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Metal–Site Dispersed Zinc–Chromium Oxide Derived from Chromate–Intercalated Layered Hydroxide for Highly Selective Propane Dehydrogenation

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Abstract: Propane dehydrogenation (PDH) is a crucial approach for propylene production. However, commonly used CrO_x -based catalysts have issues including easy sintering at elevated reaction temperatures and relying on high acidity supports. In this work, we develop a strategy, to strongly anchor and isolate active sites against their commonly observed aggregation during reactions, by taking advantage of the net trap effect in chromate intercalated Zn–Cr layered hydroxides as precursors. Furthermore, the intercalated chromate overcomes the collapse of traditional layered hydroxides during their transformation to metal oxide, thus exposing more available active sites. A joint fine modulation including crystal structure, surface acidity, specific surface area, and active sites dispersion is performed on the final mixed metal oxides for propane dehydrogenation. As a result, $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}$ -MMO delivers attractive propane conversion (~27%) and propylene selectivity (>90%) as compared to other non-noble-metal-based catalysts.

Keywords: layered hydroxide; chromate intercalation; spinel; propane dehydrogenation



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1. Introduction

Propylene has a wide range of applications in producing chemicals such as polypropylene, propylene oxide, and isopropyl alcohol [1–4]. However, traditional production processes, such as steam cracking and fluidized bed catalytic cracking, have low propylene yields, high energy consumption, and high costs [5,6]. Therefore, there is an urgent need to develop efficient propylene production technologies. Propane direct dehydrogenation (PDH), which relies on noble metal Pt-based and CrO_x -based catalysts, provides a more economic and environmentally friendly route to propylene synthesis than conventional processes [7,8]. CrO_x -catalysts have greater cost advantages over Pt-based catalysts, but the aggregation of the active sites in CrO_x -based catalysts at elevated reaction temperatures and the deactivation of catalysts due to the high acidity of commonly used supports (e.g., Al_2O_3) remain to be solved [9]. Furthermore, the PDH process requires catalysts with a relatively high surface area to make full use of active sites and manage heat transfer to avoid side-reactions, while commonly prepared metal oxides for PDH suffer from low surface area, especially those annealed at elevated temperature to obtain high mechanical strength. Therefore, the design of a CrO_x -based catalyst with high surface area, accompanying with stably dispersed active sites and the fine modulation of catalyst acidity, is desperately needed to improve the performance of PDH.

Layered hydroxides are a class of two-dimensional (2D) nanosheet materials, whose laminates are constructed by M^{2+} and M^{3+} hydroxides [10,11]. The net trap effect in layered hydroxide laminates is promising to stably anchor each metal cation during high temperature treatment. As a result, mixed metal oxides (MMOs) derived from layered hydroxides can immobilize the elemental distribution and avoid site aggregation, addressing one major problem in PDH catalyst synthesis [12]. Furthermore, exchangeable anions, for example,

chromate in the interlayer of layered hydroxides, can firstly contribute to more available PDH active sites; secondly, chromates do not decompose at elevated temperatures, thus preserving the structural integrity of the MMO and maintaining a larger surface area. This overcomes the issues of structural collapse and surface area reduction typically linked to the use of carbonate–intercalated hydroxide precursors. [13]. Third, the tunable interlayer anions and lamellar cations offer significant potential for regulating the surface acidity of MMOs [14].

Following the merits discussed above, we prepared catalysts for propane dehydrogenation using chromate (CrO_4^{2-}) intercalated Zn–Cr layered hydroxides (ZnCr-CrO_4^{2-}) as precursors. Chromate intercalation enables the formation of structurally stable zinc–chromium mixed metal oxides (ZnCr–MMO) with more dispersed active sites after the calcination of the layered hydroxides, which maintain a high surface area ($70.80 \text{ m}^2/\text{g}$) and are structurally stable even at a reaction temperature of 550°C . In addition, chromate intercalation also contributes to the modulation of surface acidity. Joint efforts contribute to high propane conversion ($\sim 27\%$) and selectivity ($>90\%$) at $\text{WHSV} = 8.9 \text{ h}^{-1}$ of $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}\text{-MMO}$.

2. Results and Discussion

2.1. Characterization of Catalyst Precursors

We used a co–precipitation method to synthesize precursor layered hydroxides, followed by a calcination at 600°C for 4 h under air atmosphere to obtain catalysts (Figure 1).

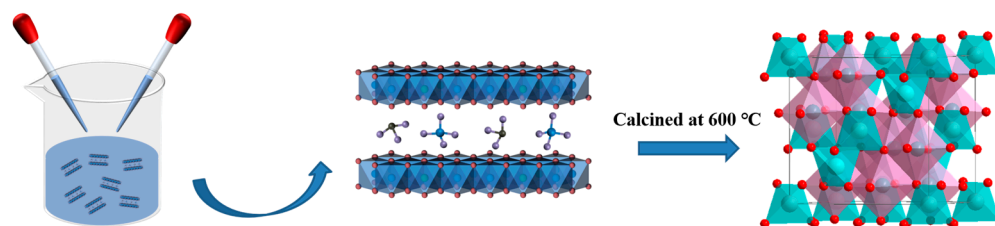


Figure 1. Schematic illustration of the pure ZnCr_2O_4 spinel preparation from chromate–intercalated precursor.

The synthesized precursors were first characterized by XRD to study the effect of chromate intercalation on the crystal structure of layered hydroxides. As shown in Figure 2a, both $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}$ and $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}$ have layered hydroxide structures. The diffraction peaks of $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}$ at 12.2° and 24.6° correspond to (003) and (006) diffraction peaks of layered hydroxides, respectively. Furthermore, the (003) and (006) diffraction peaks of $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}$ shift towards lower angles, specifically at 10.9° and 20.1° , respectively, compared to $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}$. According to Bragg’s law, this result can be attributed to the difference in anion radii in the interlayer and provides initial evidence of successful chromate intercalation. The structure is analyzed via Fourier transform infrared (FT–IR) within a range of 4000 to 400 cm^{-1} . As shown in Figure 2b, the strong broad absorption band of the layered hydroxide at about 3500 cm^{-1} corresponds to the O–H stretching vibrations of both metal hydroxyl (M–OH) group and hydroxyl group from water molecule in the interlayer. The weak absorption near 1639 cm^{-1} is usually considered the bending vibration of the interlayer or physically adsorbed water [15]. Absorption bands at 1365 cm^{-1} and 1492 cm^{-1} for $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}$ originate from C–O stretching vibrations in carbonates [16], whereas no obvious characteristic peaks belonging to CO_3^{2-} are observed in the chromate–intercalated precursor in the range of $1365\text{--}1500 \text{ cm}^{-1}$, and absorption bands originating from the Cr(VI)–O vibration appear at about 900 cm^{-1} in the grey box. The Cr(VI)–O vibrational bands of $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}$ are shifted compared to potassium chromate (887 cm^{-1}), which can be attributed to the van der Waals forces between the intercalated chromate and the laminate (also known as confinement effect). Here, we can draw the conclusion of the successful intercalation of chromate.

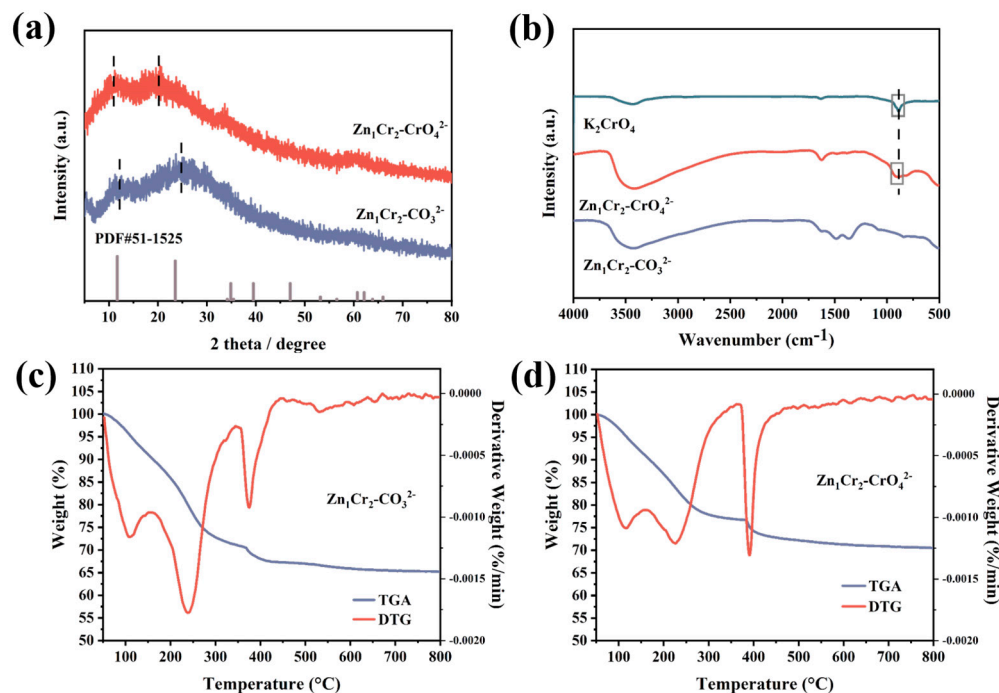


Figure 2. (a) XRD patterns, (b) FTIR spectrum, (c,d) TGA–DTA of the $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}$ and $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}$ precursors.

The morphology of materials was studied by transmission electron microscopy (TEM). As shown as Figure S1, a similar nanosheet morphology between $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}$ and $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}$ indicates that the intercalation of chromate does not affect the morphology of layered hydroxides. Thermal stability was assessed using thermogravimetric analysis (TGA). As shown in Figure 2c,d, most of the weight loss is completed before 400 °C. The $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}$ presents three weight loss peaks: the first peak (108 °C) indicates the removal of water, the second peak (240 °C) reflects the elimination of interlayer hydroxyl and interlayer anions (CO_3^{2-}), accompanied by the collapse of the layered structure, and the third peak (375 °C) corresponds to the decomposition of CO_3^{2-} and the elimination of hydroxyl groups [17]. Similar three weight loss peaks were also observed for the $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}$ precursor, but they were located at different temperatures. The first one at 114 °C is due to removal of surface adsorbed water, and the other two weight loss peaks (228 °C, 392 °C) represents the removal of interlayer hydroxyl groups. The chromate in the $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}$ interlayer did not thermally decompose, and the overall weight loss was less than that of the $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}$. Results here suggest that $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}$ has a potential high surface area since decomposition of carbonate will result in structural collapse, which is not the case in $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}$.

Subsequently, the surface structure and chemical state of the materials were analyzed using Raman spectra and X-ray photoelectron spectra (XPS). As shown in Figure S2, for $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}$ precursors, the strong peak at 536 cm^{-1} is attributed to Cr–O–H bending modes [18,19], while the strong peak of $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}$ at 850 cm^{-1} is attributed to chromate (CrO_4^{2-}) [20]. Cr 2p spectrum of $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}$ in Figure S3 displays two different valence states. The binding energies of Cr^{3+} in hydroxide are located at $\sim 578\text{ eV}$ ($2p^{3/2}$) and $\sim 588\text{ eV}$ ($2p^{1/2}$) [21], while the binding energy of Cr^{6+} in chromate is located at $\sim 580\text{ eV}$ ($2p^{3/2}$) and $\sim 590\text{ eV}$ ($2p^{1/2}$) [21].

2.2. Characterization of Spinel Formation after Precursor Calcination

The prepared layered hydroxide precursors were calcined at 600 °C for 4 h under air atmosphere to obtain mixed metal oxides. We firstly performed structural analysis of the calcined samples using XRD. As shown in Figure 3a, the diffraction peaks of $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}$ –MMO correspond well to ZnCr_2O_4 spinel phase (PDF#22–1107), while

the diffraction peak attributed to ZnO (PDF#36-1451) is observed at 31° for $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}\text{-MMO}$. ZnO is unstable under propane dehydrogenation reaction conditions and can be easily reduced to metallic zinc (Zn) with a melting point of approximately 420°C [22]. To investigate the effect of Zn/Cr ratios on the structure of the catalysts, we modulated Zn/Cr ratios and calcined each catalyst in the same way. XRD analysis in Figure S4a exhibits both ZnO and ZnCr_2O_4 phases in samples when Zn/Cr > 0.5 , while the diffraction peak of Cr_2O_3 was observed in samples where Zn/Cr < 0.5 (PDF#38-1479), which can be explained by the unbalanced A(II)/B(III) ratio in the precursor to form a pure phase spinel. In order to form a pure phase spinel structure, we chose a sample with a Zn/Cr ratio of 1:2 for further study. We calcined $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}$ at $500\text{--}800^\circ\text{C}$ to explore the effect of calcination temperature on the structure of the material. As shown by the XRD results (Figure S4b), the layered structures were destroyed during calcination at temperatures over 500°C , accompanied by the appearance of ZnCr_2O_4 spinel characteristic diffractions, which became sharper along with an elevated calcination temperature from 500 to 800°C . In addition, ZnO is formed when the temperature is further increased. We finally chose a calcination temperature of 600°C and a reaction temperature of 550°C , given the propane dehydrogenation is frequently carried out at $550\text{--}700^\circ\text{C}$ [23].

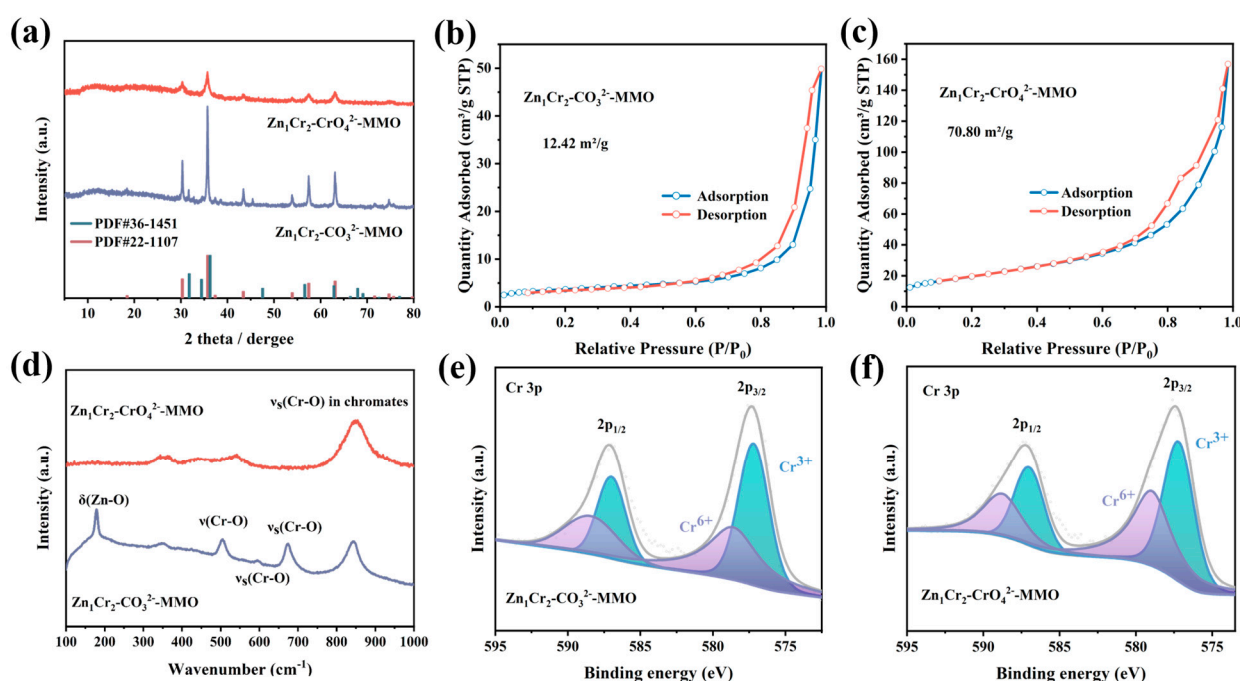


Figure 3. (a) XRD patterns of $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}\text{-MMO}$ and $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}\text{-MMO}$. N_2 adsorption-desorption isotherm and pore size distribution of $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}\text{-MMO}$ (b) and $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}\text{-MMO}$ (c). (d) Raman of $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}\text{-MMO}$ and $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}\text{-MMO}$. XPS spectra of Cr 2p over $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}\text{-MMO}$ (e) and $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}\text{-MMO}$ (f).

Figure S5 shows the TEM images of the calcined samples and the corresponding size distributions. The particle size of $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}\text{-MMO}$ is concentrated mainly in the range of $20\text{--}25\text{ nm}$, while the particle size of $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}\text{-MMO}$ is in the range of $9\text{--}11\text{ nm}$. Figure 3b,c show the N_2 isothermal adsorption-desorption isotherm of the calcined materials. Both $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}\text{-MMO}$ and $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}\text{-MMO}$ exhibit type IV isotherm and H3 hysteresis loops, which are caused by slit-shaped pores formed by the stacking of plate-like particles retained by the precursor [24]. In addition, it can be observed that the specific surface area of $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}\text{-MMO}$ ($70.80\text{ m}^2/\text{g}$) is significantly greater than that of $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}\text{-MMO}$ ($12.42\text{ m}^2/\text{g}$), which is advantageous for active sites exposure.

Raman spectra were used to analyze the changes in the surface structure of the precursor after calcination. The sharp peak at 180 cm^{-1} in $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}\text{-MMO}$ (Figure 3d) is derived from the Zn–O bending vibration of the ZnCr_2O_4 spinel. The band at 500 cm^{-1} with medium intensity and the less intense bands at 599 cm^{-1} can be assigned to the Cr–O stretching vibration (F_{2g}). The band at 673 cm^{-1} is attributed to the symmetric Cr–O stretching vibration of A_{1g} symmetry, which originates from the CrO_6 groups in the spinel structure [25]. The $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}\text{-MMO}$ catalyst exhibits a strong peak at 850 cm^{-1} (Figure 3d), which is attributed to the Cr–O stretching vibration of chromate [20], indicating that a significant amount of chromate (CrO_4^{2-}) is present on the catalyst. In addition, chemical state analysis of the calcined samples was performed using XPS. As shown in Figure 3e,f, the binding energies of Cr^{3+} in Cr_2O_3 or ZnCr_2O_4 spinel are located at $\sim 577\text{ eV}$ ($2p^{3/2}$) and $\sim 586.8\text{ eV}$ ($2p^{1/2}$), and the binding energies of Cr^{6+} in CrO_3 or CrO_4^{2-} are located at $\sim 579\text{ eV}$ ($2p^{3/2}$) and $\sim 588.8\text{ eV}$ ($2p^{1/2}$) [21,26]. The XPS results reveal the presence of both Cr (III) and Cr (VI) in the calcined samples. Additionally, it is found that $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}\text{-MMO}$ have a higher proportion of Cr (VI) on the surface. Under reaction conditions, Cr^{6+} can be reduced to Cr^{3+} as active sites to facilitate PDH conversion, while initial Cr^{3+} can be reduced to metallic Cr, a bad active site for PDH [9,27].

2.3. The Catalytic Performance of Catalysts

2.3.1. Catalytic Properties in Direct Propane Dehydrogenation

We evaluated propane dehydrogenation performance of $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}\text{-MMO}$ and $\text{ZnCr-CrO}_4^{2-}\text{-MMO}$ with different Zn/Cr ratios. The performance of all the catalysts for the PDH reaction was evaluated at 550°C , 0.1 MPa , $\text{C}_3\text{H}_8:\text{N}_2 = 1:4.32$, and $\text{WHSV} = 22.3\text{ h}^{-1}$. Figure 4a,b display the initial conversion and selectivity of various catalysts (Initial conversion and selectivity here refer to data collected 7 min after propane is fed). It is clear that the PDH performance of the catalyst using chromate–intercalated hydroxides as precursors ($\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}\text{-MMO}$) is superior to that of the catalyst with non–intercalated hydroxides as precursors ($\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}\text{-MMO}$) for Zn/Cr=1:2. The $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}\text{-MMO}$ were primarily composed of the ZnCr_2O_4 spinel phase and the crystalline ZnO phase (Figure 3a). Due to the fact that dispersed and unsaturated Cr^{3+} is typically regarded as the active site for propane dehydrogenation, Cr is inactive against propane when it enters the spinel phase [28]. Additionally, the propane conversion on crystalline ZnO is low and unstable under reaction conditions [22]. As a result, $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}\text{-MMO}$ exhibited low PDH activity, with less than 2% propane conversion. Furthermore, the PDH performance exhibited an increase with the rise in Cr ratio in catalysts with various Zn/Cr ratios. The propane conversion rate was highest (13%) when the Zn/Cr ratio was 1:2 ($\text{Zn}_1\text{Cr}_3\text{-CrO}_4^{2-}\text{-MMO}$), and decreased to 6.5% with further increase in the Cr ratio. This could be attributed to the fact that as the amount of chromium increases, the $\text{Zn}_1\text{Cr}_3\text{-CrO}_4^{2-}\text{-MMO}$ exhibited crystalline Cr_2O_3 (Figure S4). Previous studies have shown that the activity of alkane dehydrogenation decreases when accompanied by the formation of crystalline Cr [29], which was the reason for the reduced PDH conversion performance of the $\text{Zn}_1\text{Cr}_3\text{-CrO}_4^{2-}\text{-MMO}$ catalysts. Accordingly, it is presumed that the chromate is reduced during the reaction to reactive Cr^{3+} , which has a positive effect on the reaction.

In addition, $\text{Mg}_2\text{Cr}_1\text{-CrO}_4^{2-}\text{-MMO}$ was synthesized and tested for its propane dehydrogenation reactivity. As shown in Figure S6, the catalytic activity of the $\text{Mg}_2\text{Cr}_1\text{-CrO}_4^{2-}\text{-MMO}$ sample for propane dehydrogenation was not superior to that of the $\text{Zn}_2\text{Cr}_1\text{-CrO}_4^{2-}\text{-MMO}$ sample. Furthermore, the $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}\text{-MMO}$ sample exhibited the lowest reactivity. Consequently, in this study, the formation of a pure phase spinel structure as a carrier for the main active site, CrO_4^{2-} (obtained by intercalation of the precursor), without the interference of oxides with other divalent (inhibitor to PDH reaction) or trivalent ions (changed acidity could also result in catalysts deactivation) is crucial for the propane dehydrogenation reaction.

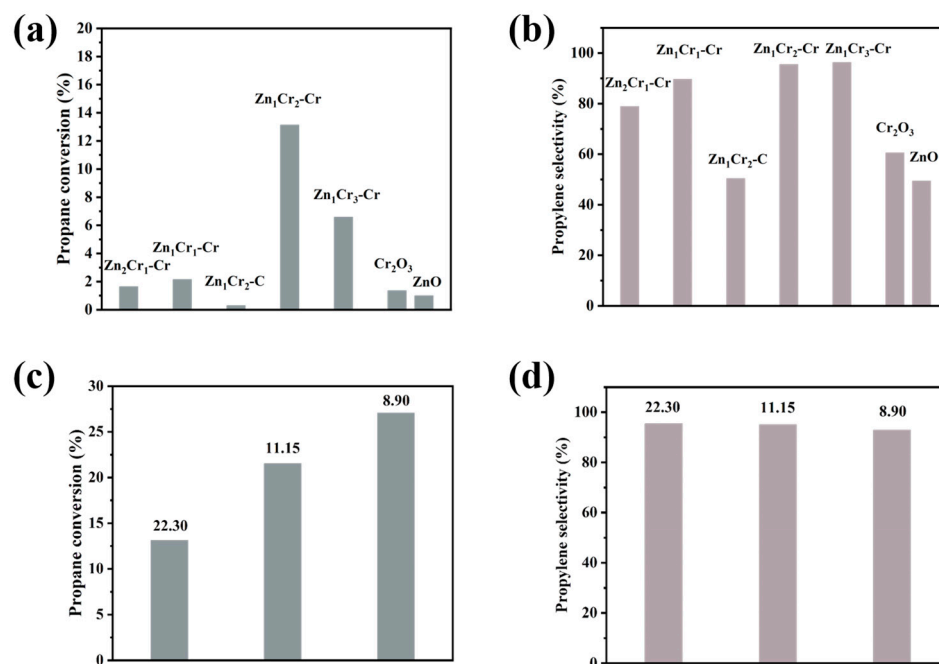


Figure 4. (a) Initial propane conversion and (b) propylene selectivity of $Zn_1Cr_2-CO_3^{2-}-MMO$ and $Zn_1Cr_2-CrO_4^{2-}-MMO$ (Reaction conditions: $550\text{ }^\circ\text{C}$, $WHSV = 22.3\text{ h}^{-1}$, $C_3H_8:N_2 = 1:4.32$). (c) Initial propane conversion and (d) propylene selectivity of $Zn_1Cr_2-CrO_4^{2-}-MMO$ with different WHSV (22.30 h^{-1} , 11.15 h^{-1} and 8.9 h^{-1}).

Figure S7a,b show the conversion and selectivity of different samples throughout prolonged periods of reaction. Although $Zn_1Cr_2-CrO_4^{2-}-MMO$ exhibits a relatively high initial PDH conversion and selectivity, it suffers a fast deactivation rate. This could be attributed to the abundance of strongly acidic sites (discussed in the following), which generate a significant amount of carbon during the reaction, covering the active sites.

In addition, the weight hourly space velocity (WHSV) has a significant impact on the catalytic performance of catalysts; therefore, we investigated the impact of various WHSV on the initial conversion and selectivity of $Zn_1Cr_2-CrO_4^{2-}-MMO$. Figure 4c,d show that the catalyst's propane conversion increases as WHSV decreases, with all catalysts exceeding 90% selectivity. At $WHSV = 8.9\text{ h}^{-1}$, the initial conversion of propane reaches approximately 27%, and the selectivity towards propylene is above 90%. Compared to previously studied chromium-based catalysts, such as supported catalysts with binary $CrZrO_x$ species ($CrZrO_x/SiO_2$) [30], rod-shaped porous alumina-supported Cr_2O_3 catalyst ($Cr-Al-800$) [31], and CrO_x supported on high-silica HZSM-5 [32], our catalyst exhibits a competitive advantage (Table S1).

2.3.2. Investigation of the Acidic Sites of Catalysts

During the PDH process, acidic sites play a key role in facilitating the cleavage of C-H and C-C bonds (conversion and selectivity), while they also result in the formation of carbon deposits (catalyst stability) [33,34]. Therefore, we modulated the acidic sites on the surface of the materials by adjusting the Zn/Cr ratio and intercalating chromate into the layered hydroxide precursor. To explore the reasons resulting in fast deactivation of the catalyst, we analyzed the surface acidity of the catalyst by NH_3 -TPD. As shown in Figure 5a, Zn_1Cr_2-MMO exhibits multiple NH_3 desorption peaks: $<250\text{ }^\circ\text{C}$ attributing to weak acidic sites, $250-400\text{ }^\circ\text{C}$ correlating to medium-strong acidic sites, and $>400\text{ }^\circ\text{C}$ corresponding to strong acidic sites. It is widely accepted that the area of the NH_3 -TPD is directly related to the amount of acid sites [35], and Table S2 lists the data after integration; the peaks are for each catalyst. For $Zn_1Cr_2-CO_3^{2-}-MMO$, the integral area was larger at temperatures above $400\text{ }^\circ\text{C}$ compared to the range of $50-250\text{ }^\circ\text{C}$, which suggests that it has more strongly acidic sites than weakly acidic sites. The intercalation of CrO_4^{2-} in the

precursor resulted in an increase in the NH_3 -TPD integral area for $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}$ -MMO compared to $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}$ -MMO, particularly at 50–250 °C. This suggests an increase in the total acidic sites of the catalyst, particularly the weakly acidic sites.

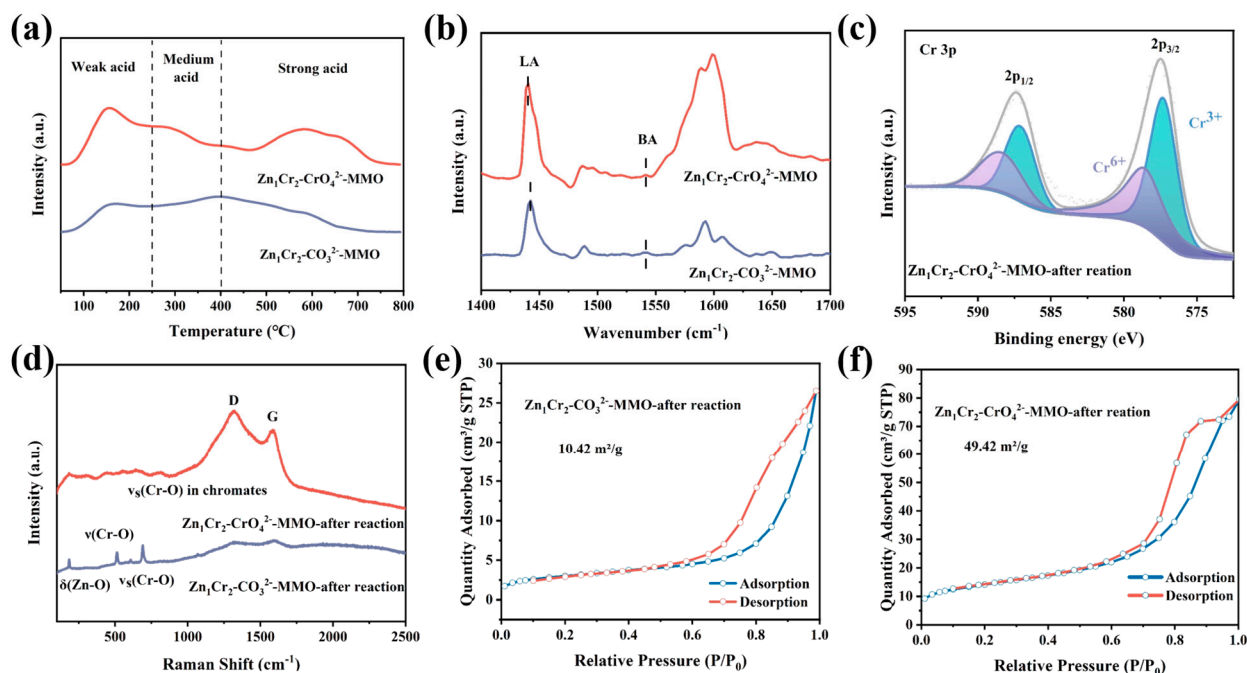


Figure 5. (a) NH_3 -TPD, (b) Py-IR of $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}$ -MMO and $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}$ -MMO. (c) XPS spectra of Cr 2p over $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}$ -MMO after reaction. (d) Raman spectra of $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}$ -MMO and $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}$ -MMO after reaction. (e) N_2 -adsorption-desorption isotherm and pore size distribution of $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}$ -MMO (e) and $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}$ -MMO after reaction (f).

Also as shown in Figure S8 and Table S2, in the catalysts with different Zn/Cr ratios, the increase in Cr content is accompanied by a rise in the medium and strong acid sites of the catalysts, reaching a maximum at a Zn/Cr ratio of 1:2. At this ratio, the medium acid site content is 0.1396 mmol/g, and the strong acid site content is 0.2503 mmol/g. When the Cr content further increases, the medium and strong acid site content of the catalyst are reduced to 0.0880 mmol/g and 0.0567 mmol/g, respectively. This may be due to the fact that the acidic sites of the catalyst increase with increasing Cr^{6+} concentration, which corresponds to an increase in the cracking capacity of the catalyst, making it more susceptible to carbon formation [36]. However, $\text{Zn}_1\text{Cr}_3\text{-CrO}_4^{2-}$ -MMO produces more crystalline Cr_2O_3 phases (Figure S4a), due to a further increase in Cr content, leading to a decrease in acidic sites.

Further, we employed pyridine infrared (Py-IR) spectroscopy to analyze the surface acidity of the samples. The peaks at 1450, 1490, and 1610 cm^{-1} are typically associated with pyridine coordinated to the Lewis acid (LA) site, while the peaks at 1490 and 1540 cm^{-1} are associated with pyridine coordinated to the Brønsted acid (BA) site [37]. As shown in Figures 5b and S8b, the characteristic bands appear primarily at 1450, 1490, and 1615 cm^{-1} , proving that the synthesized samples are all mainly Lewis acid sites. Previous studies have shown that Lewis acidic sites can facilitate C–H bond fragmentation, while excessive Brønsted acid sites are more favorable for C–C bond fragmentation [38]. Therefore, the catalysts exhibit high propylene selectivity (>90%).

2.3.3. Catalysts after Reaction

A series of characterizations were performed to investigate changes in the chemical states and structure of the catalysts after the reaction. Figure 5c and Figure S9 show the XPS after the reaction of $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}$ -MMO and $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}$ -MMO, respectively. It

can be observed that after the reaction, Cr^{3+} and Cr^{6+} were detected on the surfaces of both $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}\text{-MMO}$ and $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}\text{-MMO}$ catalysts. However, the proportion of Cr^{6+} notably decreased compared to that before the reaction, particularly in the $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}\text{-MMO}$ catalysts. This indicates that Cr^{6+} in $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}\text{-MMO}$ was reduced to Cr^{3+} and served as active sites during the propane dehydrogenation reaction, thereby positively influencing the reaction.

The Raman spectra show a weakening of the intensity of the Cr–O vibrational peaks belonging to chromate in the catalysts after reaction (Figure 5d), consistent with the XPS results. This further proves that Cr^{6+} is reduced to Cr^{3+} under the reaction conditions, and that Cr^{3+} may function as an active site. Furthermore, the Raman spectra of the $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}\text{-MMO}$ catalyst exhibit clear defects (D) and graphitization (G) peaks at approximately 1500 cm^{-1} [39], indicating the presence of carbon deposits on the catalyst. The weak peaks of carbon in the Raman spectrum of $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}\text{-MMO}$ may be attributed to its low conversion ratio (<2%), which makes the amount of carbon deposits low.

To investigate evolution in catalyst structure after the reaction and the effect of carbon formation on structure and PDH activity, we further characterized the catalyst's structure and morphology. The structure of the samples after reaction were characterized by XRD, and Figure S10 shows that in addition to the preservation of the ZnCr_2O_4 structure after the reaction, clear diffraction peaks belonging to carbon were found in $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}\text{-MMO}$. A comparable trend was observed for $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}\text{-MMO}$, although the diffraction peaks for carbon were weaker. The findings were consistent with those obtained through Raman spectroscopy.

TEM was used to analyze the morphology of the reacted catalyst. As shown in Figure S11, after the reaction, the particle size of $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}\text{-MMO}$ samples was concentrated within the range of 35–45 nm, which is significantly larger (20–25 nm) than the particle size before the reaction. In contrast, the particle size of the $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}\text{-MMO}$ catalyst after the reaction was mainly concentrated at 10–11 nm, which is similar to the particle size before the reaction (9–11 nm). It is suggested that $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}\text{-MMO}$ is structurally more stable than $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}\text{-MMO}$ and can reduce the risk of active site aggregation during propane dehydrogenation reaction conditions. In addition, $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}\text{-MMO}$ and $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}\text{-MMO}$ showed black shadows on their surfaces after the reaction, which could be attributed to the presence of carbon deposits on the catalyst surface. At the same time, carbon deposits block the pore structure of the catalyst, further reducing the BET specific surface area; the specific surface areas of $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}\text{-MMO}$ and $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}\text{-MMO}$ were reduced to 10.43 and 49.42 m^2 , respectively. (Figure 5e,f).

Subsequently, we further investigated the carbon deposits after the sample reaction by analyzing the reacted samples using thermogravimetric analysis (TGA). Figure S12 shows that the main weight loss of $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}\text{-MMO}$ occurs around 300 °C, indicating a substantial accumulation of carbon in the catalyst. This is consistent with our discussion of acidic sites above, i.e., although $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}\text{-MMO}$ has more weakly acidic sites that are favorable for the reaction, it also has a large number of strongly acidic sites that will inevitably lead to the formation of carbon deposits. A significant accumulation of carbon can cover the active sites, resulting in a decrease in catalytic activity. For the $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}\text{-MMO}$, the low weight loss is due to its low conversion rate (<2%), resulting in less carbon formation after the reaction.

3. Materials and Methods

3.1. Materials and Reagents

All chemical raw materials were analytical reagent grade. Zinc chloride (ZnCl_2 , anhydrous) and potassium chromate (K_2CrO_4) were procured from Shanghai Macklin Biochemical Technology Co., Shanghai, China. Sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3) were procured from Sinopharm Chemical Reagent Co., Ltd., Beijing, China. Chromic Chloride Hexahydrate ($\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$) was procured from West Asia Chemical Technology, Shandong) Co., Ltd., Shandong, China).

3.2. Catalyst Preparation

The co-precipitation method has been used for the preparation of CrO_4^{2-} intercalated layered hydroxide precursors (ZnCr-CrO_4^{2-} and $\text{Mg}_2\text{Cr}_1\text{-CrO}_4^{2-}$). To prevent the intercalation of carbonate into the hydroxide interlayer, nitrogen-saturated de-carbonated water was used instead of deionized water in the subsequent steps. In the case of $\text{Zn}_1\text{Cr}_2\text{-CrO}_4^{2-}$, for example, 4 mmol ZnCl_2 (anhydrous) and 8 mmol $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 50 mL of deionized water, which was labeled as Solution A; 50 mL of deionized water were used to dissolve 15 mmol NaOH and 10 mmol K_2CrO_4 . The resulting solution was labeled as solution B. The C solution was prepared by dissolving 20 mmol of K_2CrO_4 in 50 mL of deionized water. Solutions A and B were slowly added simultaneously under nitrogen protection to solution C with vigorous stirring at 50 °C for 1.5 h while maintaining a controlled pH around 9. The resulting precipitates were thoroughly washed with deionized water until pH neutrality was reached and then freeze-dried overnight for further use.

The synthesis of $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}$, Zn(OH)_2 , and Cr(OH)_3 samples was conducted using the co-precipitation method. The synthesis of $\text{Zn}_1\text{Cr}_2\text{-CO}_3^{2-}$ is presented here as an illustrative example. 4 mmol ZnCl_2 (anhydrous) and 8 mmol $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 50 mL of deionized water, which was labeled as Solution A; 50 mL of deionized water were used to dissolve 15 mmol NaOH and 6 mmol Na_2CO_3 (anhydrous), and the resulting solution was labeled as solution B. Solutions A and B were slowly added simultaneously to 50 mL of deionized water with vigorous stirring at 50 °C for 1.5 h while maintaining a controlled pH around 9. The resulting precipitates were thoroughly washed with deionized water until pH neutrality was reached and then freeze-dried overnight for further use.

The prepared layered hydroxide precursors were placed in a muffle furnace and calcined at a temperature of 600 °C for 4 h at a ramp rate of 10 °C/min. Comparison samples were also prepared by calcining at 500, 700, and 800 °C for 4 h at the same ramp rate.

3.3. Characterization

The Shimadzu XRD-6000 diffractometer (Shimadzu, Kyoto, Japan) was used to analyze the crystalline structures of all samples, using a Cu K α source ($\lambda = 0.154$ nm) and a scanning range of 5 °C to 90 °C with a scanning step of 10 °C/min. The instrument used for XPS characterization was a ESCALAB 250 (Thermo Fisher Scientific, Waltham, MA, USA), and the X-ray source was an Al K α target ($h\nu = 1486.6$ eV). FT-IR spectra were recorded on a Bruker Vector-22 Fourier Transform spectrometer (Bruker Optics, Karlsruhe, Germany) with 2 cm^{-1} resolution in the 4000 to 400 cm^{-1} range. The Raman spectra were recorded using a 785 nm laser light source (InVia Reflex, Renishaw, London, UK), covering a range of 4000 to 100 cm^{-1} . The transmission electron microscopy (TEM) using HT7700 (Hitachi, Tokyo, Japan). The specific surface area was determined using the Brunauer-Emmett-Teller (BET) method, which is based on the adsorption isotherm (ASAP-2460-4N, Micromeritics, Wikiwand, GA, USA). Prior to measurement, the samples were degassed at 180 °C for 2 h. Thermogravimetric analysis (TGA) was used to determine the thermal properties of the samples in air. The weight loss was measured using TGA/DSC 3+ (Mettler Toledo, Zurich, Switzerland) with a heating rate of 10 °C min^{-1} . NH_3 temperature-programmed desorption (NH_3 -TPD) was conducted on the Micrometric ChemiSorb 2750 (Micromeritics, Wikiwand, GA, USA). Following pretreatment, the sample was exposed to the probe molecule (NH_3) at a flow rate of 40 mL min^{-1} for 1 h to ensure maximum adsorption. Subsequently, data were recorded in He from room temperature to 800 °C at a rate of 10 °C min^{-1} . Pyridine-infrared (Py-IR) was conducted on the Bruker Tensor 27 (Bruker Optics, Karlsruhe, Germany). The samples were pressed from the support sheet, placed in the in situ cell of the infrared spectrometer, sealed, evacuated at 350 °C, held for 1 h, and then cooled to room temperature. The in situ cell was filled with bare yard vapors and left to adsorb for 1 h. Afterward, the cell was evacuated and heated to 200 °C and 350 °C, respectively, and degassed for 1 h at each temperature. Bare-infrared spectra were collected at both 200 °C and 350 °C.

3.4. Catalytic Test

The reactor was heated to a reaction temperature of 550 °C with a ramp rate of 10 °C/min using 44.2 mL min^{−1} N₂. After reaching the reaction temperature, the feed composition was changed to 10.22 mL min^{−1} C₃H₈ and 44.2 mL min^{−1} N₂ to measure the performance of the catalyst. At a constant feed composition, catalyst weights of 0.2 g, 0.4 g, and 0.5 g were employed to modulate the weight hourly space velocity (WHSV).

The reaction products were analyzed using the GC 2014 online system (Shimadzu, Kyoto, Japan) equipped with an FID detector for hydrocarbons and a TCD detector for hydrogen. Propane conversion (conv. C₃H₈) and propylene selectivity (sel. C₃H₆) were determined utilizing the internal standard method as per the following equation:

$$\text{Conv.}(\text{C}_3\text{H}_8)(\%) = \frac{F_{\text{C}_3\text{H}_8\text{inlet}} - F_{\text{C}_3\text{H}_8\text{outlet}}}{F_{\text{C}_3\text{H}_8\text{inlet}}} \times 100\% \quad (1)$$

$$\text{Sele.}(\text{C}_3\text{H}_6)(\%) = \frac{F_{\text{C}_3\text{H}_6\text{outlet}}}{\sum i(\frac{n_i}{3}) \times F_{\text{outlet}}} \times 100\% \quad (2)$$

4. Conclusions

In this study, ZnCr₂O₄ was synthesized through calcination at 600 °C with chromate interaction into a layered hydroxide interlayer as a precursor under air atmosphere. The positive effect of chromate interaction on the propane dehydrogenation reaction allowed the catalyst to form pure phase spinel after calcination at 600 °C, without the interference of the ZnO and Cr₂O₃ phases. Furthermore, intercalated chromate helped to maintain large specific surface area and expose active sites; jointly, Zn₁Cr₂–CrO₄^{2−}–MMO demonstrated a high propane dehydrogenation activity, achieving 27% propane conversion at WHSV = 8.9 h^{−1} while maintaining selectivity above 90%. Our findings suggest that MMOs prepared with oxometallate intercalated hydroxides as precursors have the potential to be applied to various reactions requiring high surface area and stable active sites against aggregation during reaction.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/molecules29133063/s1>, Figure S1: TEM of (a) Zn₁Cr₂–CO₃^{2−} and (b) Zn₁Cr₂–CrO₄^{2−} precursors; Figure S2: Raman spectrum of the Zn₁Cr₂–CO₃^{2−} and Zn₁Cr₂–CrO₄^{2−} precursors; Figure S3: XPS spectra of Cr 2p over the Zn₁Cr₂–CrO₄^{2−} precursor; Figure S4: XRD patterns of (a) different compositions of Zn₁Cr₂–CrO₄^{2−}–MMO and (b) Zn₁Cr₂–CrO₄^{2−} calcined at different temperatures; Figure S5: TEM of (a) Zn₁Cr₂–CO₃^{2−}–MMO and (b) Zn₁Cr₂–CrO₄^{2−}–MMO; Figure S6: (a) Initial propane conversion and (b) propylene selectivity of Mg₂Cr₁–CrO₄^{2−}–MMO, Zn₁Cr₂–CO₃^{2−}–MMO and Zn₁Cr₂–CrO₄^{2−}–MMO (Reaction conditions: 550 °C, WHSV = 22.3 h^{−1}, C₃H₈:N₂ = 1:4.32); Figure S7: (a) Propane conversion and (b) propylene selectivity of Zn₁Cr₂–CO₃^{2−}–MMO and Zn₁Cr₂–CrO₄^{2−}–MMO (Reaction conditions: 550 °C, WHSV = 22.3 h^{−1}, C₃H₈:N₂ = 1:4.32). (c) Propane conversion and (d) propylene selectivity of Zn₁Cr₂–CrO₄^{2−}–MMO with different WHSV; Figure S8: (a) NH₃–TPD and (b) Py–IR of different proposition ZnCr–CrO₄^{2−}–MMO; Figure S9: XPS spectra of Cr 2p over Zn₁Cr₂–CO₃^{2−}–MMO after reaction; Figure S10: XRD patterns of Zn₁Cr₂–CO₃^{2−}–MMO (a) and Zn₁Cr₂–CrO₄^{2−}–MMO (b) after reaction; Figure S11: TEM of Zn₁Cr₂–CO₃^{2−}–MMO (a) and Zn₁Cr₂–CrO₄^{2−}–MMO (b) after reaction; Figure S12: TGA of Zn₁Cr₂–CO₃^{2−}–MMO and Zn₁Cr₂–CrO₄^{2−}–MMO after reaction; Table S1: Comparison of catalytic performance in this work with previous works; Table S2: NH₃ desorption property of the catalysts [30–32,37,38,40–48].

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References

- Wang, Y.; Chen, S.; Sun, J.; Xie, Y.; Zhao, Z.-J.; Pei, C.; Gong, J. Roles of V-O sites for non-oxidative propane dehydrogenation over supported vanadium oxides. *Sci. China Mater.* **2023**, *66*, 1062–1070. [\[CrossRef\]](#)
- Atanga, M.A.; Rezaei, F.; Jawad, A.; Fitch, M.; Rownaghi, A.A. Oxidative dehydrogenation of propane to propylene with carbon dioxide. *Appl. Catal. B Environ.* **2018**, *220*, 429–445. [\[CrossRef\]](#)
- Zhao, Z.-J.; Chiu, C.-C.; Gong, J. Molecular understandings on the activation of light hydrocarbons over heterogeneous catalysts. *Chem. Sci.* **2015**, *6*, 4403–4425. [\[CrossRef\]](#) [\[PubMed\]](#)
- Ye, C.; Peng, M.; Li, Y.; Wang, D.; Chen, C.; Li, Y. Atomically dispersed Pt in ordered PtSnZn intermetallic with Pt-Sn and Pt-Zn pairs for selective propane dehydrogenation. *Sci. China Mater.* **2022**, *66*, 1071–1078. [\[CrossRef\]](#)
- Hu, Z.-P.; Yang, D.; Wang, Z.; Yuan, Z.-Y. State-of-the-art catalysts for direct dehydrogenation of propane to propylene. *Chin. J. Catal.* **2019**, *40*, 1233–1254. [\[CrossRef\]](#)
- Lavrenov, A.; Saifulina, L.; Buluchevskii, E.; Bogdanets, E. Propylene production technology: Today and tomorrow. *Catal. Ind.* **2015**, *7*, 175–187. [\[CrossRef\]](#)
- Wang, G.; Zhu, X.; Li, C. Recent progress in commercial and novel catalysts for catalytic dehydrogenation of light alkanes. *Chem. Rec.* **2020**, *20*, 604–616. [\[CrossRef\]](#) [\[PubMed\]](#)
- Nawaz, Z. Light alkane dehydrogenation to light olefin technologies: A comprehensive review. *Rev. Chem. Eng.* **2015**, *31*, 413–436. [\[CrossRef\]](#)
- Chen, S.; Chang, X.; Sun, G.; Zhang, T.; Xu, Y.; Wang, Y.; Pei, C.; Gong, J. Propane dehydrogenation: Catalyst development, new chemistry, and emerging technologies. *Chem. Soc. Rev.* **2021**, *50*, 3315–3354. [\[CrossRef\]](#)
- Wang, Q.; O'Hare, D. Recent advances in the synthesis and application of layered double hydroxide (LDH) nanosheets. *Chem. Rev.* **2012**, *112*, 4124–4155. [\[CrossRef\]](#)
- Evans, D.; Slade, R. Layered double hydroxides. *Struct. Bond.* **2006**, *119*, 1–87.
- He, S.; An, Z.; Wei, M.; Evans, D.G.; Duan, X. Layered double hydroxide-based catalysts: Nanostructure design and catalytic performance. *Chem. Commun.* **2013**, *49*, 5912–5920. [\[CrossRef\]](#)
- Yuan, Z.; Kumar, A.; Zhou, D.; Feng, J.; Liu, B.; Sun, X. Highly efficient semi-hydrogenation of acetylene over Ni supported mesoporous MgAl_2O_4 spinel derived from aluminate-intercalated layered double hydroxide. *J. Catal.* **2022**, *414*, 374–384. [\[CrossRef\]](#)
- Zhang, J.; Yan, T.; Yang, Y.; Sun, J.; Lin, Y.; Wei, M. Zn-Zr-Al oxides derived from hydrotalcite precursors for ethanol conversion to diethyl carbonate. *Chin. J. Catal.* **2019**, *40*, 515–522. [\[CrossRef\]](#)
- Zhong, L.; He, X.; Qu, J.; Li, X.; Lei, Z.; Zhang, Q.; Liu, X. Precursor preparation for Ca-Al layered double hydroxide to remove hexavalent chromium coexisting with calcium and magnesium chlorides. *J. Solid State Chem.* **2017**, *245*, 200–206. [\[CrossRef\]](#)
- Shabanian, M.; Hajibeygi, M.; Raeisi, A. FTIR characterization of layered double hydroxides and modified layered double hydroxides. In *Layered Double Hydroxide Polymer Nanocomposites*; Woodhead Publishing: Sawston, UK, 2020; pp. 77–101.
- Theiss, F.L.; Ayoko, G.A.; Frost, R.L. Thermogravimetric analysis of selected layered double hydroxides. *J. Therm. Anal. Calorim.* **2012**, *112*, 649–657. [\[CrossRef\]](#)
- Gomes, A.S.O.; Simic, N.; Wildlock, M.; Martinelli, A.; Ahlberg, E. Electrochemical investigation of the hydrogen evolution reaction on electrodeposited films of $\text{Cr}(\text{OH})_3$ and Cr_2O_3 in mild alkaline solutions. *Electrocatalysis* **2017**, *9*, 333–342. [\[CrossRef\]](#)
- Gomes, A.S.O.; Yaghini, N.; Martinelli, A.; Ahlberg, E. A micro-Raman spectroscopic study of $\text{Cr}(\text{OH})_3$ and Cr_2O_3 nanoparticles obtained by the hydrothermal method. *J. Raman Spectrosc.* **2017**, *48*, 1256–1263. [\[CrossRef\]](#)
- Christiansen, M.B.; Sørensen, M.A.; Sanyova, J.; Bendix, J.; Simonsen, K.P. Characterisation of the rare cadmium chromate pigment in a 19th century tube colour by Raman, FTIR, X-ray and EPR. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2017**, *175*, 208–214. [\[CrossRef\]](#)
- Sun, J.; Qi, G.C.; Tan, Y.; An, C.Q. Characterization of chromate conversion film on tinplate substrate by XPS and electrochemistry methods. *Surf. Interface Anal.* **2009**, *41*, 449–452. [\[CrossRef\]](#)
- Zhao, D.; Tian, X.; Doronkin, D.E.; Han, S.; Kondratenko, V.A.; Grunwaldt, J.-D.; Perechodjuk, A.; Vuong, T.H.; Rabeah, J.; Eckelt, R.; et al. In situ formation of ZnO_x species for efficient propane dehydrogenation. *Nature* **2021**, *599*, 234–238. [\[CrossRef\]](#)
- Sun, M.-L.; Hu, Z.-P.; Wang, H.-Y.; Suo, Y.-J.; Yuan, Z.-Y. Design Strategies of Stable Catalysts for Propane Dehydrogenation to Propylene. *ACS Catal.* **2023**, *13*, 4719–4741. [\[CrossRef\]](#)

24. Reichle, W.; Kang, S.; Everhardt, D. The nature of the thermal decomposition of a catalytically active anionic clay mineral. *J. Catal.* **1986**, *101*, 352–359. [\[CrossRef\]](#)
25. Song, H.; Laudenschleger, D.; Carey, J.J.; Ruland, H.; Nolan, M.; Muhler, M. Spinel-structured ZnCr_2O_4 with excess Zn is the active $\text{ZnO}/\text{Cr}_2\text{O}_3$ catalyst for high-temperature methanol synthesis. *ACS Catal.* **2017**, *7*, 7610–7622. [\[CrossRef\]](#)
26. Aguilar, M.; Barrera, E.; Palomar-Pardavé, M.; Huerta, L.; Muhl, S. Characterization of black and white chromium electrodeposition films: Surface and optical properties. *J. Non-Cryst. Solids* **2003**, *329*, 31–38. [\[CrossRef\]](#)
27. Cavani, F.; Koutyrev, M.; Trifiro, F.; Bartolini, A.; Ghisletti, D.; Iezzi, R.; Santucci, A.; Del Piero, G. Chemical and physical characterization of alumina-supported chromia-based catalysts and their activity in dehydrogenation of isobutane. *J. Catal.* **1996**, *158*, 236–250. [\[CrossRef\]](#)
28. Sattler, J.J.H.B.; Ruiz-Martinez, J.; Santillan-Jimenez, E.; Weckhuysen, B.M. Catalytic dehydrogenation of light alkanes on metals and metal oxides. *Chem. Rev.* **2014**, *114*, 10613–10653. [\[CrossRef\]](#)
29. Hakuli, A.; Kytöki, A.; Krause, A. Dehydrogenation of i-butane on $\text{CrO}_x/\text{Al}_2\text{O}_3$ catalysts prepared by ALE and impregnation techniques. *Appl. Catal. A Gen.* **2000**, *190*, 219–232. [\[CrossRef\]](#)
30. Han, S.; Zhao, Y.; Otroshchenko, T.; Zhang, Y.; Zhao, D.; Lund, H.; Vuong, T.H.; Rabeah, J.; Bentrup, U.; Kondratenko, V.A.; et al. Unraveling the Origins of the Synergy Effect between ZrO_2 and CrO_x in Supported CrZrO_x for Propene Formation in Nonoxidative Propane Dehydrogenation. *ACS Catal.* **2019**, *10*, 1575–1590. [\[CrossRef\]](#)
31. Gao, X.-Q.; Lu, W.-D.; Hu, S.-Z.; Li, W.-C.; Lu, A.-H. Rod-shaped porous alumina-supported Cr_2O_3 catalyst with low acidity for propane dehydrogenation. *Chin. J. Catal.* **2019**, *40*, 184–191. [\[CrossRef\]](#)
32. Hu, Z.; Wang, Y.; Yang, D.; Yuan, Z.-Y. CrO supported on high-silica HZSM-5 for propane dehydrogenation. *J. Energy Chem.* **2020**, *47*, 225–233. [\[CrossRef\]](#)
33. Ren, Y.; Wang, J.; Hua, W.; Yue, Y.; Gao, Z. $\text{Ga}_2\text{O}_3/\text{HZSM}-48$ for dehydrogenation of propane: Effect of acidity and pore geometry of support. *J. Ind. Eng. Chem.* **2012**, *18*, 731–736. [\[CrossRef\]](#)
34. Schreiber, M.W.; Plaisance, C.P.; Baumgärtl, M.; Reuter, K.; Jentys, A.; Bermejo-Deval, R.; Lercher, J.A. Lewis-Brønsted acid pairs in Ga/H-ZSM-5 to catalyze dehydrogenation of light alkanes. *J. Am. Chem. Soc.* **2018**, *140*, 4849–4859. [\[CrossRef\]](#)
35. Węgrzyniak, A.; Jarczewski, S.; Węgrzynowicz, A.; Michorczyk, B.; Kuśtrowski, P.; Michorczyk, P. Catalytic behavior of chromium oxide supported on nanocasting-prepared mesoporous alumina in dehydrogenation of propane. *Nanomaterials* **2017**, *7*, 249. [\[CrossRef\]](#)
36. Fridman, V.Z.; Xing, R. Investigating the $\text{CrO}_x/\text{Al}_2\text{O}_3$ dehydrogenation catalyst model: II. Relative activity of the chromium species on the catalyst surface. *Appl. Catal. A Gen.* **2017**, *530*, 154–165. [\[CrossRef\]](#)
37. Lin, G.; Su, Y.; Duan, X.; Xie, K. High-density lewis acid sites in porous single-crystalline monoliths to enhance propane dehydrogenation at reduced temperatures. *Angew. Chem. Int. Ed.* **2021**, *60*, 9311–9315. [\[CrossRef\]](#)
38. Yue, Y.; Fu, J.; Wang, C.; Yuan, P.; Bao, X.; Xie, Z.; Basset, J.-M.; Zhu, H. Propane dehydrogenation catalyzed by single Lewis acid site in Sn-Beta zeolite. *J. Catal.* **2021**, *395*, 155–167. [\[CrossRef\]](#)
39. Zhu, X.; Wang, T.; Xu, Z.; Yue, Y.; Lin, M.; Zhu, H. Pt-Sn clusters anchored at Al^{3+} penta sites as a sinter-resistant and regenerable catalyst for propane dehydrogenation. *J. Energy Chem.* **2022**, *65*, 293–301. [\[CrossRef\]](#)
40. Dai, Y.; Gu, J.; Tian, S.; Wu, Y.; Chen, J.; Li, F.; Du, Y.; Peng, L.; Ding, W.; Yang, Y. $\gamma\text{-Al}_2\text{O}_3$ sheet-stabilized isolate Co^{2+} for catalytic propane dehydrogenation. *J. Catal.* **2020**, *381*, 482–492. [\[CrossRef\]](#)
41. Wei, S.; Dai, H.; Long, J.; Lin, H.; Gu, J.; Zong, X.; Yang, D.; Tang, Y.; Yang, Y.; Dai, Y. Nonoxidative propane dehydrogenation by isolated Co^{2+} in BEA zeolite: Dealumination-determined key steps of propane CH activation and propylene desorption. *Chem. Eng. J.* **2023**, *455*, 140726. [\[CrossRef\]](#)
42. Wang, W.; Wu, Y.; Liu, T.; Zhao, Y.; Qu, Y.; Yang, R.; Xue, Z.; Wang, Z.; Zhou, F.; Long, J. Single Co sites in ordered SiO_2 channels for boosting nonoxidative propane dehydrogenation. *ACS Catal.* **2022**, *12*, 2632–2638. [\[CrossRef\]](#)
43. Liu, G.; Zhao, Z.-J.; Wu, T.; Zeng, L.; Gong, J. Nature of the active sites of $\text{VO}_x/\text{Al}_2\text{O}_3$ catalysts for propane dehydrogenation. *ACS Catal.* **2016**, *6*, 5207–5214. [\[CrossRef\]](#)
44. Xie, L.; Wang, R.; Chai, Y.; Weng, X.; Guan, N.; Li, L. Propane dehydrogenation catalyzed by in-situ partially reduced zinc cations confined in zeolites. *J. Energy Chem.* **2021**, *63*, 262–269. [\[CrossRef\]](#)
45. Liu, J.; Liu, Y.; Ni, Y.; Liu, H.; Zhu, W.; Liu, Z. Enhanced propane dehydrogenation to propylene over zinc-promoted chromium catalysts. *Catal. Sci. Technol.* **2020**, *10*, 1739–1746. [\[CrossRef\]](#)
46. Natarajan, P.; Khan, H.A.; Jaleel, A.; Park, D.S.; Kang, D.-C.; Yoon, S.; Jung, K.-D. The pronounced effect of Sn on RhSn catalysts for propane dehydrogenation. *J. Catal.* **2020**, *392*, 8–20. [\[CrossRef\]](#)
47. Xie, Y.; Luo, R.; Sun, G.; Chen, S.; Zhao, Z.-J.; Mu, R.; Gong, J. Facilitating the reduction of V-O bonds on VO_x/ZrO_2 catalysts for non-oxidative propane dehydrogenation. *Chem. Sci.* **2020**, *11*, 3845–3851. [\[CrossRef\]](#)
48. Wang, Y.; Suo, Y.; Ren, J.-T.; Wang, Z.; Yuan, Z.-Y. Spatially isolated cobalt oxide sites derived from MOFs for direct propane dehydrogenation. *J. Colloid. Interf. Sci.* **2021**, *594*, 113–121. [\[CrossRef\]](#)

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