K-doped $LaFeO_3$ perovskites for CO_2 hydrogenation to light olefins

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Introduction

CO_2 valorization through thermocatalytic hydrogenation represents a promising pathway for the production of green value-added chemicals such as light olefins. In this study, $LaFeO_3$ perovskite (LFO) and its potassium-promoted derivatives (K/LFO, with a nominal K:Fe=1.7) are synthesized using three synthesis routes, namely sol-gel (sg), hydrothermal (ht) and mechanochemical method (m). The catalysts were systematically characterized (via XRD, Raman, FTIR, SEM and XPS analysis) to determine their phase composition, surface chemistry, morphology, and oxidation state distribution of the iron active sites, and evaluated at 340 - 400 ^oC, 20 bar, WHSV= 5.5 $L \cdot gcat^{-1} \cdot h^{-1}$ and a feed ratio of H_2:CO_2=3:1 with the aim to reveal structure-performance relationships.

Results and Discussion

Structural and spectroscopic analyses revealed that the mechanochemical route produced a defect-rich perovskite with enhanced Fe^{2+}/Fe^{3+} redox flexibility and oxygen vacancies, whereas the sol-gel and hydrothermal routes yielded more stoichiometric, less reducible lattices. Upon K incorporation, the structural reconstruction was pronounced, accompanied by the appearance of Fe_3O_4 and FeC_x phases. Catalytic evaluation studies demonstrated a strong dependence on both synthesis and potassium promotion. The mechanochemical K/LFO-m catalyst exhibited the highest CO_2 conversion (50%) and light-olefin selectivity (17%) at 340 ^oC , outperforming the sol-gel and hydrothermal counterparts (Fig 1). This superior activity was associated with sustained oxygen-vacancy contribution, stabilized reduced iron species, homogeneous K dispersion, and the formation of iron carbide phases which facilitated CO_2 activation and C-C coupling. Moreover, the effect of reaction temperature demonstrated that CO_2 conversion increases with an increase in temperature, while C_2-$C_4^=$ selectivity reaches a plateau over 370 ^oC, and further temperature increase hinders paraffin formation. Overall, the findings highlight the critical interplay between defect chemistry and alkali promotion in tuning perovskite-derived Fe active sites for efficient CO_2-to-olefins conversion.

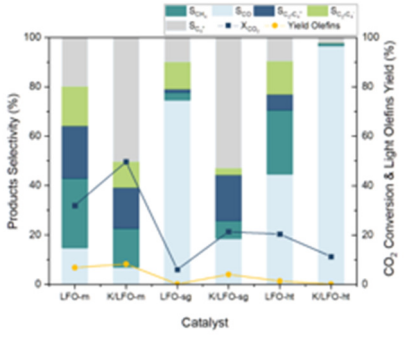


Figure 1: Catalytic activity and product distribution over LFO and K/LFO catalytic systems.

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