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Oxidative dehydrogenation of ethane to ethylene in the presence of HCl over CeO_2-based catalysts

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ABSTRACT

This article reports a new catalytic route for the oxidative dehydrogenation of ethane to ethylene in the presence of HCl at moderate temperatures. CeO_2 was found to be the most efficient catalyst for the production of ethylene from the variety of metal oxides examined in this work. CeO_2 nanocrystals with rod and cube morphologies showed higher ethane conversions and ethylene selectivities than CeO_2 nanoparticles. The modification of CeO_2 by MnO_x further enhanced the catalytic performance. Ethane conversion of 94% and ethylene selectivity of 69% were obtained after 2 h of reaction at 723 K over an 8 wt% MnO_x–CeO_2 catalyst. This catalyst was stable and the ethylene yield could be sustained at 65%–70% over 100 h of reaction. The presence of HCl played a key role in the selective production of C_2H_4, and some of the C_2H_4 was probably formed from chloroethane by dehydrochlorination.

Ethylene is one of the most important building-blocks of the chemical industry. Currently, ethylene is primarily produced from petroleum via steam cracking of naphtha. The depletion of crude oil has stimulated the development of non-petroleum routes for the production of ethylene. At the same time, the emergence and the growing importance of shale gas particularly in the US [1] has been a strong incentive to use this lower alkane resource for the production of ethylene and propylene, as shale gas contains not only methane but also ethane and propane in substantial amounts [2]. In the Middle East, this abundant source of ethane feedstock has made the production of ethylene from ethane a highly attractive route [3].

The non-oxidative dehydrogenation of C_2H_6 to C_2H_4 is strong endothermic and a thermodynamically limited reaction. A reaction temperature of ~973 K is required to obtain an equilibrium C_2H_6 conversion of ~40% [3]. Although Cr- and Pt-based catalysts have been employed for the dehydrogenation of C_2H_6, the high temperature and the need to repeatedly regenerate the catalyst owing to the coke deposition increase the process cost [4]. In contrast, oxidative dehydrogenation is an exothermic reaction and can be performed at moderate temperatures (< 773 K) with high C_2H_6 conversions. However, the selectivity can be an issue, leading to deep oxidation, i.e., the formation of CO and CO_2 (CO_x), in the presence of O_2. To increase the alkene selectivity at high alkane conversion is a particularly challenging task [5]. Various catalysts have been reported for the oxidative dehydrogenation of C_2H_6 to C_2H_4 [3,6,7]. Among these catalysts, MoVTeNb mixed oxides [8,9] and Ni-based mixed oxides [10] have been shown to work at moderate temperatures (< 773 K), but the C_2H_4 yield of these

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catalysts (< 50%) is not high enough for commercial consideration. However, some non-redox metal oxides with chloride modification catalyze the oxidative dehydrogenation of C_2H_6 to C_2H_4 at higher temperatures (typically > 873 K) [11–14]. The yield of C_2H_4 exceeded 70% at > 900 K over a Li-Na-Mg-Dy-O-Cl catalyst [14]. Cl^- anions were shown to play a crucial role in the oxidative dehydrogenation of C_2H_6 to C_2H_4 for this catalyst [14]. The covering of the surface sites, where the deep oxidation occurs, with Cl^- may increase the selectivity. Moreover, the formation of active species such as ClO^- or Cl• in the presence of O_2 may enhance the activity [3,14]. However, the loss of Cl^- may occur at high reaction temperatures in the presence of O_2, causing deactivation of the catalyst.

Recently, we reported a novel two-step route for the production of lower olefins from CH_4 [15]. In the first step, the oxidative chlorination of CH_4 in the presence of HCl and O_2 produces CH_3Cl with high selectivity, which can further be converted to lower olefins, i.e., C_2H_4, C_3H_6, and C_4H_8, over zeolite catalysts in the second step. The reactions in the two steps can be expressed as follows:

Step 1, $CH_4 + HCl + 1/2\ O_2 \rightarrow CH_3Cl + H_2O$ (1)

Step 2, $CH_3Cl \rightarrow 1/n\ C_nH_{2n}\ (n = 2–4) + HCl$ (2)

The HCl generated in the second step can be recycled back into the first step, and the net reaction of this two-step route is the oxidative dehydrogenation of CH_4 to lower olefins. We have demonstrated that CeO_2 is an efficient catalyst for the first step [15] and modified H-ZSM-5 or H-ZSM-34 works efficiently for the second step reaction [16,17].

Although HCl may cause corrosion problems, it would be of interest to investigate the conversion of C_2H_6 in the presence of HCl and O_2 because of the following reasons. First, it is known that some CH_4 resources such as the shale gas contain a considerable fraction of C_2H_6 in addition to CH_4. Thus, it is useful to know the behavior of C_2H_6 when our catalytic system with HCl and O_2 [15] is applied to the transformation of these CH_4 resources. Second, catalysts containing Cl^- such as Li-Na-Mg-Dy-O-Cl are known to be capable of providing higher C_2H_4 yields for the oxidative dehydrogenation of C_2H_6, and the Cl^- anions on catalyst surfaces have been shown to play a pivotal role [3,11–14]. This inspires us to develop a novel catalytic process for the oxidative dehydrogenation of C_2H_6 in the presence of HCl, which would avoid the loss of Cl^-.

The catalytic reactions were performed on the fixed-bed flow reactor operating at atmospheric pressure. Each catalyst was pretreated in the quartz reactor in a O_2-He gas flow at 823 K for 0.5 h, followed by a purge under He. After the temperature had decreased to the reaction temperature (typically 723 K), the reactant gas flow was introduced into the reactor to start the reaction. The products were analyzed by on-line gas chromatography.

Table 1 shows the catalytic performance of various metal oxides, which were purchased from Alfa Aesar or Sinopharm Chemical Reagent Co. Ltd. (China), for the conversion of C_2H_6 to C_2H_4 in the presence of HCl and O_2. Under our reaction conditions, the metal oxides with redox abilities exhibited higher C_2H_6 conversions. C_2H_4 was the main oxidation product for most of the metal oxides except for CuO and Cr_2O_3, which provided a higher selectivity for C_2H_5Cl. C_2H_3Cl and C_2H_4Cl were also formed with low selectivity over some catalysts. Two rare earth metal oxides, CeO_2 and Eu_2O_3, showed higher C_2H_4 selectivities (> 60%). Among all the metal oxides examined, CeO_2 exhibited the highest C_2H_4 yield (49%). CeO_2 has also been shown to be an efficient catalyst for the oxidative chlorination of CH_4 to CH_3Cl [15]. In our previous paper [15], we proposed that HCl was activated by Ce^{4+} on the CeO_2 surfaces through electron transfer, forming an active Cl species responsible for the conversion of CH_4, and the reduced Ce^{3+} was then reoxidized to Ce^{4+} by O_2. CeO_2 was the best catalyst for this process likely because of its excellent redox ability and stability. We speculate that the conversion of C_2H_6 here may follow a similar

Table 1
Catalytic performance of various metal oxides for C_2H_6 conversion in the presence of HCl and O_2.

Catalyst	C_2H_6 conversion (%)	Selectivity (%)						C_2H_4 yield (%)
		C_2H_4	C_2H_5Cl	C_2H_3Cl	$C_2H_4Cl_2$	CO	CO_2	
None	0							0
MgO	8	38	15	0.4	0	4.1	43	2.8
V_2O_5	63	23	3.1	0.2	0	46	27	14
Cr_2O_3	39	5.5	41	0.7	0	14	38	2.1
MnO_2	71	23	4.6	1.2	0	43	28	17
Fe_2O_3	60	51	19	3.1	1.6	3.7	21	31
Co_3O_4	34	29	11	0.5	0.4	0	41	9.9
NiO	3	17	0.5	0	0	0	83	0.5
CuO	41	10	36	2.0	1.5	4.1	43	2.8
ZnO	2	6.1	0	0	0	0	94	0.1
La_2O_3	9	35	2.7	0.2	0	11	50	3.3
CeO_2	80	61	4.6	6.4	3.2	6.6	16	49
Pr_6O_{11}	72	15	0	0	0	5.6	75	11
Nd_2O_3	20	36	0.5	0.6	0	18	45	7.3
Eu_2O_3	51	66	0.6	5.6	0	12	15	34
Gd_2O_3	8	29	1.3	2.0	0	14	44	3.2
Tb_4O_7	69	15	0	1.3	0	9.8	74	9.9
Dy_2O_3	13	38	1.1	1.3	0	14	45	4.9
Ho_2O_3	23	21	0	1.3	0	8.7	69	4.8
Er_2O_3	4	36	2.4	1.8	0	6.3	54	1.6

Reaction conditions: catalyst, 1.0 g; $P(C_2H_6)$ = 20 kPa; $P(O_2)$ = 20 kPa; $P(HCl)$ = 61 kPa; F = 40 mL/min; T = 723 K; time on stream, 2 h.