Direct conversion of propane to propylene by O$_2$ in the presence of HCl over NiO-modified CeO$_2$ nanocrystals

Qinghong Zhang,* Quanhua Xie, Huaming Zhang, Jinline Kang, Jun Cheng and Ye Wang

State Key Laboratory of Physical Chemistry of Solid Surfaces, Collaborative Innovation Center of Chemistry for Energy Materials, National Engineering Laboratory for Green Chemical Productions of Alcohols, Ethers and Esters, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, China

*Corresponding author: +86-592-2183047, zhangqh@xmu.edu.cn

Abstract: Here, we report a new strategy for the oxidative dehydrogenation of propane by O$_2$ with outstanding propylene yield in the presence of HCl. CeO$_2$ is an efficient catalyst for the conversion of C$_3$H$_8$ to C$_3$H$_6$ by (O$_2$ + HCl). This reaction is structure sensitive and the catalytic behavior depends on the exposed facet of CeO$_2$. A C$_3$H$_6$ yield of 55% has been attained at C$_3$H$_8$ selectivity of ~80% over NiO-modified CeO$_2$ nanorods. C$_3$H$_8$ is activated by the chlorine species generated from HCl oxidation on oxygen vacancy sites. NiO enhances the adsorption and activation of HCl, thus increasing C$_3$H$_6$ selectivity.

Keywords: Oxidative dehydrogenation of propane, Propylene, CeO$_2$ nanocrystals.

1. Introduction

Oxidative dehydrogenation of C$_3$H$_8$ is an attractive reaction for C$_3$H$_6$ production, but the over-oxidation results in low C$_3$H$_6$ selectivity at considerable C$_3$H$_8$ conversions and the formation of undesirable CO$_2$. To increase the selectivity of the target product, which is more reactive than the substrate, is a challenging goal in selective oxidation catalysis.$^1$ Despite some recent encouraging progress, high propylene selectivity (>70%) is still difficult to achieve at a high propane conversion (>30%).

The use of halogen (X$_2$) as an oxidant for the functionalization of lower alkanes can avoid the formation of CO$_2$ and has attracted much attention in recent years, but the regeneration of X$_2$ from HX via the Deacon reaction is necessary and is a cost-demanding process. Some studies have been devoted to the conversion of CH$_4$ and other lower alkanes by (O$_2$ + HX), but only a few studies have reported the conversion of propane by this strategy.$^{2,3}$ Besides lower olefins, RX (R = alkyl group) was also formed in the conversion of lower alkanes.$^3$ Here, we report the direct conversion of C$_3$H$_8$ to C$_3$H$_6$ by (O$_2$ + HCl) with a high single-pass yield using CeO$_2$-based catalyst. We demonstrate that the reaction is structure sensitive and the modification of CeO$_2$ by NiO can further enhance C$_3$H$_6$ yield. The roles of HCl and the reaction mechanism will be discussed.

2. Experimental

CeO$_2$ nanocrystals with different morphologies were synthesized by hydrothermal methods. The modification of CeO$_2$ nanorods with different additives was performed by an impregnation method. The catalytic reaction was carried out on a fixed-bed flow reactor. The carbon-containing products were analyzed by online gas chromatography.

3. Results and discussion

We first investigated the catalytic behaviors of various metal-oxide catalysts for the conversion of C$_3$H$_8$ by (O$_2$ + HCl). The result shows that CeO$_2$ is a promising catalyst, not only because CeO$_2$ demonstrates the highest single-pass C$_3$H$_6$ yield among all the catalysts examined but also because it shows high stability. The catalytic behavior of CeO$_2$ depended on its morphology or the exposed facets. The rates of C$_3$H$_8$ conversion and C$_3$H$_6$ formation decreased in the order of nanorods (exposing {110} + {100}) > nanocubes (exposing {100}) > nano-octahedra (exposing {111}) ≈ nanoparticle (exposing {111}). Thus, the {110} facet shows higher activity than the {100} facet, which was significantly higher than the {111} facet. We further compared the C$_3$H$_6$ selectivity at similar C$_3$H$_8$ conversion levels and found that the C$_3$H$_6$ selectivity decreased in the following sequence: nanocube > nanorod > nano-octahedron = nanoparticle. Thus, the {100}
facet is the most selective for C$_3$H$_6$ formation, followed by the {110} and {111} facets. In short, the CeO$_2$-catalyzed conversion of C$_3$H$_8$ is a structure-sensitive reaction. The {110} facet is the most active for C$_3$H$_8$ conversion, whereas the {100} facet is the most selective for C$_3$H$_6$ formation.

We investigated the effect of various modifiers on the catalytic behavior of CeO$_2$ nanorods. Among all the modifiers examined, NiO was the most efficient for promoting C$_3$H$_6$ formation. Both O$_2$ and C$_3$H$_8$ conversions increased after the doping of NiO with a low content (Figure 1). The C$_3$H$_6$ selectivity increased gradually from 55% to 72% with an increase in NiO content to 8 wt%. At the same time, the selectivities of CO and CO$_2$ decreased, and the selectivity of organic chlorides kept low (<4%).

Our studies revealed that HCl played a crucial role in the selective formation of C$_3$H$_6$ over CeO$_2$ based catalysts. CO$_2$ was the major product in the absence of HCl (Figure 2A), indicating that CeO$_2$ and NiO–CeO$_2$ were complete oxidation catalysts for the oxidation of C$_3$H$_8$ by O$_2$. Both C$_3$H$_8$ conversion and C$_3$H$_6$ selectivity increased with the partial pressure of HCl. C$_3$H$_8$ conversion of ~70% and C$_3$H$_6$ selectivity of ~80% were attained over the 8 wt% NiO–CeO$_2$ catalyst at a P(HCl) of 25 kPa (Figure 2B). The single-pass C$_3$H$_6$ yield reached ~55%. We confirmed that ~98% HCl could be recovered.

We performed mechanistic studies for CeO$_2$ and 8 wt% NiO–CeO$_2$ catalysts. We uncovered that the oxidation of HCl by O$_2$ to Cl$_2$ (the Deacon reaction) occurred on our catalysts, but the formation of Cl$_2$ was inhibited by the presence of C$_3$H$_8$. We characterized the CeO$_2$ nanocrystals with different morphologies and the NiO–CeO$_2$ catalysts with different NiO contents by UV-Raman and HCl chemisorption studies. The correlation of the characterization results with the catalytic behaviors suggests that C$_3$H$_8$ conversion activity depends on the concentration of oxygen vacancies, while the chemisorption amount of HCl determines C$_3$H$_6$ selectivity. In combination with DFT calculations, we propose that HCl is activated on oxygen vacancies in the presence of O$_2$, generating Cl species for the activation of C$_3$H$_8$ and the selective formation of C$_3$H$_6$.

4. Conclusions

CeO$_2$ is an efficient and stable catalyst for the conversion of C$_3$H$_8$ to C$_3$H$_6$ by O$_2$ in the presence of HCl. The reaction is structure sensitive and the catalytic behavior depends on the exposed facet of CeO$_2$. CeO$_2$ nanorods and nanocubes show the highest activity and the highest C$_3$H$_6$ selectivity, respectively. The modification of CeO$_2$ nanorods with NiO increases catalytic performances, offering a C$_3$H$_6$ yield of ~55%. HCl plays a crucial role in selective formation of C$_3$H$_6$. The oxygen vacancy participates in the activation of HCl, generating active Cl species for the selective formation of C$_3$H$_6$.

References