction conditions.

The present results corroborate the main general finding of the previous studies [1], say, that the deactivation is much faster for the formation of CO than for the formation of ethene, but presently this deactivation rate can be quantified. The deactivation rate for CO formation is roughly 10–12 times faster than that of ethene formation. As discussed above these deactivation rates are only dependent on the number of active sites. In fact, an important catalyst sintering was observed after reaction [1]. If one assumes that the decrease of activity is only due to surface area reduction, taking into account the stoichiometry of reactions (1) and (2), one may estimate that rate of deactivation of the unselective reaction (2) is around 1.5 times faster than that of the selective reaction (1). So, besides a catalyst surface area reduction, and hence the total number of active sites, the unselective sites are decreasing at a much faster rate than the active sites are.

Besides, the used experimental strategies allows to uncouple deactivation and catalytic reaction and to measure the steady-state formation rate for each product and its apparent energy of activation, even in the temperature region where deactivation occurs. Their values seem to indicate that the unselective reaction has lower activation energy than the ODH. This trend is commonly found in ODH of lower alkanes with oxygen, for which an increase of temperature produces an improvement of selectivity at isoconversion.

4. Conclusions

The kinetic parameters of the ODH of ethane with CO_2 over Ca-doped nanosized ceria (rates, activation energy) as well as those of the catalyst deactivation itself have been simultaneously measured. A strategy based in a relatively short experimentation time has been employed. The differences in deactivation rates for CO and ethene formation seems to indicate that the deactivation process involves not only the catalyst sintering but also a change in the proportion of selective and unselective active sites. In the steady-state kinetics (absence of catalyst deactivation), activation energy of ethene formation is slightly higher than that of CO formation. Further studies are presently being conducted to complete the kinetic study and obtain the complete rate expression. The use of the proposed experimental methodology can be extended to study the kinetics of other catalytic reactions subject to fast catalytic deactivation.

Acknowledgements

The financial support of the Spanish Interministry Committee for Science and Technology (CICYT) under Projects MAT2002-03803 and MAT2003-01696, and the European Commission through the Co-ordination Action CONCORDE (NMP4-CT-2004-505834) is gratefully acknowledged.

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