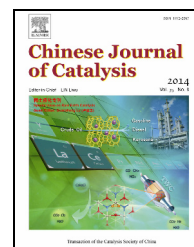


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Oxidative dehydrogenation of ethane to ethylene in the presence of HCl over CeO₂-based catalysts

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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. CeO₂ was found to be the most efficient catalyst for the production of ethylene from the variety of metal oxides examined in this work. CeO₂ nanocrystals with rod and cube morphologies showed higher ethane conversions and ethylene selectivities than CeO₂ nanoparticles. The modification of CeO₂ 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-CeO₂ 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 C₂H₄, and some of the C₂H₄ was probably formed from chloroethane by dehydrochlorination.

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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 C₂H₆ to C₂H₄ is strong endothermic and a thermodynamically limited reaction. A reaction temperature of ~973 K is required to obtain an

equilibrium C₂H₆ conversion of ~40% [3]. Although Cr- and Pt-based catalysts have been employed for the dehydrogenation of C₂H₆, 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 C₂H₆ conversions. However, the selectivity can be an issue, leading to deep oxidation, i.e., the formation of CO and CO₂ (CO_x), in the presence of O₂. 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 C₂H₆ to C₂H₄ [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 C₂H₄ yield of these

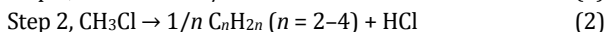
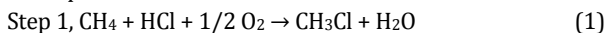
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catalysts (< 50%) is not high enough for commercial consideration. However, some non-redox metal oxides with chloride modification catalyze the oxidative dehydrogenation of C₂H₆ to C₂H₄ at higher temperatures (typically > 873 K) [11–14]. The yield of C₂H₄ 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 C₂H₆ to C₂H₄ 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 O₂ may enhance the activity [3,14]. However, the loss of Cl⁻ may occur at high reaction temperatures in the presence of O₂, causing deactivation of the catalyst.

Recently, we reported a novel two-step route for the production of lower olefins from CH₄ [15]. In the first step, the oxidative chlorination of CH₄ in the presence of HCl and O₂ produces CH₃Cl with high selectivity, which can further be converted to lower olefins, i.e., C₂H₄, C₃H₆, and C₄H₈, over zeolite catalysts in the second step. The reactions in the two steps can be expressed as follows:



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 CH₄ to lower olefins. We have demonstrated that CeO₂ 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 C₂H₆ in the presence of HCl and O₂ because of the following reasons. First, it is known that some CH₄ resources such as the shale gas contain a considerable fraction of C₂H₆ in addition to CH₄. Thus, it is useful to know the behavior of C₂H₆ when our catalytic system with HCl and O₂ [15] is applied to the transformation of these CH₄ re-

sources. Second, catalysts containing Cl⁻ such as Li-Na-Mg-Dy-O-Cl are known to be capable of providing higher C₂H₄ yields for the oxidative dehydrogenation of C₂H₆, 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 C₂H₆ 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 O₂-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 C₂H₆ to C₂H₄ in the presence of HCl and O₂. Under our reaction conditions, the metal oxides with redox abilities exhibited higher C₂H₆ conversions. C₂H₄ was the main oxidation product for most of the metal oxides except for CuO and Cr₂O₃, which provided a higher selectivity for C₂H₅Cl. C₂H₃Cl and C₂H₄Cl₂ were also formed with low selectivity over some catalysts. Two rare earth metal oxides, CeO₂ and Eu₂O₃, showed higher C₂H₄ selectivities (> 60%). Among all the metal oxides examined, CeO₂ exhibited the highest C₂H₄ yield (49%). CeO₂ has also been shown to be an efficient catalyst for the oxidative chlorination of CH₄ to CH₃Cl [15]. In our previous paper [15], we proposed that HCl was activated by Ce⁴⁺ on the CeO₂ surfaces through electron transfer, forming an active Cl species responsible for the conversion of CH₄, and the reduced Ce³⁺ was then reoxidized to Ce⁴⁺ by O₂. CeO₂ was the best catalyst for this process likely because of its excellent redox ability and stability. We speculate that the conversion of C₂H₆ here may follow a similar

Table 1

Catalytic performance of various metal oxides for C₂H₆ conversion in the presence of HCl and O₂.

Catalyst	C ₂ H ₆ conversion (%)	Selectivity (%)						C ₂ H ₄ yield (%)
		C ₂ H ₄	C ₂ H ₅ Cl	C ₂ H ₃ Cl	C ₂ H ₄ Cl ₂	CO	CO ₂	
None	0							0
MgO	8	38	15	0.4	0	4.1	43	2.8
V ₂ O ₅	63	23	3.1	0.2	0	46	27	14
Cr ₂ O 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 ₂ O ₃	60	51	19	3.1	1.6	3.7	21	31
Co ₃ O 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 ₂ O 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 ₆ O ₁₁	72	15	0	0	0	5.6	75	11
Nd ₂ O ₃	20	36	0.5	0.6	0	18	45	7.3
Eu ₂ O ₃	51	66	0.6	5.6	0	12	15	34
Gd ₂ O ₃	8	29	1.3	2.0	0	14	44	3.2
Tb ₄ O ₇	69	15	0	1.3	0	9.8	74	9.9
Dy ₂ O ₃	13	38	1.1	1.3	0	14	45	4.9
Ho ₂ O ₃	23	21	0	1.3	0	8.7	69	4.8
Er ₂ O ₃	4	36	2.4	1.8	0	6.3	54	1.6

Reaction conditions: catalyst, 1.0 g; P(C₂H₆) = 20 kPa; P(O₂) = 20 kPa; P(HCl) = 61 kPa; F = 40 mL/min; T = 723 K; time on stream, 2 h.

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