Direct conversion of propane to propylene by O_2 in the presence of HCl over NiO-modified CeO_2 nanocrystals

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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_3H_8 to C_3H_6 by (O_2 + HCl). This reaction is structure sensitive and the catalytic behavior depends on the exposed facet of CeO_2. A C_3H_6 yield of 55% has been attained at C_3H_6 selectivity of ~80% over NiO-modified CeO_2 nanorods. C_3H_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_3H_6 selectivity.

Keywords: Oxidative dehydrogenation of propane, Propylene, CeO_2 nanocrystals.

1. Introduction

Oxidative dehydrogenation of C_3H_8 is an attractive reaction for C_3H_6 production, but the over-oxidation results in low C_3H_6 selectivity at considerable C_3H_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_3H_8 to C_3H_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_3H_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_3H_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_3H_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_3H_8 conversion and C_3H_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_3H_6 selectivity at similar C_3H_8 conversion levels and found that the C_3H_6 selectivity decreased in the following sequence: nanocube > nanorod > nanooctahedron ≈ nanoparticle. Thus, the {100} facet is the most selective for C_3H_6 formation, followed by the {110} and {111} facets. In short, the CeO_2-catalyzed conversion of C_3H_8 is a structure-sensitive reaction. The {110} facet is the most active for C_3H_8 conversion, whereas the {100} facet is the most selective for C_3H_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_3H_6 formation. Both O_2 and C_3H_8 conversions increased after the doping of NiO with a low content (Figure 1). The C_3H_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%).

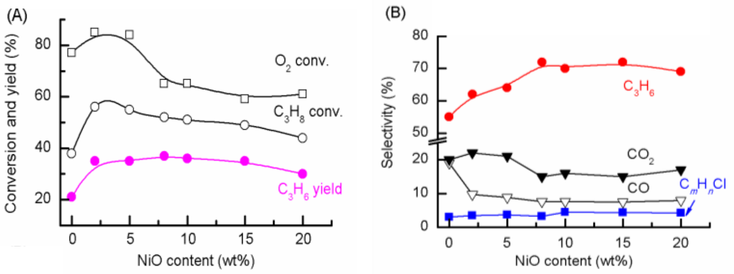

Figure 1. Effect of NiO content on catalytic behaviors of NiO−CeO_2 catalysts.

Our studies revealed that HCl played a crucial role in the selective formation of C_3H_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_3H_8 by O_2. Both C_3H_8 conversion and C_3H_6 selectivity increased with the partial pressure of HCl. C_3H_8 conversion of ~70% and C_3H_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_3H_6 yield reached ~55%. We confirmed that ~98% HCl could be recovered.

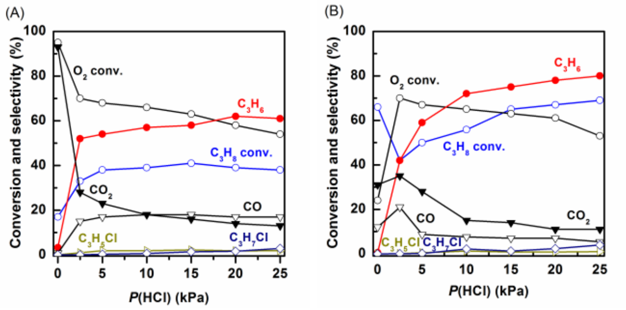

Figure 2. Effect of HCl pressure on catalytic behaviors over (A) CeO_2 and (B) 8 wt% NiO−CeO_2 catalysts.

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_3H_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_3H_8 conversion activity depends on the concentration of oxygen vacancies, while the chemisorption amount of HCl determines C_3H_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_3H_8 and the selective formation of C_3H_6.

4. Conclusions

CeO_2 is an efficient and stable catalyst for the conversion of C_3H_8 to C_3H_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_3H_6 selectivity, respectively. The modification of CeO_2 nanorods with NiO increases catalytic performances, offering a C_3H_6 yield of ~55%. HCl plays a crucial role in selective formation of C_3H_6. The oxygen vacancy participates in the activation of HCl, generating active Cl species for the selective formation of C_3H_6.

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