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CeO_2: an active and selective catalyst for the oxidative dehydrogenation of ethane with CO_2

XU Yide (徐奕德)

(State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China)

and Vicente Cortes CORBERAN

(Institute de Catalisis y Petroleoquimica, C.S.I.C, Campus U.A.M, Cantoblanco, 28049 Madrid, Spain)

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Abstract It was assumed that the homogeneous dehydrogenation of C_2H_6 occurred in the gas phase was independent of the presence of catalysts and this is applicable to the oxidative dehydrogenation of ethane with CO_2 over CeO_2. On the basis of this assumption, a method was developed to analyze the contribution of C_2H_4 formation from heterogeneous catalysis. In this study, ceria was found to be active and selective for the oxidative dehydrogenation of ethane with CO_2 and the selectivity to C_2H_4 was above 60% and the actual contribution for C_2H_4 formation from heterogeneous catalysis was about 55%—75% in the range of 953—993 K.

Keywords: ceria, catalyst, oxidative dehydrogenation with CO_2, ethane.

A crucial point in the oxidative dehydrogenation of light alkanes is that various oxygen species on the catalyst surface and/or in the bulk are in dynamic equilibrium with the O_2 in the gas phase. Therefore, different oxidative reactions, involving with reactants, intermediates and products, will take place simultaneously. There are a few papers reported that inert CO_2 rather than gaseous O_2 was used as an oxygen source and/or oxidant[1—5]. One group claimed that CO_2 was involved in the reaction as an oxidant, providing a monoatomic oxygen species, $O_{ads.}$, via its dissociation on catalyst surface[1]. Meanwhile, Krylov et al. reported that the manganese containing catalysts were most active for the oxidative dehydrogenation of C_2H_6 and C_3H_8 with CO_2 into C_2-C_3 olefins when temperatures higher than 1 073 K and attributed a redox mechanism on their catalysts[2].

CeO_2-based catalysts have received much attention recently in the total oxidation of CO and hydrocarbons for their redox properties and the ability to store and release oxygen of CeO_2[6]. Although CeO_2 has been proven useful in total oxidative reaction, its ability to catalyze selective or partial oxidations is poor when gaseous O_2 was used. All the results reported in literature showed that oxidation of hydrocarbons over CeO_2 yields CO_2 as the main product, with selectivity close to 100%; only trace of partial oxidation products like CO are observed.

Recently, we have found that CeO_2 is active and selective for the oxidative dehydrogenation of ethane (ODE) with CO_2 to C_2H_4, accompanying the formation of CO and H_2O either as selective or non-selective reaction product[7]. Since CO_2 is more inert as an oxygen source and/or oxidant, a higher reaction temperature is needed. Therefore, one should expect that at such a high temperature homogeneous dehydrogenation of light alkane in the gas phase could not be avoided. It was suggested that the homogeneous dehydrogenation of C_2H_6, occurred in the gas phase, was independent of the presence of catalyst[1]. Accordingly, the actual contribution from heterogeneous catalysis in the ODE with CO_2 over a catalyst may be estimated from the results obtained from the blank test and the results of corresponding catalytic test under the same conditions. In this study we attempt to analyze the actual contribution for the formation of C_2H_4 from heterogeneous catalysis and to show the unique catalytic performance of ceria for the ODE with CO_2.

1 Materials and methods

Ceria used in this work was prepared by the precipitation of cerium nitrate (C. P. grade) using oxalic acid solution (A. R. grade) as a precipitant. The precipitate was dried at 393 K and finally calcined in air at 1 123 K for 6 h. The calcined sample was pressed, crushed and sieved into granules of 20—40 mesh for further use. ODE with CO_2 was carried out in a fixed bed tubular, a down-flow reactor as described in our previous report[7]. The blank test was carried out in the same way. In the initial stage, the conversions of C_2H_6 and CO_2 were calculated on the basis that all hydrocarbons in the tailgas (C_2H_4 and CH_4) resulted from the transformation of C_2H_6, while the CO was from CO_2. Selectivities and differential rates were calculated in the conventional way. These initial data will be properly treated on the assumption that the homogeneous dehydrogenation of C_2H_6 to C_2H_4 occurred in the gas phase was independent of the catalysts so as to analyze the actual contribution for C_2H_4 formation from heterogeneous catalysis.

2 Results and discussion

Under the experimental conditions used in this work we noticed that the highest yield of conversion of CO_2 observed in the homogeneous reaction in gas phase between C_2H_6 and CO_2 was only about 0.1% (fig. 1). This indicates that the homogeneous reaction between C_2H_6 and CO_2 in gas phase is negligible. The main reaction in gas phase is the dehydrogenation of C_2H_6, which is highly selective as expected, and its hydrocracking is minor. Therefore, the homogeneous reaction in gas phase can be expressed by the following two reactions:

$$C_2H_6 \Leftrightarrow C_2H_4 + H_2 \qquad (1)$$

$$C_2H_6 + H_2 \Leftrightarrow 2CH_4 \qquad (2)$$

The plot of the yield of C_2H_4 at different C_2H_6 conversions at 973 K is a straight line passing through the origin and increases with the conversion of C_2H_6, showing that C_2H_4 is the primary product (fig. 2). Whereas the yield of CH_4 increases with the conversion of C_2H_6, the line does not pass through the

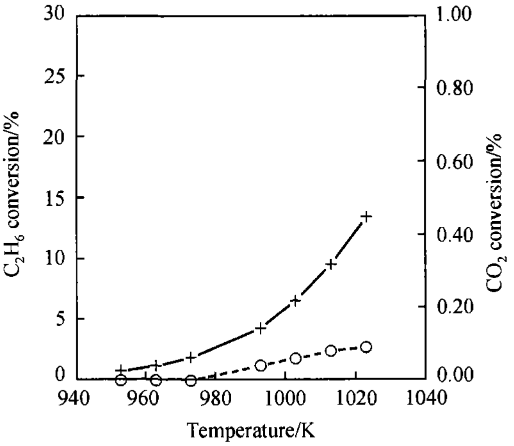


Fig. 1. Typical temperature dependences of C_2H_6 (+) and CO_2(O) conversions in homogeneous reaction at a total flow rate of 200 mL/min (C_2H_6 : CO_2 : He = 10 : 20 : 170 mL/min).

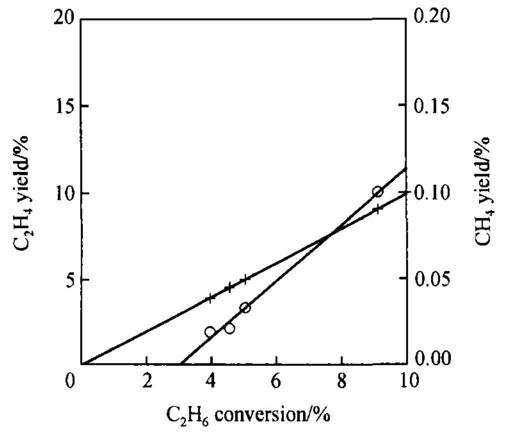


Fig. 2. The yields of C_2H_4(+) and CH_4(O) at different conversions at 973 K with the ratios of C_2H_6 : CO_2 : He keeping constant.

origin (fig. 2). This is evident that the CH_4 is not the primary product of the reaction. The apparent activation energy for homogeneous dehydrogenation of C_2H_6 is high as shown in table 1.

Figures 3 and 4 show the typical temperature dependence of C_2H_6 and CO_2 conversions and C_2H_4, CH_4 and CO yields over CeO_2 at a total flow rate of 200 mL/min (C_2H_6 : CO_2 : He = 10 : 20 : 170 mL/min) after substracting the contribution from the homogeneous reaction. It is clear from these two figures that ceria shows a fairly good catalytic performance for the ODE with CO_2. The reaction can be expressed by

$$C_2H_6 + CO_2 \Rightarrow C_2H_4 + CO + H_2O. \qquad (3)$$

Table 1 Apparent activation energies for homogeneous dehydrogenation of ethane at various contact times in the temperature range of 953—1 023 K

Contact time, $g \cdot s \cdot mL^{-1}$	Activation energy $kJ \cdot mol^{-1}$	Correlation coefficient
12	307.2 ± 21	0.997
6	331.1 ± 6.7	0.999
4	336.9 ± 10	0.999
3	342.8 ± 14.2	0.999

We also notice that even at the highest reaction temperature the CH_4 yield (from ethane hydrocracking) is less than 0.1% (fig. 4), indicating that ceria have little cracking activity for C_2H_6 in the range of 953—1 023 K. Therefore, we consider that the formation of CH_4 results from homogeneous hydrocracking. We also notice that in all cases, the total depletion rates of C_2H_6 are always smaller than the total depletion rates of CO_2, suggesting that there is a non-selective oxidation of C_2H_6 with CO_2 on the catalyst surface. Since no carbon deposit could be found on ceria surface, according to ref. [2], we may suggest the non-selective catalytic reaction as:

$$C_2H_6 + 5CO_2 \Rightarrow 7CO + 3H_2O. \qquad (4)$$

Referring to heterogeneous reactions (3) and (4), we can further separate the heterogeneous depletion rates of C_2H_6 and CO_2, and the formation rate of CO into two categories. One is selective and responsible for the formation of C_2H_4, and the other is non-selective and leads only 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 the reaction (3) is (148.8 ± 14.2) kJ/mol, which is in good agreement with the ODE with gaseous O_2 over various catalysts[7], while the corresponding reaction order with respect to C_2H_6 is 0.95 ± 0.05, which is quite good and reasonable. All these results confirm that the analysis for the reaction is correct. The temperature effect on the heterogeneous catalytic selectivity to C_2H_4, the effectiveness of CO_2(the percentage of CO_2 taking part in the

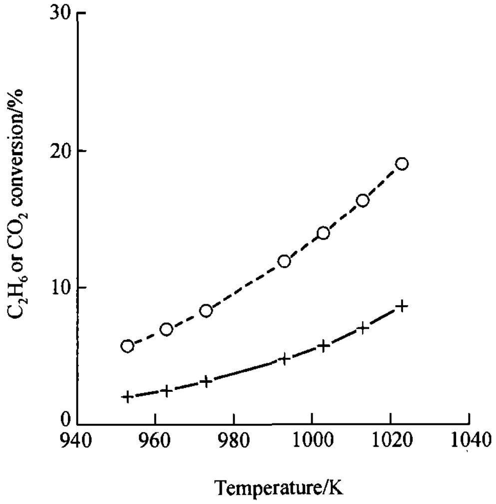


Fig. 3. Typical temperature dependences on C_2H_6 (+) and CO_2 (O) conversions over CeO_2 after substracting the contribution from homogeneous reactions at a total flow rate of 200 mL/min ($C_2H_6 : CO_2 : He = 10:20:170$ mL/min).

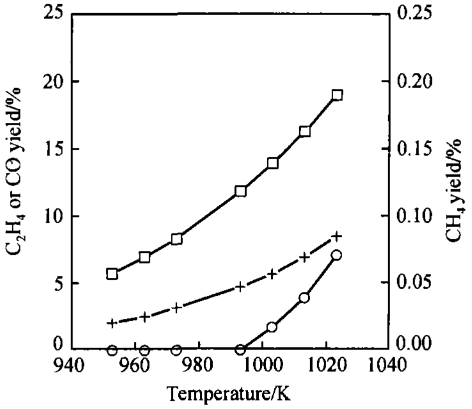


Fig. 4. Typical temperature dependences on C_2H_4 (+), CH_4 (O) and CO (□) yields over CeO_2 after subtracting the contribution from homogeneous reactions at a total flow rate of 200 mL/min ($C_2H_6 : CO_2 : He = 10:20:170$ mL/min).

reaction (3)), the actual contribution to the formation of C_2H_4 from heterogeneous ODE with CO_2 and the total selectivity to C_2H_4 (including the contribution from heterogeneous catalysis and homogeneous reaction) over CeO_2 are shown in fig. 5. Although the actual contribution for the formation of C_2H_4 from heterogeneous ODE with CO_2 decreases resulted from an exponential increase in homogeneous dehydrogenation in gas phase, the heterogeneous catalytic selectivity to C_2H_4 and the effectiveness of CO_2 remain relatively stable with the increase of reaction temperature.

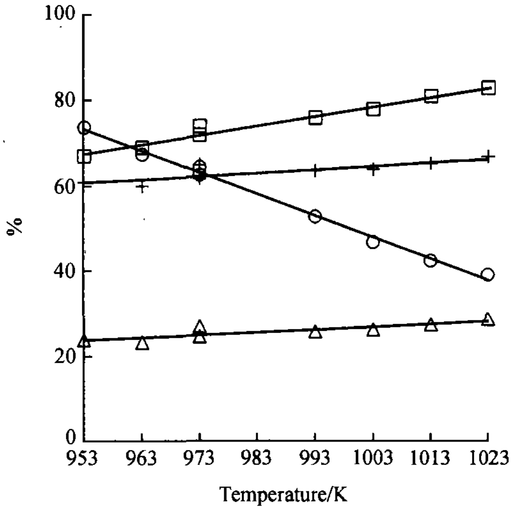
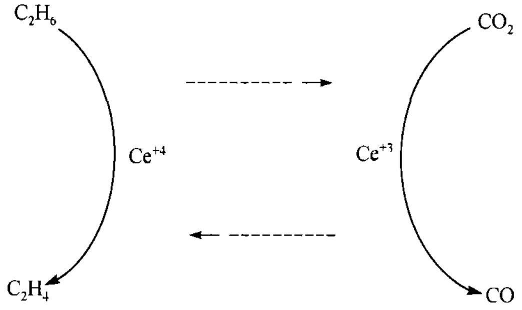


Fig. 5. The temperature effect of the catalytic selectivity to C_2H_4 (+), the effectiveness of CO_2 (Δ), the actual catalytic contribution for the formation of C_2H_4 from heterogeneous ODE with CO_2 (O) and the total heterogeneous and homogeneous selectivity to C_2H_4 (□) over CeO_2 at a total flow rate of 200 mL/min ($C_2H_6 : CO_2 : He = 10 : 20 : 170$ mL/min).

Our present study gives evidence that the ODE with CO_2 over ceria is a real heterogeneous catalytic reaction. The reaction is rather complicated because of the coexistence of homogeneous dehydrogenation of C_2H_6 in gas phase and heterogeneous catalysis on the catalyst surface. As far as the ODE with CO_2 over CeO_2 catalyst is concerned, it seems that CeO_2 plays the role of a redox catalyst in the reaction. Therefore, we suggest that the catalytic reaction takes place *via* the reduction of the catalyst by C_2H_6 and its oxidation by CO_2, as expressed as follows:



or expressed by the following equations:

$$2CeO_2 + C_2H_6 \Rightarrow Ce_2O_3 + C_2H_4 + H_2O, \tag{5}$$

$$Ce_2O_3 + CO_2 \Rightarrow 2CeO_2 + CO. \tag{6}$$

Table 2 Apparent activation energies and the reaction orders with respect to C_2H_6 in heterogeneous reactions at a total flow rate of 200 mL/min

Depletion rate of C_2H_6a)	Activation energy	Correlation coefficient	Reaction order	Correlation coefficient
	$kJ \cdot mol^{-1}$		n	
$r_{C_2H_6\text{-ht}}$	144.2 ± 9.6	0.998	0.83 ± 0.05	0.999
$r_{C_2H_6\text{-ht3}}$	148.8 ± 14.2	0.995	0.95 ± 0.05	0.999
$r_{C_2H_6\text{-ht4}}$	133.8 ± 7.9	0.998	0.55 ± 0.06	0.996

a) $r_{C_2H_6\text{-ht}}$, the depletion rate of C_2H_6 contributed from the heterogeneous catalysis; $r_{C_2H_6\text{-ht3}}$ and $r_{C_2H_6\text{-ht4}}$: the depletion rates of C_2H_6 contributed from the reaction (3) and the reaction (4) respectively.

The complete reaction, i.e. (5) + (6) constitutes the reaction equation (3). Therefore, the redox properties and the ability to store and release oxygen of CeO_2 are available for using CO_2 as an oxygen source and/or oxidant in the ODE with CO_2 over CeO_2. The features for this reaction are that the selectivity to C_2H_4 of the heterogeneous reaction can reach to the level of over 60% under a proper reaction condition, and besides H_2O, CO is the only non-selective product. A more detailed study on the oxidative dehydrogenation of light alkanes with CO_2 on CeO_2 and CeO_2-based catalysts now is underway.

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