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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

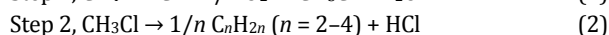
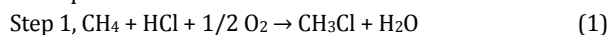
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catalysts (< 50%) is not high enough for commercial consideration. However, some non-redox metal oxides with chloride modification catalyze the oxidative dehydrogenation of C₂H₆ to C₂H₄ at higher temperatures (typically > 873 K) [11–14]. The yield 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 C₂H₄Cl 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.

Table 2Catalytic performance of CeO₂ with different morphologies for the conversion of C₂H₆ in the presence of HCl and O₂.

Type of CeO ₂	A _{BET} (m ² /g)	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
Commercial	8	40	41	22	2.7	1.1	10	23	16
Nanoparticle	150	76	44	0.3	14	3.1	6.8	31	36
Nanorod	99	84	50	0.3	14	2.7	8.3	25	42
Nanocube	23	82	54	6.3	7.1	4	4.5	24	48

Reaction conditions: catalyst, 0.50 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.

reaction mechanism, with C₂H₄ as the major product instead of the alkyl chloride.

We have reported that the morphology of CeO₂ affects its catalytic behavior in the oxidative chlorination of CH₄ [15]. Table 2 compares the catalytic performance of CeO₂ nanorods, nanocubes, and nanoparticles, which have been synthesized by the hydrolysis of cerium(III) salts combined with a hydrothermal treatment under different conditions [15,18]. The commercial CeO₂ was also a nanoparticulate sample but with a lower surface area. For better comparison, we used a smaller amount of catalyst (0.50 g) for this series of catalysts. As displayed in Table 2, CeO₂ nanoparticles with a high surface area showed a higher C₂H₆ conversion than the commercial CeO₂. The CeO₂ nanorods and nanocubes showed even higher C₂H₆ conversions although their surface areas were lower than the CeO₂ nanoparticles. Moreover, the latter two CeO₂ catalysts afforded higher C₂H₄ selectivities. Recent studies have shown that the redox properties and catalytic performance of CeO₂ are dependent on its morphology and the exposed surface structure [18,19]. In our previous work, we showed that the nanorods exposed the {110} (51%) and {100} (49%) planes, while the nanocubes and the nanoparticles exclusively exposed the {100} and {111} planes respectively [15]. Our previous studies demonstrated that the {110} and {100} planes were more active for the oxidative chlorination of CH₄ than the {111} plane [15]. Here, we suggest that the {100} and {110} planes of CeO₂ are also more efficient than the {111} plane for the conversion of C₂H₆ to C₂H₄ in the presence of HCl and O₂.

To further increase the yield of C₂H₄, we investigated the effect of various modifiers on the catalytic performance of the CeO₂ nanorods, which show better C₂H₄ yields and can be easily synthesized. The modified CeO₂ catalysts were prepared by the

impregnation method, i.e., impregnation of CeO₂ nanorods in aqueous solutions by various metal nitrates, followed by drying and calcination at 823 K. Table 3 shows that some modifiers can enhance the C₂H₆ conversion or C₂H₄ selectivity. In particular, the MgO-CeO₂, MnO_x-CeO₂, and CoO_x-CeO₂ catalysts exhibited significantly higher C₂H₄ yields than CeO₂ alone. The yields of C₂H₄ were ≥60% for these three modified catalysts. Although the MgO-CeO₂ catalyst exhibited the highest selectivity of C₂H₄ after 2 h of reaction, both the conversion of C₂H₆ and the selectivity of C₂H₄ decreased with time on stream. Mg was lost from the catalyst bed during the reaction, which caused the decrease in catalytic performance.

We examined the effect of Mn content on the MnO_x-CeO₂ catalyst. The catalyst has been denoted as *y* wt% MnO_x-CeO₂, where *y* represents the content of Mn as a weight percentage. As displayed in Fig. 1, the modification of CeO₂ with an appropriate content of Mn (≤10 wt%) improved both C₂H₆ conversion and C₂H₄ selectivity. Too high a Mn content was detrimental to the C₂H₆ conversion and thus the C₂H₄ yield. At a Mn content of 8 wt%, the C₂H₆ conversion and C₂H₄ yield were the highest, reaching 94% and 65%, respectively, at 723 K. In addition to C₂H₄ (selectivity, 69%), C₂H₃Cl, i.e., vinyl chloride, the monomer for the production of poly-vinyl chloride (PVC), was also formed with a selectivity of 14%. Thus, the selectivity to useful products reached ~85% at a C₂H₆ conversion of 94% at 723 K over the 8 wt% MnO_x-CeO₂ catalyst.

We performed a long-term reaction for the conversion of C₂H₆ in the presence of HCl and O₂ over the 8 wt% MnO_x-CeO₂ catalyst. As displayed in Fig. 2, C₂H₆ conversion decreased only slightly with time on stream and remained at ~88% after 100 h of reaction. The selectivity for C₂H₃Cl decreased to ~3% after ~35 h. The selectivity for C₂H₄ increased gradually from ~70%

Table 3Catalytic performance of the modified CeO₂ 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
CeO ₂	84	50	0.3	14	2.7	8.3	25	42
Na ₂ O-CeO ₂	73	39	34	8.9	0.7	5.8	12	28
MgO-CeO ₂	84	72	2.9	7.4	1.9	3.2	13	60
V ₂ O ₅ -CeO ₂	82	55	0.3	3.9	0.3	24	17	45
Cr ₂ O ₃ -CeO ₂	78	59	0.5	9	1.6	12	17	46
MnO _x -CeO ₂	91	67	0.6	11	1	5.5	14	61
Fe ₂ O ₃ -CeO ₂	80	41	0.2	16	2.5	9.5	31	32
CoO _x -CeO ₂	89	68	1.6	9.5	2.9	5.0	13	60
NiO-CeO ₂	89	55	0.9	12	3.7	5.4	24	49
CuO-CeO ₂	78	30	0.3	17	4.4	4.2	44	23
ZnO-CeO ₂	86	62	1	10	0.8	6.4	19	54

Reaction conditions: catalyst, 0.50 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.

*The content of the modifier in each catalyst was 10 wt%.

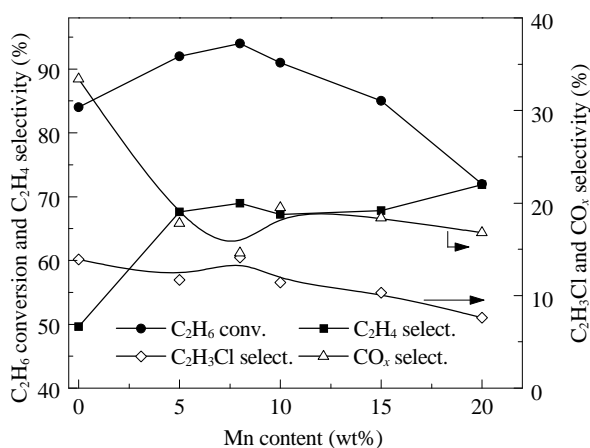


Fig. 1. Effect of Mn content on the catalytic performance of the $\text{MnO}_x\text{-CeO}_2$ catalysts. Reaction conditions: catalyst, 0.50 g; $P(\text{C}_2\text{H}_6) = 20$ kPa; $P(\text{O}_2) = 20$ kPa; $P(\text{HCl}) = 61$ kPa; $F = 40$ mL/min; $T = 723$ K; time on stream, 2 h.

to 75%–80%. During the 100 h, the yield of C_2H_4 was sustained at 65%–70%. Thus, our catalyst was stable for the oxidative dehydrogenation of C_2H_6 to C_2H_4 in the presence of HCl and O_2 .

We have clarified that HCl plays a critical role in the selective formation of C_2H_4 . As shown in Fig. 3, the presence of HCl was not only required for the C_2H_6 conversion, but also changed the product selectivity significantly over the 8 wt% $\text{MnO}_x\text{-CeO}_2$ catalyst. In the absence of HCl, CO_2 was the only product, indicating that only combustion of C_2H_6 proceeded over the present catalyst in the absence of HCl. Increasing the partial pressure of HCl decreased the selectivity of CO_x sharply and increased the selectivity for C_2H_4 . As the partial pressure of HCl exceeded 6 kPa, the selectivity of C_2H_4 reached its peak at ~70%. $\text{C}_2\text{H}_3\text{Cl}$ and $\text{C}_2\text{H}_4\text{Cl}_2$ were also formed and their selectivities increased as the partial pressure of HCl increased. These observations demonstrate that the presence of HCl is required for the selective formation of C_2H_4 from C_2H_6 . Concerning the role of HCl in this process, we speculate that an active Cl species, which is responsible for the activation of C_2H_6 , may be formed on the catalyst surface. During the conversion of C_2H_6

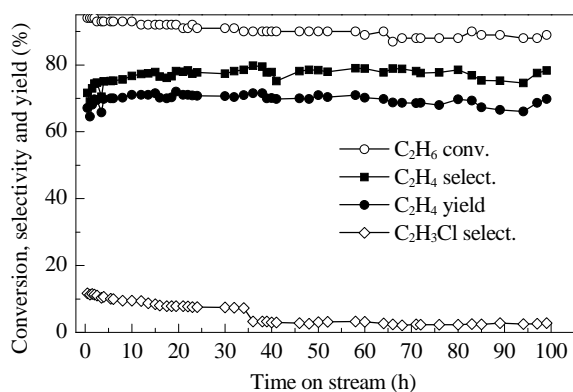


Fig. 2. Dependence of the catalytic performance of the 8 wt% $\text{MnO}_x\text{-CeO}_2$ catalyst on time on stream. Reaction conditions: catalyst, 0.50 g; $P(\text{C}_2\text{H}_6) = 20$ kPa; $P(\text{O}_2) = 20$ kPa; $P(\text{HCl}) = 61$ kPa; $F = 40$ mL/min; $T = 723$ K.

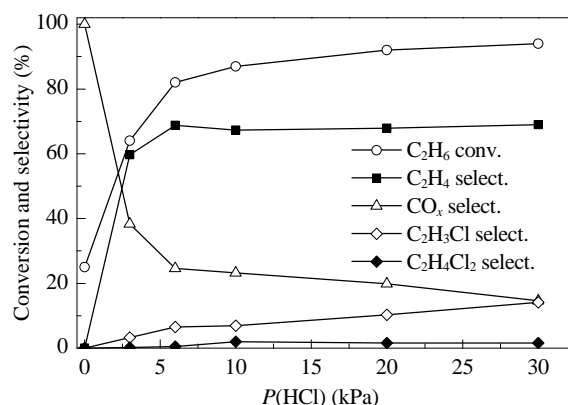


Fig. 3. Effect of HCl partial pressure on the catalytic performance of the 8 wt% $\text{MnO}_x\text{-CeO}_2$ catalyst. Reaction conditions: catalyst, 0.50 g; $P(\text{C}_2\text{H}_6) = 20$ kPa; $P(\text{O}_2) = 20$ kPa; $F = 40$ mL/min; $T = 723$ K.

with HCl and O_2 , we did not observe the formation of Cl_2 . However, Cl_2 was formed in the absence of C_2H_6 over our catalyst and 12% yield of Cl_2 was attained at 723 K. These results in combination with the significant effect of HCl in the formation of C_2H_4 (Fig. 3) suggest that HCl is activated on our catalyst surfaces, generating an active Cl species, which accounts for the selective formation of C_2H_4 . Future studies are needed for the elucidation of these active Cl species.

To understand the reaction pathway for the formation of C_2H_4 , we investigated the effect of the contact time, expressed as W (catalyst weight)/ F (gas flow rate), on product selectivities at 673 K. As shown in Fig. 4, the selectivity for $\text{C}_2\text{H}_5\text{Cl}$ decreased and the selectivity for C_2H_4 increased with increasing contact time. This suggests that some of the C_2H_4 arises from $\text{C}_2\text{H}_5\text{Cl}$, which is formed as one of the primary products similar to CH_3Cl in the case of oxidative chlorination of CH_4 in the presence of HCl and O_2 [15]. More CO_x and $\text{C}_2\text{H}_3\text{Cl}$ were also formed at longer contact times, suggesting that these two products were secondary products. However, the extrapolation to zero contact time or zero conversion leads to ~60% but not a zero selectivity for C_2H_4 (Fig. 4), indicating that a large part of C_2H_4 may be formed as a primary product directly from C_2H_6 . Further studies

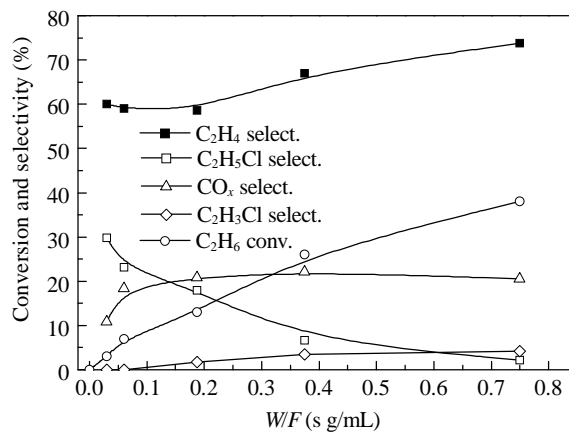


Fig. 4. Effect of contact time on the product distribution over the 8 wt% $\text{MnO}_x\text{-CeO}_2$ catalyst. Reaction conditions: catalyst, 0–0.50 g; $P(\text{C}_2\text{H}_6) = 20$ kPa; $P(\text{O}_2) = 20$ kPa; $F = 40$ mL/min; $T = 673$ K.

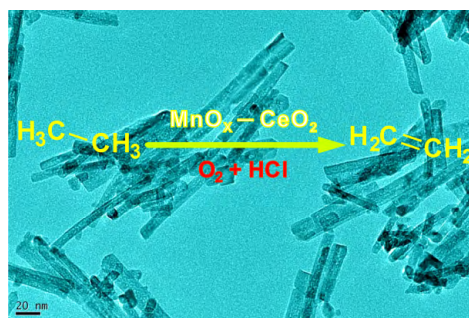
Graphical Abstract

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

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The presence of HCl significantly accelerates the oxidative dehydrogenation of C₂H₆ into C₂H₄ under moderate conditions over CeO₂-based catalysts. C₂H₄ yields of 65%–70% have been obtained over an 8 wt% MnO_x-CeO₂ catalyst at 723 K.



are needed to clarify the C₂H₄ formation mechanism.

In conclusion, we have reported a novel route for the oxidative dehydrogenation of C₂H₆ to C₂H₄ at moderate temperatures in the presence of HCl. CeO₂ is an efficient catalyst for this route and the modification of CeO₂ by MnO_x further increases the activity and selectivity for C₂H₄ formation. The 8 wt% MnO_x-CeO₂ catalyst provides C₂H₄ yield of 65%–70% at 723 K and the catalyst is stable in these conditions. We have demonstrated that HCl plays a critical role in the selective production of C₂H₄.

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HCl存在下CeO₂基催化剂上乙烷氧化脱氢制乙烯

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摘要: 报道了一种HCl存在时温和条件下的乙烷氧化脱氢制乙烯催化转化新途径。研究发现, 在多种金属氧化物催化剂中, CeO₂呈现最佳乙烯生成的催化性能。与纳米粒子相比, 具有棒状和立方体状形貌的CeO₂纳米晶具有较高的乙烷转化率和乙烯选择性。以MnO_x修饰CeO₂可进一步提高催化性能。在8 wt% MnO_x-CeO₂催化剂上, 723 K反应2 h时乙烷转化率和乙烯选择性分别为94%和69%。该催化剂性能稳定, 反应100 h乙烯收率可保持在65%–70%。HCl的存在对乙烯的选择性生成起着至关重要的作用, 一部分乙烯来自于氯乙烷的脱HCl反应。

关键词: 乙烷; 乙烯; 氧化脱氢; 氯化氢; 二氧化铈

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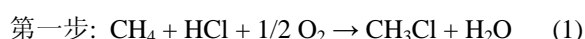
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乙烯是现代化学工业中最重要的基干原料之一。目前, 乙烯主要通过石脑油裂解制得。随着原油的不断耗竭, 开发经非石油路径制乙烯的新途径已引起广泛的关注。另一方面, 近年来随着美国等国页岩气的开采成功, 页岩气的重要性不断提升^[1]。页岩气中除主要成分甲烷外, 还含有大量的乙烷和丙烷等低碳烷烃^[2]。这也为利用低碳烷烃制乙烯和丙烯的研究注入新的动力。事实上, 在中东地区, 丰富的乙烷资源已使由乙烷制备乙烯成为非常具有吸引力的转化路径。

由乙烷无氧脱氢制乙烯是一个强吸热和热力学受限反应。在约973 K时乙烷的热力学平衡转化率约为40%^[3]。虽然铬基和铂基催化剂被应用于乙烷的脱氢反应, 但是高的反应温度以及由于积碳导致的催化剂重复再生大大增加了该过程的成本^[4]。比较而言, 氧化脱氢是一个放热反应, 可以在更为温和的反应温度下(<773 K)获得高的乙烷转化率。然而, 在有氧条件下生成CO和CO₂(CO_x)的深度氧化反应对乙烯选择性产生不利影响。在高烷烃转化率下获得高烯烃选择性是一个极具挑战性的研究课题^[5]。当前已有多种催化剂被用于乙烷氧化脱氢制乙烯的反应^[3,6,7]。其中, MoVTNb复合氧化物^[8,9]和镍基复合氧化物^[10]可以在较温和的条件下催化该反应(<773 K), 但是这类催化剂上乙烯的收率偏低(<50%), 不能满足工业化的需求。另一方面, 一些经氯修饰的非氧化还原性的金属氧化物在较高的反应温度下(>873 K)能够有效催化乙烷氧化脱氢制乙烯^[11–14]。例如, 在900 K以上Li-Na-Mg-Dy-O-Cl催化剂的乙烯收率可达到70%以上^[14]。在该类催化剂上, 氯离子被认为发挥了关键作用^[14]。由于催化剂表面覆盖氯离子, 抑制了其表面可能导致的深度氧化反应, 从而提升了乙烯的选择性。而且, 催化剂表面在氧气氛下可能产生活性Cl物种, 例如ClO⁻或Cl[•], 有可能提高催化活性^[3,14]。然而高温下催化剂上Cl的流失易导致催化剂失活。

最近, 我们报道了一种两步法由甲烷制备低碳烯烃的新催化途径^[15]。首先, 在HCl和O₂的存在下由CH₄高选择性生成CH₃Cl, 然后CH₃Cl在分子筛表面进一步反应生成低碳烯烃C₂H₄, C₃H₆, C₄H₈等, 其反应过程如下所示:



在第二步中生成的HCl可以循环到第一步, 从而将该两步法的净反应可以归结为由甲烷氧化脱氢制低碳烯烃。我们的研究已经表明, CeO₂是第一步反应的高效催化剂^[15], 而经修饰的H-ZSM-5或H-ZSM-34在第二步

反应中可获得较高的低碳烯烃选择性^[16,17]。

尽管HCl可能带来设备腐蚀等问题, 但研究HCl和O₂存在下的C₂H₆选择氧化反应仍具有重要意义。其原因在于以下两个方面。首先, 现有的甲烷资源, 如页岩气等, 其中含有相当量的乙烷, 因此当我们上述的催化体系^[15]应用于页岩气等甲烷资源的转化时, 需要知道在甲烷转化的过程中, 乙烷如何反应。其次, 对于C₂H₆氧化脱氢制乙烯, 含Cl⁻催化剂如Li-Na-Mg-Dy-O-Cl表现出了极佳的C₂H₄收率, 催化剂表面的Cl⁻离子起着至关重要的作用^[3,11–14]。受该体系启发, 我们希望发展一条HCl存在下的乙烷氧化脱氢的新途径, 该途径可避免Cl⁻的流失, 保持稳定的催化活性。

我们在常压固定床微型反应装置上进行催化反应。催化剂首先在He和O₂混合气流中在823 K预处理30 min, 而后切换到He气流吹扫30 min。待温度降至反应温度后(723 K), 通入反应气开始反应。所有产物用气相色谱在线分析。

我们首先考察了HCl和O₂存在下C₂H₆转化反应中各种金属氧化物的催化性能。实验中所用金属氧化物购自阿法埃莎或国药集团化学试剂有限公司。如表1所示, 拥有较好氧化还原能力的金属氧化物均表现出了较高的乙烷转化率。除CuO呈现了较高的C₂H₃Cl选择性外, 其他金属氧化物上C₂H₄为主要产物。在一些催化剂上还有少量C₂H₃Cl和C₂H₄Cl₂生成。稀土金属氧化物CeO₂和Eu₂O₃表现出较高的C₂H₄选择性(>60%)。在所研究的金属氧化物催化剂中, CeO₂显示了最高的C₂H₄收率(49%)。需要指出, CeO₂也是CH₄氯化制CH₃Cl反应中最有效的催化剂^[15]。我们曾提出CeO₂表面的Ce⁴⁺通过电子转移活化HCl产生活性Cl物种, 活性Cl物种活化CH₄, O₂将Ce³⁺重新氧化为Ce⁴⁺^[15]。CeO₂突出的氧化还原能力和稳定性使其成为CH₄氯化反应的最佳催化剂。我们推测, C₂H₆转化反应可能服从相似的反应机理, 但主要产物是C₂H₄, 而不是乙烷氯化物。

我们曾报道CeO₂形貌极大地影响其在CH₄氯化反应中的催化性能^[15]。表2比较了CeO₂纳米棒、纳米立方体和纳米粒子在HCl和O₂存在下C₂H₆转化反应中的催化性能。这些不同形貌的CeO₂纳米晶通过Ce(III)盐水解结合不同条件下的水热处理制得^[15,18]。与形貌亦为纳米粒子但表面积较小的商品CeO₂相比, 我们制备的大比表面积的CeO₂纳米粒子具有较高的C₂H₆转化率。尽管与CeO₂纳米粒子相比, CeO₂纳米棒和纳米立方体的比表面积较小, 但它们显示更高的C₂H₆转化率和C₂H₄选择

性。最近的研究揭示, CeO_2 的氧化还原能力和催化性能与其形貌有关^[18,19]。我们之前的工作表明^[15], CeO_2 纳米棒主要暴露{110}和{100}两种晶面, 其相对比例分别为51%和49%, 而 CeO_2 纳米立方体和 CeO_2 纳米粒子则几乎仅一种晶面, 分别为{100}和{111}面。上述结果说明, 在HCl存在的乙烷氧化脱氢反应中, CeO_2 {110}和{100}面比{111}面具有更高的催化活性。

为了进一步提高 C_2H_4 的收率, 我们考察了各种氧化物对具有较高 C_2H_4 收率和易于制备的 CeO_2 纳米棒的修饰效果。该系列催化剂共浸渍法制备, 即在各种金属硝酸盐溶液中加入 CeO_2 纳米棒, 浸渍后搅拌蒸干, 并于823 K下焙烧制得。由表3可见, 一些金属氧化物修饰可提高 C_2H_6 转化率或 C_2H_4 选择性。其中 MgO-CeO_2 , $\text{MnO}_x\text{-CeO}_2$ 和 $\text{CoO}_x\text{-CeO}_2$ 表现出最好的催化性能, C_2H_4 收率可达到60%。尽管 MgO-CeO_2 在反应2 h时拥有最高的乙烯选择性, 但是随反应进行, C_2H_6 转化率和 C_2H_4 选择性均下降。我们观察到反应过程中Mg从催化剂床层流失, 这主要导致催化剂失活。

我们考察了Mn含量对 $\text{MnO}_x\text{-CeO}_2$ 催化性能的影响。该系列催化剂表示为 $y \text{ wt}\% \text{ MnO}_x\text{-CeO}_2$, 其中 y 为Mn重量百分含量。如图1所示, 当Mn含量小于10 wt%时, 随Mn含量增加, C_2H_6 转化率和 C_2H_4 选择性提高。过量的Mn反而降低 C_2H_6 转化活性, 并从而降低 C_2H_4 的收率; 当Mn含量为8 wt%时, 显示最佳催化性能, 723 K时, C_2H_6 转化率为94%, C_2H_4 收率为65%。此时, 除 C_2H_4 外, 还观察到氯乙烯($\text{C}_2\text{H}_3\text{Cl}$)的生成, 其选择性为14%。 $\text{C}_2\text{H}_3\text{Cl}$ 是生产重要的聚合物聚氯乙烯(PVC)的单体。因此, 在723 K时, 8 wt% $\text{MnO}_x\text{-CeO}_2$ 催化剂上, C_2H_6 的转化率为94%, 高附加值产物($\text{C}_2\text{H}_4 + \text{C}_2\text{H}_3\text{Cl}$)选择性约达85%。

图2进一步考察了8 wt% $\text{MnO}_x\text{-CeO}_2$ 催化剂的稳定性。随着反应的进行, C_2H_6 转化率略有降低, 100 h后可以保持在88%。反应35 h后, $\text{C}_2\text{H}_3\text{Cl}$ 选择性降至~3%。 C_2H_4 选择性从~70%逐渐上升至75%–80%。反应100 h后, C_2H_4 收率可维持在65%–70%。因此, 8 wt% $\text{MnO}_x\text{-CeO}_2$ 催化剂

在HCl和 O_2 存在下的 C_2H_6 氧化脱氢反应中性能稳定。

我们已探明, HCl对 C_2H_4 的生成起关键作用。如图3所示, HCl的存在不仅提高8 wt% $\text{MnO}_x\text{-CeO}_2$ 催化剂上 C_2H_6 转化率, 同时改变了产物的选择性。未添加HCl时, C_2H_6 只发生燃烧反应生成 CO_2 。HCl的加入显著抑制 CO_x 的生成, 同时提高 C_2H_4 选择性。当HCl分压超过6 kPa后, C_2H_4 选择性达70%。随HCl分压的进一步增大, $\text{C}_2\text{H}_3\text{Cl}$ 和 $\text{C}_2\text{H}_4\text{Cl}_2$ 的选择性亦有所增加。这些结果表明, HCl的存在可诱导 C_2H_6 高选择性地生成 C_2H_4 。有关HCl作用的本质, 我们推测可能在催化剂表面生成的活性氯物种参与了 C_2H_6 的转化。本实验表明, 在HCl和 O_2 存在下的乙烷转化反应中无 Cl_2 生成。而在相同条件下无 C_2H_6 存在的HCl和 O_2 反应中, 可以观察 Cl_2 的生成, 在723 K, Cl_2 收率为12%。结合图3的HCl在乙烯生成中的关键作用, 我们认为HCl可在催化剂表面被活化, 产生活性氯物种, 负责乙烯的生成。有关Cl的本质尚待进一步研究。

为了解 C_2H_4 生成的反应途径, 我们考察了673 K下接触时间(W (催化剂质量)/ F (气体流速))对8 wt% $\text{MnO}_x\text{-CeO}_2$ 催化性能的影响。如图4所示, 随着接触时间的增加, $\text{C}_2\text{H}_3\text{Cl}$ 的选择性降低, C_2H_4 的选择性增加, 这表明一部分的 C_2H_4 可能由 $\text{C}_2\text{H}_3\text{Cl}$ 产生。与HCl和 O_2 存在下的 CH_4 氯氧化生成 CH_3Cl 反应类似^[15], $\text{C}_2\text{H}_3\text{Cl}$ 是HCl和 O_2 存在下 C_2H_6 选择氧化的初始产物之一。 CO_x 和 $\text{C}_2\text{H}_3\text{Cl}$ 随着接触时间的增加有所增加, 这表明这些产物是反应过程中的次级产物。在接触时间或转化率外推至0时, C_2H_4 的选择性仍有60%(图4), 可见大部分的 C_2H_4 可能作为初级产物直接由 C_2H_6 生成。今后仍需开展进一步的研究以探明 C_2H_4 的生成机理。

总之, 本文报道了HCl存在时温和条件下的乙烷氧化脱氢制乙烯的催化转化新途径。 CeO_2 是该反应的高效催化剂, MnO_x 修饰 CeO_2 可进一步提高 C_2H_6 转化率和 C_2H_4 选择性。在8 wt% $\text{MnO}_x\text{-CeO}_2$ 催化剂上, 723 K下可获得65%–70%的乙烯收率, 且该催化剂性能稳定。结果表明, HCl在 C_2H_4 的生成中起关键作用。