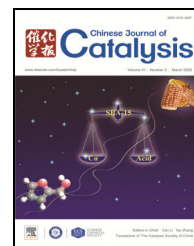


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Article

Co–Cr–O mixed oxides for low-temperature total oxidation of propane: Structural effects, kinetics, and spectroscopic investigation

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ABSTRACT

A series of Co–Cr–O mixed oxides with different Co/Cr molar ratios are synthesized and tested for the total oxidation of propane. The reaction behaviors are closely related to the structural features of the mixed oxides. The catalyst with a Co/Cr molar ratio of 1:2 (1Co2Cr) and a spinel structure has the best activity (with a reaction rate of $1.38 \mu\text{mol g}^{-1} \text{s}^{-1}$ at 250°C), which is attributed to the synergistic roles of its high surface acidity and good low-temperature reducibility, as evidenced by the temperature-programmed desorption of ammonia, reduction of hydrogen, and surface reaction of propane. Kinetic study shows that the reaction orders of propane and oxygen on the 1Co2Cr catalyst (0.58 ± 0.03 and 0.34 ± 0.05 , respectively) are lower than those on the 2Co1Cr catalyst (0.77 ± 0.02 and 0.98 ± 0.16 , respectively) and 1Co5Cr (0.66 ± 0.05 and 1.30 ± 0.11 , respectively), indicating that the coverages of propane and oxygen on 1Co2Cr are higher than those on the other catalysts due to its higher surface acidity and higher reducibility. In addition, in-situ diffuse reflectance infrared spectroscopic investigation reveals that the main surface species on 1Co2Cr during the reaction are polydentate carbonate species, which accumulate on the surface at low temperatures ($< 250^\circ\text{C}$) but decompose at relatively high temperatures.

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1. Introduction

Alkanes are one of the major volatile organic compounds (VOCs) that are massively produced from automobile exhaust and various industrial processes, such as coal processing, petroleum refining, and natural gas processing [1,2]. Increasingly stringent environmental legislation urges the development of efficient technologies for the abatement of VOCs. Catalytic total oxidation (catalytic combustion) has been considered a promising strategy due to its advantages, such as low light-off temperature, low energy consumption, high purification efficiency, and no secondary pollution. For the catalytic combustion of

light alkanes, e.g., methane and propane, noble metals such as Pt and Pd are very effective as catalysts [3–10]. However, the high cost and vulnerability to poisoning have become the major limitations to their commercial applications. Transition metal oxides are appealing alternatives due to their low cost, resistance to toxicity, and high thermal stability. Admittedly, it has been reported that various transition metal oxides (or mixed oxides) such as Cu, Mn, Co, Fe, and Ni oxides are active in the catalytic combustion of propane [11–22].

Among transition metal oxides, cobalt oxides (Co_3O_4) have attracted much attention due to their high activity in propane combustion. For example, porous Co_3O_4 oxides prepared via an

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aqueous precipitation method showed a reaction rate of $1.69 \mu\text{mol g}^{-1} \text{s}^{-1}$ at 200°C for propane combustion [15], and the high activity was attributed to the improved accessibility of the reactants to the surface of the catalyst, which exhibited a large porosity (up to 76%). The activity could be further improved by the addition of a secondary metal. A Ni-doped nano-array Co_3O_4 catalyst ($\text{Ni}_{0.27}\text{Co}_{2.73}\text{O}_4$) afforded a reaction rate of $5.58 \mu\text{mol g}^{-1} \text{s}^{-1}$ at 250°C , which was higher than that afforded by the pure Co_3O_4 (c.a. $3.00 \mu\text{mol g}^{-1} \text{s}^{-1}$ at 250°C). The promoting role of Ni was ascribed to the promoted surface lattice oxygen activity [16]. Faure and Alphonse [23] also reported that a $\text{Co}_{2.3}\text{Mn}_{0.7}\text{O}_4$ spinel oxide exhibited better activity than the pure cobalt oxide for both CO and propane oxidation, due to its high surface area (up to $250 \text{ m}^2 \text{ g}^{-1}$) and high Co concentration. Therefore, the formation of Co–M–O (M is a secondary metal) mixed oxides appears to be a promising approach to improving the catalytic activity toward propane combustion. In this sense, Co–Cr–O mixed oxides might be effective because such a combination is very effective in oxidation reactions, such as the catalytic combustion of methane [24] and chlorinated VOCs (CVOs) [25,26]. The enhanced activities of these Co–Cr–O mixed oxides could be attributed to the Cr-related high-surface acidity and high reducibility of the oxygen species, which are also two crucial parameters in VOCs combustion [27–29].

In this work, a series of Co–Cr–O mixed oxides with different Co/Cr molar ratios were synthesized and tested for the total oxidation of propane. Detailed characterizations were conducted to clarify the structural and surface properties of these catalysts, which were further correlated to their performances. Moreover, kinetic investigation and in-situ spectroscopic studies were performed to interpret the different behaviors and possible reaction pathways on the catalysts, as well as the surface species. It was found that the catalyst properties were strongly dependent on the Co/Cr molar ratio, which consequently influenced the catalytic behaviors profoundly.

2. Experimental

2.1. Catalyst preparation

The Co–Cr–O mixed oxides with different Co/Cr molar ratios were prepared by a sol–gel method. Considering the mixed oxide with a Co/Cr molar ratio of 1:2 as an example, 0.05 mol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.10 mol of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and 0.30 mol of citric acid were dissolved in 50 mL of deionized H_2O . The solution was stirred at 80°C for 6 h to obtain a gel, which was dried at 100°C for 24 h. Finally, the solid substance was calcined at 600°C in static air for 4 h. The resulting catalyst was denoted as 1Co2Cr. Other catalysts were prepared in a similar manner and were denoted as $x\text{Co}y\text{Cr}$, where x/y was the nominal Co/Cr molar ratio in the catalyst. The pure cobalt oxide and chromium oxide were denoted as CoO_x and CrO_x , respectively.

2.2. Catalyst characterizations

The specific surface areas of the catalysts were measured by N_2 absorption at 77 K on a BK200C surface area analyzer. The

catalysts were pretreated under vacuum at 150°C for 4 h. The Brunauer–Emmet–Teller (BET) method was employed to calculate the specific area.

The exact Co and Cr contents in the catalysts were determined by X-ray fluorescence (XRF) spectroscopy using an ARL ADVANT’X Intelli Power 4200 scanning X-ray fluorescence spectrometer. The result was analyzed using a UniQuant non-standard sample quantitative analysis software.

The crystalline structures of the catalysts were determined by X-ray diffraction, which was conducted with a Bruker X-ray diffractometer (XRD, D8 Advance type) using $\text{Cu K}\alpha$ radiation at 40 kV and 40 mA. The scanning 2θ range was 20° – 70° , with a step size of 0.02°s^{-1} . The crystallite sizes and lattice parameters of the catalysts were analyzed using the JADE 6.0 software.

The Raman spectra of the catalysts were collected on a Renishaw Invia confocal microprobe under ambient condition (laser power = 3 mW; dwell time = 30 s; number of scans = 30; resolution = 1 cm^{-1}). The wavelength of the excitation laser was 325 nm. Prior to the measurement, the sample was heated by an infrared lamp (80°C , 15 min) to remove the water in the sample.

The reducibility of the catalyst was measured by the hydrogen–temperature-programmed reduction (H_2 -TPR) technique, which was performed on a home-made apparatus. Forty milligrams of the catalyst was loaded in the reactor and was pretreated at 300°C for 1 h in a flow of 10 vol% O_2 + 90 vol% N_2 (30 mL min^{-1}). After the sample was cooled to room temperature, it was heated in a flow of 5 vol% H_2 + 95 vol% N_2 (30 mL min^{-1}) to 700°C at a ramping rate of $10^\circ\text{C min}^{-1}$. The signal was recorded by a thermal conductivity detector (TCD), and the H_2 consumption was calibrated by the reduction of a known amount of CuO powder.

The surface acidity of the catalyst was measured by ammonia–temperature-programmed desorption (NH_3 -TPD). In a typical measurement, 300 mg of the catalyst was loaded in the home-made reactor and pretreated at 300°C for 1 h in a flow of 10 vol% O_2 + 90 vol% N_2 (30 mL min^{-1}). Subsequently, it was cooled to 100°C and exposed to a flow of pure NH_3 (30 mL min^{-1}) for 1 h. After the catalyst was purged by pure N_2 (30 mL min^{-1}) at 100°C for 30 min, it was heated to 600°C at a ramping rate of $10^\circ\text{C min}^{-1}$. The signal of the desorbed NH_3 was recorded by mass spectrometry (MS, Hiden, QIC-20) at $m/e = 17$.

The oxidation states of the elements in the catalysts were determined by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi). Monochromated Al $K\alpha$ served as the X-ray source (1486.6 eV). The binding energy of each element in the catalyst was corrected by the C 1s line ($E_{\text{C1s}} = 284.6 \text{ eV}$).

The temperature-programmed surface reaction of propane (C_3H_8 -TPSR) was carried out in the home-made apparatus. The catalyst (300 mg) loaded in a quartz tubular reactor was pretreated at 300°C for 1 h in a flow of 10 vol% O_2 + 90 vol% N_2 (30 mL min^{-1}). After the catalyst was cooled to room temperature, it was exposed to a flow of 5 vol% C_3H_8 + 95 vol% N_2 (30 mL min^{-1}) and heated to 600°C at a ramping rate of $10^\circ\text{C min}^{-1}$. The outlet signals of C_3H_8 , CO_2 , and H_2O were recorded by mass spectrometry (MS, Hiden, QIC-20) at $m/e = 27, 44$, and

18, respectively.

The in-situ diffuse reflectance infrared spectroscopy (DRIFTS) of propane oxidation was performed on a Thermal-Fischer Nicolet iS50 FTIR spectrometer equipped with an MCT detector. A certain amount of the catalyst was loaded in a PIKE DRIFT accessory and was pretreated in 10 vol% O₂ + 90 vol% N₂ (30 mL min⁻¹) at 450 °C for 30 min, followed by N₂ purge for another 30 min. Thereafter, it was cooled to room temperature in a N₂ flow (30 mL min⁻¹), and the background spectra were recorded at different temperatures. Afterward, a mixture flow of 0.2 vol% C₃H₈ + 2 vol% O₂ balanced with N₂ (30 mL min⁻¹) was introduced, and the catalyst was heated to 450 °C at a ramping rate of 10 °C min⁻¹. The spectra were collected at certain temperatures, which were subtracted with corresponding backgrounds.

2.3. Catalyst activity testing and kinetic investigation

The performance of the catalysts toward the total oxidation of propane was tested in a fixed-bed micro-reactor. Fifty milligrams of the catalyst (60–80 mesh) was diluted with 50 mg of quartz sand of the same size and loaded in a tubular quartz reactor (i.d. = 6 mm). A thermal couple was placed in the middle of the catalyst bed to monitor the reaction temperature. A gas mixture consisting of 0.2 vol% C₃H₈ and 2 vol% O₂ (balanced by N₂) with a total flow rate of 67 mL min⁻¹ (GHSV = 80000 mL g⁻¹ h⁻¹) was employed. The outlet gas was analyzed using a gas chromatograph (Shimadzu GC-2014) equipped with a flame-ionized detector (FID) and capillary column (DB-WAX, 30 m × 0.25 mm × 0.25 μm). The conversion of propane was calculated using the following equation:

$$X_{\text{C}_3\text{H}_8} (\%) = ([\text{C}_3\text{H}_8]_{\text{in}} - [\text{C}_3\text{H}_8]_{\text{out}}) \times 100 \% / [\text{C}_3\text{H}_8]_{\text{in}}$$

where $X_{\text{C}_3\text{H}_8}$ is the conversion of propane; $[\text{C}_3\text{H}_8]_{\text{in}}$ and $[\text{C}_3\text{H}_8]_{\text{out}}$ are the concentrations of propane in the inlet and outlet, respectively.

The reaction behaviors of the catalysts were also tested under wet reaction conditions, where 2.5 vol% of water vapor was introduced by passing the reactants through a water bubbler at 0 °C.

Kinetic studies of the total oxidation of propane over some

representative catalysts were conducted under differential reaction modes (with propane conversion less than 15%). The absence of mass and heat transfer limitations were verified. For example, the Weisz–Prater criterion (C_{WP}) was used for internal diffusion; the Mears criterion (C_{M}) was used for external diffusion, and the Mears' criterion (C_{M}) was used for heat transfer (see Supporting Information for detailed calculations). The reaction orders of propane and oxygen were measured at propane partial pressures in the range of 0.202–0.505 kPa and oxygen partial pressures in the range of 4.04–9.09 kPa.

3. Results and discussion

3.1. General characterizations of the catalysts

The synthesized catalysts have significantly different specific surface areas, depending on their compositions. As shown in Table 1, the pure CoO_x has a very low surface area (2 m² g⁻¹), and the surface area gradually increases with the addition of Cr in the samples. The 1Co2Cr mixed oxide has the largest surface area (86 m² g⁻¹); however, further addition of Cr results in a decline in the surface area, as the pure CrO_x has a surface area of 27 m² g⁻¹. Furthermore, the actual Co/Cr molar ratios are close to those of the nominal values because the catalysts were prepared by a sol–gel method and no metal species were lost during the procedure.

The crystalline structures of the catalysts were determined by XRD, and the profiles are shown in Fig. 1. The CoO_x and 5Co1Cr catalysts exhibit typical spinel structures of Co₃O₄ (JCPDS No. 42–1467), while the 2Co1Cr catalyst shows a mixture of the spinel Co₃O₄ and Co₂CrO₄ (JCPDS No. 24–0326). Analyses of the lattice parameters further indicate the substitution of Co cations by Cr cations in the spinel Co₃O₄ matrix, as the lattice parameters increase from 0.8082 nm for CoO_x to 0.8101 nm for 2Co1Cr because the ionic radius of the Cr³⁺ cation (0.0615 nm) is larger than that of the Co³⁺ cation (0.0545 nm). For the 1Co1Cr and 1Co2Cr catalysts, only the standard spinel structure of CoCr₂O₄ (JCPDS No. 22–1084) is observed. It should be noted that the Co/Cr molar ratio in the 1Co1Cr sample is inconsistent with the stoichiometric formula of the spinel

Table 1

Specific surface areas, actual Co/Cr molar ratios, crystallite sizes, and lattice parameters of various xCo_yCr catalysts.

Catalyst	A_{BET} /m ² g ⁻¹	Actual Co/Cr molar ratio	Crystallite size /nm	Lattice parameter /nm
CoO _x	2	—	> 100	0.8082/0.8082/0.8082
5Co1Cr	6	4.89/1	36.9	0.8085/0.8085/0.8085
2Co1Cr	15	2.05/1	9.0 ^a 20.7 ^b	0.8101/0.8101/0.8101 ^a 0.8273/0.8273/0.8273 ^b
1Co1Cr	20	0.95/1	22.6	0.8273/0.8273/0.8273
1Co2Cr	86	1/2.13	8.0	0.8327/0.8327/0.8327
1Co5Cr	38	1/4.78	14.8 ^c 15.7 ^d	0.4953/0.4953/1.3574 ^c 0.8331/0.8331/0.8331 ^d
CrO _x	27	—	18.8	0.4960/0.4960/1.3605

^a Spinel Co₃O₄ (JCPDS No. 42–1467); ^b Co₂CrO₄ (JCPDS No. 24–0326);

^c Cr₂O_{2.4} (JCPDS No. 51–0959); ^d spinel CoCr₂O₄ (JCPDS No. 22–1084).

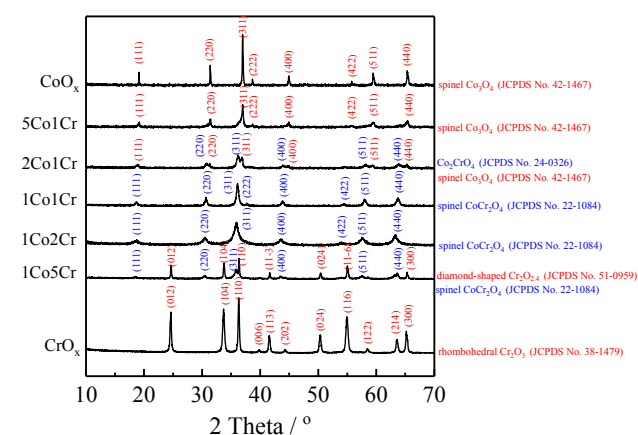


Fig. 1. XRD patterns of various xCo_yCr catalysts.

CoCr₂O₄. Moreover, compared to the case with 1Co2Cr, the diffractions of the 1Co1Cr sample slightly shift toward relatively high angles, indicating the disordering of the spinel structure due to the nonstoichiometry of the Co/Cr molar ratio in the 1Co1Cr mixed oxide [24]. In fact, the formula of a CoCr spinel oxide could be expressed as Co²⁺[Co³⁺_{2-x}Cr³⁺_x]O₄, and in such a structure, Co³⁺ could partially occupy the octahedral sites when Cr³⁺ cations are insufficient. When the content of Cr³⁺ increases, the Cr³⁺ cations could re-occupy the octahedral sites and replace the Co³⁺ cations [30]. This explains the observed CoCr₂O₄ spinel structure in both 1Co1Cr and 1Co2Cr catalysts, which is further verified by the larger lattice parameter of 1Co2Cr (0.8327 nm) than that of 1Co1Cr (0.8273 nm) because of the replacement of the Co³⁺ cations by the Cr³⁺ cations in the octahedral sites. However, the possible formation of the spinel Co₃O₄ oxide in 1Co1Cr cannot be ruled out as the patterns are quite similar. The 1Co5Cr sample consists of a mixture of a CoCr₂O₄ spinel oxide and a diamond-shaped Cr₂O_{2.4} oxide (JCPDS No. 51–0959). Once more, the lattice parameters of the CoCr₂O₄ spinel oxide in the 1Co5Cr catalyst (0.8331 nm) are larger than those in 1Co1Cr and 1Co2Cr, confirming the replacement of the Co³⁺ cations by Cr³⁺ cations [26]. However, the evolution of the Cr₂O_{2.4} oxide suggests a phase segregation with excessive Cr species. The pure CrO_x shows different diffraction characteristics of the rhombohedral Cr₂O₃ oxide (JCPDS No. 38–1479). The crystallite sizes and lattice parameters of the catalyst were analyzed by the JADE software, and the results are summarized in Table 1. It is found that CoO_x has the largest crystallite size (> 100 nm), and the addition of Cr results in a decline in the crystallite size, with the 1Co2Cr having the smallest size (8.0 nm). The changes in the crystallite sizes of the mixed oxides explain the varying surface areas of the samples, and it appears that the Cr–Co interaction helps to inhibit the growth of crystallite, thus increasing the surface area.

The structural properties of the catalysts are further investigated by Raman spectroscopy (Fig. 2). CoO_x and 5Co1Cr show

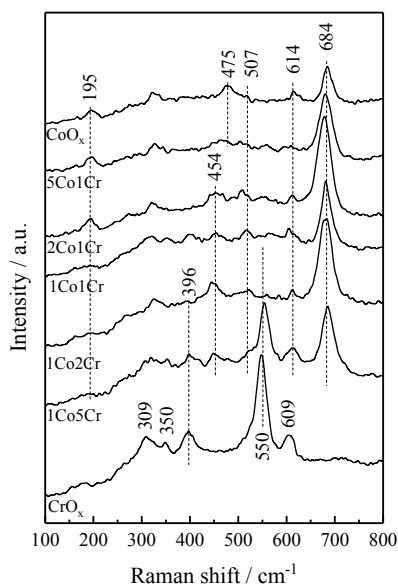


Fig. 2. Raman spectra of various xCoyCr catalysts.

five bands at 195, 475, 507, 614, and 684 cm⁻¹, which are characteristic of the spinel Co₃O₄ oxide corresponding to the F_{2g}, E_g, F_{2g}, F_{2g}, and A_{1g} vibration modes, respectively [31]. For 2Co1Cr, 1Co1Cr, and 1Co2Cr, there are also five bands at 195, 454, 507, 614, and 684 cm⁻¹, which could be respectively assigned to the F_{2g}, E_g, F_{2g}, F_{2g}, and A_{1g} vibration modes of the spinel CoCr₂O₄ oxide [32,33]. Note that 2Co1Cr contains mixed phases of Co₃O₄ and CoCr₂O₄, although the Raman vibrations of these two oxides are similar due to their similar spinel structures. For the 1Co5Cr catalyst, in addition to the bands indicative of the spinel CoCr₂O₄, new bands at 309, 350, 396, and 550 cm⁻¹ are observed, which are assigned to the CrO_x oxide [34]. The phase transformation is completed on the CrO_x oxide, in which only the features of CrO_x are observed. The Raman spectroscopic results are in good agreement with the XRD results (Fig. 1), illustrating the structural change in the oxides depending on the Co/Cr molar ratios.

The catalyst reducibility was determined by the H₂-TPR technique and the profiles are shown in Fig. 3. The CrO_x catalyst only shows a broad and weak reduction peak at 150–300 °C attributed to the reduction of Cr⁶⁺ to Cr³⁺ [35], and its total H₂ consumption is 0.42 mmol g⁻¹. The 1Co5Cr, 1Co2Cr, and 1Co1Cr catalysts show one reduction peak at 200–300 °C and a reduction peak at a high temperature (> 550 °C), which are attributed to the reduction of Cr⁶⁺ to Cr³⁺ [36] and the reduction of Cr³⁺ to lower oxidation states [24] in a CoCr₂O₄ spinel oxide, respectively. The total H₂ consumptions of these catalysts are 0.48, 1.17, and 2.92 mmol g⁻¹. For the Co-rich catalysts (those with a Co/Cr ratio higher than 1), the reduction profiles change considerably. The 2Co1Cr and 5Co1Cr catalysts both show a weak reduction peak at a low temperature (< 300 °C) and an intensive and overlapped peak at 300–550 °C. The peak centered at 380 °C is due to the reduction of Co₃O₄ to CoO [38], and the peak centered at 500 °C is due to the reduction of CoO to metallic Co [14,37]. The H₂ consumptions of the two catalysts are 7.68 and 13.42 mmol g⁻¹. The CoO_x catalyst showed an asymmetric reduction peak centered at 430 °C, which could be attributed to the combined reduction of Co₃O₄ to CoO and sequentially to metallic Co [38,39], and its H₂ consumption is 17.87 mmol g⁻¹. Moreover, the reduction of the Co³⁺ species in

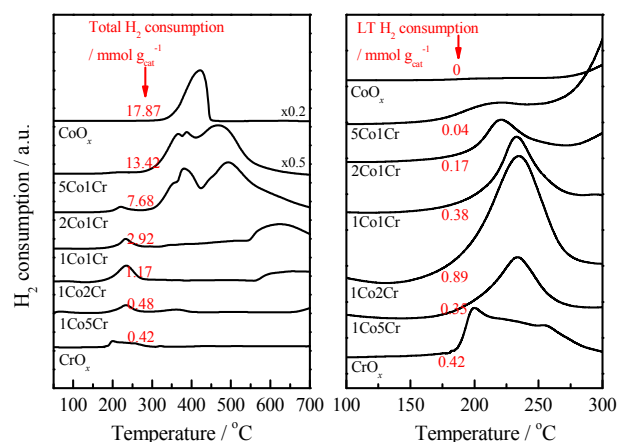


Fig. 3. H₂-TPR profiles of various xCoyCr catalysts.

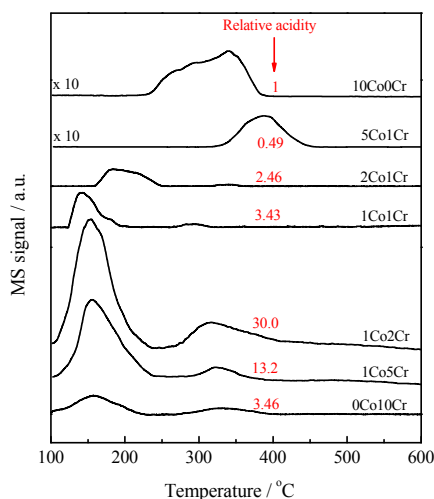


Fig. 4. NH_3 -TPD profiles of various $x\text{Co/Cr}$ catalysts.

the 2Co1Cr and 5Co1Cr catalysts to Co^{2+} is easier than that in the CoO_x catalyst, while that of Co^{2+} to metallic Co is more difficult. This is likely due to the strong interaction between cobalt oxide and chromium oxide [24]. The right panel of Fig. 3 presents the TPR profiles of the catalyst at a low-temperature (LT) range (100–300 °C) because the LT reducibility reflects the mobility of the oxygen species in the catalyst, which is crucial in the oxidation reaction, particularly at low reaction temperatures [40]. Unlike the total H_2 consumption, the LT H_2 consumption of the catalysts follow the order of 1Co2Cr (0.89 mmol g^{-1}) > CrO_x (0.42 mmol g^{-1}) > 1Co1Cr (0.38 mmol g^{-1}) > 1Co5Cr (0.35 mmol g^{-1}) > 2Co1Cr (0.17 mmol g^{-1}) > 5Co1Cr (0.04 mmol g^{-1}) > CoO_x (0 mmol g^{-1}).

Fig. 4 shows the NH_3 -TPD profiles of the catalysts. The CrO_x , 1Co5Cr, 1Co2Cr, 1Co1Cr, and 2Co1Cr catalysts show similar profiles, although their peak areas are very different. The five catalysts show NH_3 desorption peaks at 100–230 °C, indicating the presence of weak acid sites in these catalysts. In addition, relatively weak desorption peaks at 300–400 °C are observed, suggesting the presence of surface acid sites with medium strength. In contrast, the 5Co1Cr and CoO_x catalysts give only

very weak desorption peaks at 250–450 °C, indicating the presence of medium acid sites and the absence of weak acid sites in these two catalysts. The total numbers of surface acid sites in the catalysts differ considerably. The CoO_x and 5Co1Cr catalysts have a very low relative surface acidity (0.49–1); the 2Co1Cr, 1Co1Cr, and oCo10Cr catalysts have medium surface acidities (2.46–3.46), while 1Co2Cr and 1Co5Cr have a high surface acidity (13.2–30.0). The significantly different values are related to the crystalline structure, crystallite size, and surface area of the catalysts. It was reported that CrO_x has a high surface acidity due to the presence of high-valent Cr^{6+} species, while CoO_x is less acidic [25]. Notably, the 1Co2Cr mixed oxide has the highest surface acidity due to its spinel structure [24]. Moreover, it is found that the surface acidity of the catalysts generally follows the order of the surface area, which is understandable because the relatively small crystallite size of the oxide particles (high surface area) leads to an increased number of defects on the surface and more exposed cations, such as Cr^{6+} and Co^{3+} . This explains the observed highest surface acidity on the 1Co2Cr sample as it has the highest surface area (86 $\text{m}^2 \text{g}^{-1}$, Table 1).

The oxidation states of the Co, Cr, and O species in the catalysts were determined by XPS (Fig. 5). The Co $2p_{3/2}$ spectra (Fig. 5(a)) could be resolved to three components at binding energies (BEs) of 780.3, 782.0, and 788.1 eV, assigned to Co^{2+} , Co^{3+} , and the satellite peak of Co^{2+} , respectively [41]. These components gradually shift toward high BEs with increasing Cr content in the catalyst (up to 0.5 eV), suggesting the charge transfer from Co to Cr species. The Cr $2p_{3/2}$ spectra (Fig. 5(b)) could be deconvoluted to three components at BEs of 575.3, 576.6, and 578.5 eV, which are assigned to $\text{Cr}(\text{OH})_3$ or Cr_2O_3 , Cr^{3+} (occupied octahedral sites) and Cr^{6+} [25,26], respectively. The Cr $2p_{3/2}$ peaks gradually shift toward low BEs with increasing contents of Co in the catalyst (up to 0.5 eV). This observation is in good agreement with Fig. 5(a), further suggesting that the Co–Cr interaction results in the charge transfer between the Co and Cr species. For the O 1s spectra, Fig. 5(c) shows that all the catalysts contain a major component at BEs in the range of 529.8–530.2 eV, assigned to the lattice oxygen (labeled as “ O_{latt} ”), and a minor component at a BE of 531.6 eV

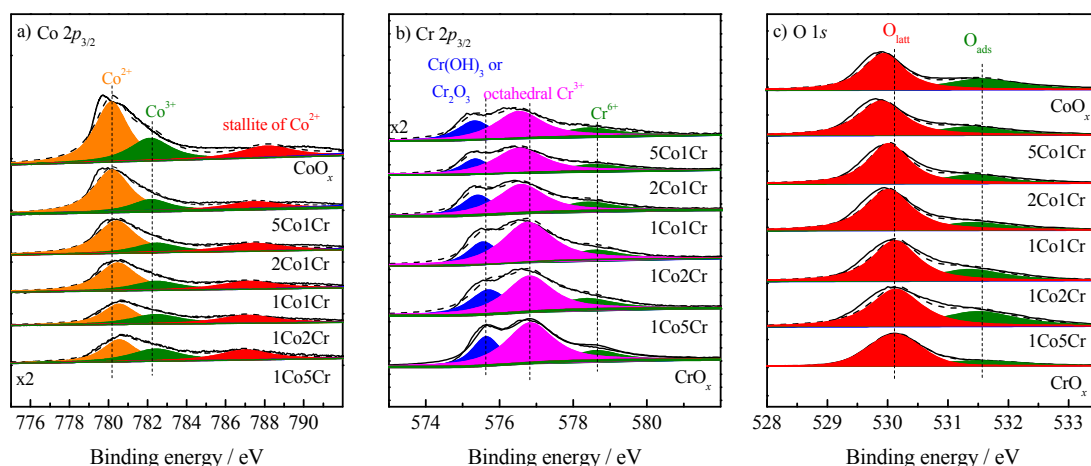
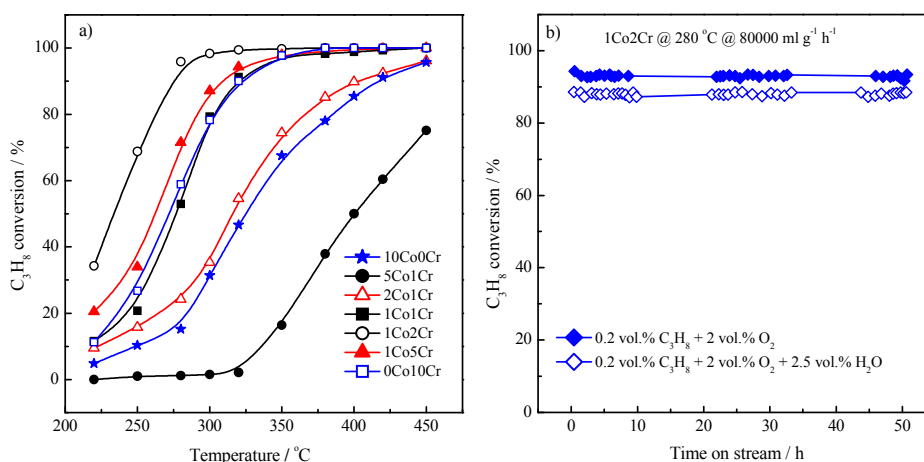


Fig. 5. XPS spectra of Co 2p (a), Cr 2p (b), and O 1s (c) in various $x\text{Co/Cr}$ catalysts.

Table 2XPS analysis of the Cr, Co, and O species in various xCo_yCr catalysts.

Catalyst	Surface concentration / %						Surface molar ratio		
	Co ²⁺	Co ³⁺	Cr ³⁺	Cr ⁶⁺	O _{latt}	O _{ads}	Co ³⁺ /Co ²⁺	Cr ⁶⁺ /Cr ³⁺	O _{ads} / O _{latt}
CoO _x	68.1	31.9	—	—	65.9	34.1	0.47	—	0.52
5Co1Cr	77.6	22.4	81.6	18.4	74.1	25.9	0.29	0.23	0.35
2Co1Cr	75.3	24.7	82.5	17.6	75.6	24.4	0.33	0.21	0.32
1Co1Cr	71.5	28.5	83.8	16.2	70.0	30.0	0.40	0.19	0.43
1Co2Cr	58.6	41.4	85.3	14.7	77.8	22.2	0.70	0.17	0.29
1Co5Cr	54.8	45.2	85.9	14.1	62.7	37.3	0.83	0.16	0.59
CrO _x	—	—	85.6	14.4	80.3	19.7	—	0.17	0.25

**Fig. 6.** (a) Propane conversions of various xCoCr catalysts at different temperatures; (b) catalyst stability of 1Co2Cr under dry and wet reaction conditions.

indicative of the surface oxygen or hydroxyl group (labeled as “O_{ads}”) [42]. Note that the position of the O_{latt} component in the catalysts also shifts toward lower BEs with increasing Co content, which reflects the different properties of the mixed oxides. The surface concentrations of various species are summarized in Table 2. The results show that the co-presence of Co and Cr in the mixed oxides results in changes in the surface contents of the Co and Cr species. The Co³⁺/Co²⁺ ratio generally increases with increasing Cr content in the catalyst (from 0.29 for the 5Co1Cr to 0.83 for the 1Co5Cr), while the Cr⁶⁺/Cr³⁺ ratio gradually declines (from 0.23 for 5Co1Cr to 0.16 for 1Co5Cr), which further suggests the Co–Cr interaction and charge transfer between these two species.

3.2. Catalytic activities of the catalysts

The catalytic behaviors of the catalysts at elevated reaction temperatures are shown in Fig. 6(a). The activities follow the order of 1Co2Cr > 1Co5Cr > CrO_x > 1Co1Cr > 2Co1Cr > CoO_x > 5Co1Cr. Table 3 summarizes the detailed results of the catalysts, which shows that the 1Co2Cr catalyst affords the highest propane conversion at 250 °C (68.8%), with the highest mass-specific reaction rate of $1.38 \times 10^{-6} \text{ mol g}^{-1} \text{ s}^{-1}$. However, if the mass reaction rates are normalized based on the surface areas of the catalysts, it is found that the catalysts give similar areal reaction rates of approximately $1.6\text{--}2.1 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1}$ with the exception of those on CoO_x ($10.3 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1}$)

and 5Co1Cr ($0.2 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1}$). The large deviations on the latter two catalysts might be due to the large errors in the measurements of the surface areas of these two catalysts as the values are very low. Fig. 6(b) shows the stability of the representative 1Co2Cr catalyst under dry (C₃H₈ + O₂) and wet (C₃H₈ + O₂ + H₂O) conditions at 280 °C. The catalyst exhibits good stability in a 50-h reaction, under either dry or wet condition, although the activity is slightly suppressed (with the propane conversion declining by ca. 6%) in the presence of 2.5 vol% in the feedstock. The inhibiting role of water vapor is usually due to the competitive adsorption of water and the reactants on the catalytic sites, which has been reported in the total oxidation of methane over CoO_x–CrO_x mixed oxides [24] and Co₃O₄/CeO₂ catalysts [43].

The findings in the current work indicate that the Co–Cr

Table 3

Summary of the catalytic performance of the catalysts at 250 °C.

Catalyst	Propane conversion / %	Specific reaction rate	
		$/ \times 10^{-6} \text{ mol g}^{-1} \text{ s}^{-1}$	$/ \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1}$
CoO _x	10.3	0.21	10.3
5Co1Cr	1.0	0.01	0.2
2Co1Cr	15.7	0.32	2.1
1Co1Cr	20.7	0.42	2.1
1Co2Cr	68.8	1.38	1.6
1Co5Cr	33.9	0.68	1.8
CrO _x	26.7	0.54	2.0

mixed oxides are effective for the total oxidation of propane. The highest reaction rate is obtained on 1Co2Cr (1.38×10^{-6} mol g⁻¹ s⁻¹ at 250 °C), which is comparable to those reported in the literature. For example, at 250 °C, it was reported that a NiCeO_x catalyst gave a reaction rate of 0.11×10^{-6} mol g⁻¹ s⁻¹ [17]; a FeO_x catalyst gave a reaction rate of 0.05×10^{-6} mol g⁻¹ s⁻¹ [20]; a CoO_x catalyst gave a reaction rate of 1.23×10^{-6} mol g⁻¹ s⁻¹ [21]; a Ni_{0.27}Co_{2.73}O₄ catalyst gave a reaction rate of 5.58×10^{-6} mol g⁻¹ s⁻¹ [16]; and a Co1Ce1 catalyst gave a reaction rate of 4.46×10^{-6} mol g⁻¹ s⁻¹ [42]. More detailed comparisons are summarized in Table S1.

It is well documented in literature that for propane combustion, the surface acidity and reducibility of the catalyst are two crucial parameters governing the catalytic performance. The acidic sites in the catalyst are believed to provide adsorption centers for the propane molecules [27] and/or activate the propane molecule by cleaving the C–H bond [44], which has been verified over the Pt catalysts supported on acidic zeolites, such as KL, HY, ZSM–5, and beta zeolites [29]. Garetto et al. [29] found that the supported Pt/Zeolites catalysts were more active than the Pt/Al₂O₃ catalysts, owing to the comparatively high propane uptake related to the high surface acidity of the zeolite supports. Conversely, the reducibility of the catalyst is related to the adsorption and/or activation of oxygen species, which is an essential process during the oxidation reaction [14]. Based on the NH₃-TPD (Fig. 4) and H₂-TPR (Fig. 3) results, in the current work, the influences of these two parameters on the catalytic behaviors of various catalysts are demonstrated in Fig. 7. Evidently, the reaction rate increases with as both the surface acidity and LT-H₂ consumption increase, suggesting the synergistic effects of the two parameters on the catalytic performance. Therefore, the best activity on 1Co2Cr is owing to its highest surface acidity and highest LT-H₂ consumption. It is worthwhile to discuss the structure of the 1Co2Cr catalyst, which is a spinel-type cobalt chromite oxide (CoCr₂O₄), as shown in Fig. 1. In the CoCr₂O₄ structure, Co and Cr cations are confined in a solid matrix, in which the high-spin divalent Co²⁺ cations mostly occupy the tetrahedral sites, while

the low-spin trivalent Cr³⁺ cations occupy the octahedral sites [45]. For the spinel-type oxides (AB₂O₄) in catalytic reactions, the octahedral B-site cations are the active sites because these cations are exposed at the surface, while the tetrahedral A-site cations are usually inactive [25]. The CoCr₂O₄ spinel oxide has been widely applied in the catalytic combustion of VOCs (including chlorinated-VOCs, CVOCs), and its excellent performance is attributed to the presence of B-site Cr species (Cr³⁺ or Cr⁶⁺) in the oxide [25,46,47]. Chen et al. [24] prepared a series of Co–Cr–O mixed oxides for methane combustion, and they found that the catalyst with a Co/Cr molar ratio of 1:2 showed the best performance due to its spinel structure and the presence of high-valent Cr⁶⁺ species, which enhanced the adsorption of chemisorbed oxygen species. Another important issue that should be addressed is the catalyst surface area. Although the mixed oxides were prepared under identical conditions, the surface areas change from very low (2 m² g⁻¹ for the CoO_x) to high (86 m² g⁻¹ for the 1Co2Cr), which strongly depends on the element compositions. The 2Co1Cr, 1Co1Cr, 1Co2Cr, and 1Co5Cr catalysts all contain the spinel CoCr₂O₄ oxide, although their surface areas vary from 15 to 86 m² g⁻¹. Generally, oxides with relatively small crystallite sizes (high surface areas) contain more defect sites than the bulk oxides. This leads to easy adsorption of oxygen species and thus high reducibility. The different surface areas of the above-mentioned catalysts account for the observed overall mass reaction rates, as they give similar areal reaction rates (c. a. 2.0×10^{-8} mol m⁻² s⁻¹). Moreover, it was reported that Co₃O₄ oxides are effective for propane combustion [15,18]; however, CoO_x and 5Co1Cr are less active in the current work, probably due to their very low surface areas and consequently low surface acidity (Fig. 4) and poor redox properties (Fig. 3).

3.3. C₃H₈-TPSR and kinetic investigation

To further investigate the different behaviors of the catalysts, C₃H₈-TPSR experiments were conducted on the three samples (1Co5Cr, 1Co2Cr, and 2Co1Cr) representing high, medium, and low reaction rates. As shown in Fig. 8(a), the 1Co5Cr catalyst shows consumption of C₃H₈ (a negative peak) at 480 °C, accompanied by a simultaneous appearance of a characteristic CO₂ signal. For the 1Co2Cr catalyst (Fig. 8(b)), distinct consumption of C₃H₈ is observed at about 190 °C, along with the formation of H₂O and CO₂. In addition, much less intense consumption of C₃H₈ is detected at 536 °C. For the 2Co1Cr catalyst, Fig. 8(c) shows the C₃H₈ consumption and CO₂ formation at 510 °C. These profiles reflect different behaviors of the catalysts. Since there is no O₂ feed during the process, the formation of CO₂ on the catalyst is likely due to the reaction between propane and the surface oxygen (or lattice oxygen) species. Moreover, the finding on 1Co2Cr suggests that there are two different oxygen species involved in the reaction, and the formation of CO₂ at ca. 200 °C might explain the relatively high activity on this catalyst, particularly at a low-temperature region. However, the nature of the oxygen species cannot be explicated at present and will be further discussed based on the kinetic results.

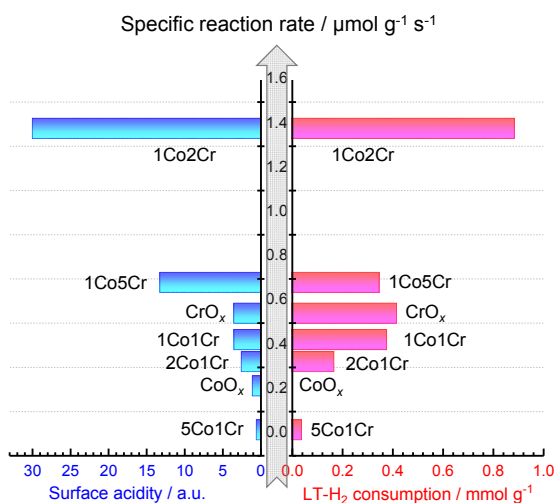


Fig. 7. Influences of the surface acidity and LT-reducibility on the reaction rates of the catalysts.

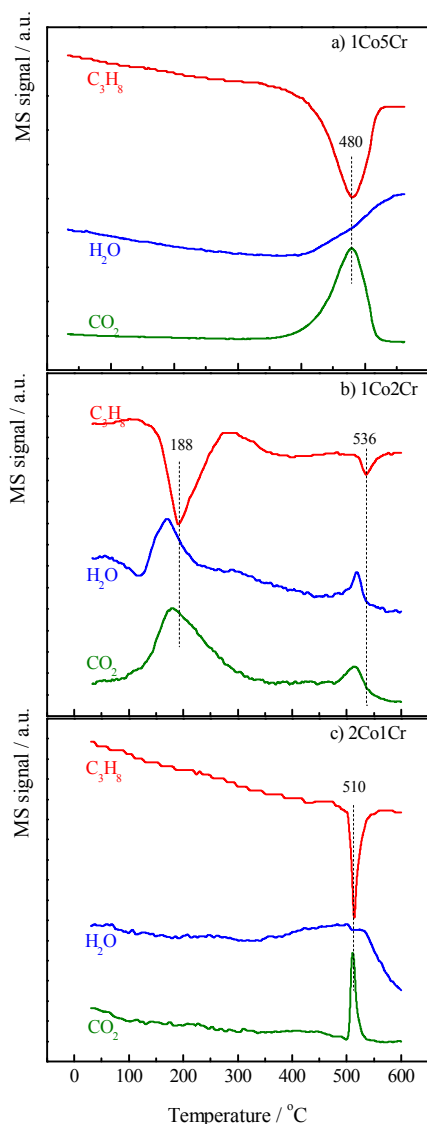


Fig. 8. C_3H_8 -TPSR profiles of the 1Co5Cr (a), 1Co2Cr (b), and 2Co1Cr (c) catalysts.

A kinetic study was also conducted on the 1Co5Cr, 1Co2Cr, and 2Co1Cr catalysts to gain some mechanistic insights. Under differential reaction mode (detailed results are summarized in Table S2), Fig. 9 shows that the reaction rate increases with increasing partial pressures of both C_3H_8 (Fig. 9(a)) and O_2 (Fig. 9(b)). By linear regression of the data in Table S2, the reaction orders of C_3H_8 and O_2 , as well as the apparent rate constant could be deduced, which are summarized in Table 4. Thus, the power-law rate expressions for the catalysts are $r = 7.32 \times 10^{-8} [\text{C}_3\text{H}_8]^{0.77} [\text{O}_2]^{0.98}$ for 2Co1Cr; $r = 42.60 \times 10^{-8} [\text{C}_3\text{H}_8]^{0.58} [\text{O}_2]^{0.34}$ for 1Co2Cr; $r = 9.49 \times 10^{-8} [\text{C}_3\text{H}_8]^{0.66} [\text{O}_2]^{1.30}$ for 1Co5Cr. Firstly, the apparent rate constant follows the order of 1Co2Cr (42.60×10^{-8}) $\gg$ 1Co5Cr (9.49×10^{-8}) $>$ 2Co1Cr (7.32×10^{-8}), suggesting the highest intrinsic activity of the 1Co2Cr catalyst. This trend fits well with that of the overall activities (Table 3). Secondly, the reaction order of C_3H_8 follows the order of 1Co2Cr (0.58 ± 0.03) $<$ 1Co5Cr (0.66 ± 0.05) $<$ 2Co1Cr (0.77 ± 0.02),

indicating that the C_3H_8 surface coverages on these catalysts follow an opposite trend (highest propane coverage on 1Co2Cr and lowest coverage on 2Co1Cr). This finding is probably related to the different surface acidity of the catalysts, as the surface acid sites are the adsorption centers for the C_3H_8 molecules [44]. The NH_3 -TPD results (Fig. 4) clearly show that 1Co2Cr has the highest surface acidity; therefore, it provides the most abundant sites for C_3H_8 adsorption. Thirdly, the reaction order of O_2 follows the order of 1Co2Cr (0.34 ± 0.05) $\ll$ 2Co1Cr (0.98 ± 0.16) $<$ 1Co5Cr (1.30 ± 0.11), implying that the adsorption of the oxygen molecules on 1Co2Cr is quite strong, while those on 2Co1Cr and 1Co5Cr are rather weak. It should be noted that the XPS results (Fig. 5(c)) reveal the presence of surface oxygen species on all the catalysts, which seems inconsistent with the hard adsorption of O_2 on the 2Co1Cr and 1Co5Cr catalysts. The discrepancy may lie in the different reaction conditions of the measurements. Note that the kinetic study was conducted at a relatively high temperature (245 °C, Table S2), which is favorable for the desorption of oxygen. Moreover, the different reaction orders of O_2 on the catalysts could explain the findings of the C_3H_8 -TPSR results (Fig. 8). Since the formation of CO_2 is observed at a very high temperature (ca. 500 °C) on the 1Co5Cr and 2Co1Cr catalysts (Figs. 8(a) and (c)) and oxygen molecules hardly adsorb on these two catalysts (reaction order of 1, Table 4), it could be deduced that the oxygen species on the catalysts are likely lattice oxygen instead of the adsorbed surface oxygen species. In contrast, the 1Co2Cr catalyst induces CO_2 formation at relatively low temperatures (ca. 200 °C, Fig. 8(b)) and O_2 molecules could readily adsorb on its surface; this low-temperature CO_2 formation could be due to the reaction between C_3H_8 and adsorbed oxygen species rather than the lattice oxygen. The obtained reaction orders of C_3H_8 (0.58 ± 0.03) and O_2 (0.34 ± 0.05) on the 1Co2Cr catalyst are similar to those reported on the NiCeO_x mixed oxides, in which the reaction orders of C_3H_8 were 0.42–0.57 and those of O_2 were 0.57–0.58 [17]. Additionally, Heynderickx et al. [48] reported C_3H_8 reaction orders of 0.21–0.27 and O_2 reaction orders of 0.22–0.25 over a $\text{CuO-CeO}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst. Furthermore, the parity plots and residual analyses (Fig. S1) show that the experimental values are well consistent with the theoretical values, thereby verifying the validity of the derived kinetic parameters. The calculated apparent activation energies for the 2Co1Cr, 1Co2Cr, and 1Co5Cr catalysts are 161.3 ± 12.5 , 128.5 ± 11.6 , and 161.3 ± 12.7 kJ mol $^{-1}$, respectively. These values are comparable to those reported for the NiCeO_x catalysts (99.1–113.4 kJ mol $^{-1}$) [17], although they are higher than those reported for the Ni-doped Co_3O_4 (32.5–83.8 kJ mol $^{-1}$) [16], Ni- and Co-doped ferrite catalysts (15.8–39.6 kJ mol $^{-1}$) [49], and $\text{Co}_3\text{O}_4/\text{ZSM-5}$ catalysts (62.8–104.0 kJ mol $^{-1}$) [14].

The mechanisms of propane combustion over transition metal oxides have been investigated in the literature. For example, very detailed kinetic modeling has been performed on $\text{VO}_x\text{-TiO}_2/\text{SiO}_2$ [50] and $\text{CuO-CeO}_2/\gamma\text{-Al}_2\text{O}_3$ catalysts [48,51]. Thybaut and co-workers concluded that on the $\text{VO}_x\text{-TiO}_2/\text{SiO}_2$ catalysts, the propane combustion follows a Mars–van Krevelen (MvK) mechanism involving one active site in the reduction and reoxidation step [50], while on the $\text{CuO-CeO}_2/\gamma\text{-Al}_2\text{O}_3$ cat-

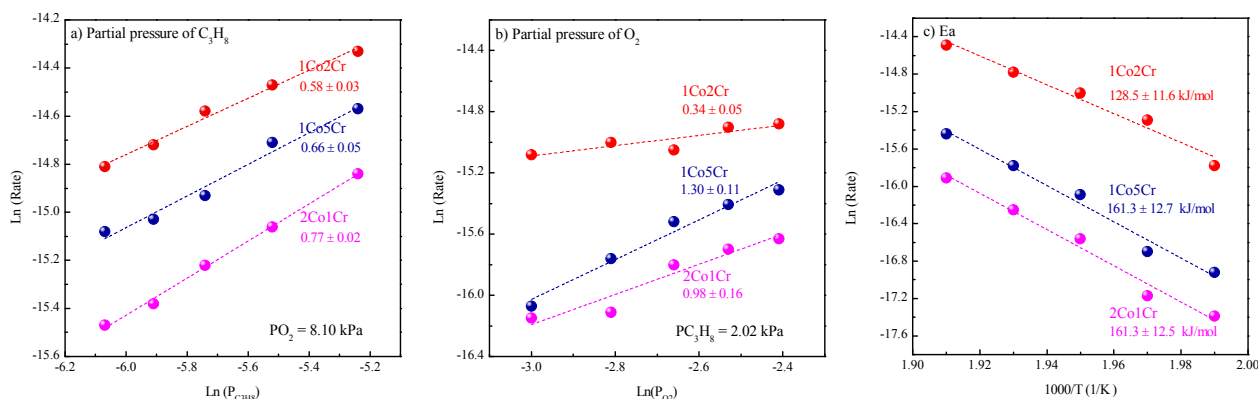
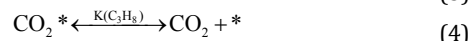
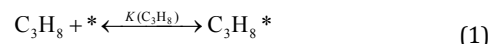


Fig. 9. Dependence of the reaction rates on the partial pressures of propane (a) and oxygen (b); (c) Arrhenius plots of the 2Co1Cr, 1Co2Cr, and 1Co5Cr catalysts.

alyst, the reaction follows a Langmuir–Hinshelwood (LH) mechanism involving the surface reaction between the adsorbed propane and dissociatively adsorbed oxygen species as the rate-determining step (RDS) [48]. Although the MvK mechanism (redox mechanism) is generally employed to explain the catalytic behaviors of various transition metal oxides [16,50], such mechanism appear to not be applicable in the current work. One evidence is that the C₃H₈–TPSR results (Fig. 8) over the employed catalysts clearly show the formation of CO₂ only at very high temperatures (ca. 500 °C) due to the reaction of C₃H₈ and lattice oxygen on the catalysts, which cannot explain the observed low temperature activities of the catalysts (Fig. 6) if the lattice oxygen is the active species in the reaction. Besides, if the reaction follows the MvK mechanism, one distinct feature in the kinetics is that the reaction order of O₂ would be near zero because the gaseous O₂ is not directly involved in the reaction (the role of gaseous O₂ is to fill the surface oxygen vacancy on the catalyst surface). However, our kinetic results reveal that the reaction orders of O₂ on the three catalysts are higher than zero (in the cases of 2Co1Cr and 1Co5Cr, the orders are close to 1), which unambiguously indicate that the reaction pathways are different from the MvK mechanism. In the current work, the three catalysts employed in the kinetic studies all have a C₃H₈ reaction order of 0.58–0.66, indicating the adsorption of propane molecules on the catalyst surface. However, the reaction order of O₂ for 1Co2Cr is 0.34, while those for 2Co1Cr and 1Co5Cr are close to 1, which suggests that oxygen molecules could adsorb on 1Co2Cr but hardly on 2Co1Cr and 1Co5Cr. Considering that the apparent activation energies of the three catalysts are similar (128.5–161.3 kJ mol^{−1}), it is likely that the reaction routes on

the catalysts are the same. It is reasonable to assume that the reaction on the catalysts follows a LH model, although the adsorption capability of propane and oxygen on the catalysts are quite different. Therefore, the reaction routes could be described as follows, which is similar to that reported in the literature [48].



The reaction routes mainly include the following: (1) propane and oxygen adsorb non-competitively on different active sites (propane, likely on acidic Cr sites (*)) and oxygen dissociation on Co sites (#), (Eqs. (1) and (2)); (2) the two adsorbed species react to cleave the first C–H bond in the propane molecule, which is the RDS, and the fast sequential oxidation to form CO₂ and H₂O (Eq. (3)); (3) the desorption of CO₂ and H₂O from the catalyst surface (Eqs. (4) and (5)).

3.4. DRIFTS investigation

In-situ DRIFT spectroscopic studies were also performed, attempting to obtain some information on the surface species or reaction intermediates during the reaction. The CrO_x and 1Co2Cr catalysts were chosen, and the results are illustrated in Fig. 10. For the CrO_x catalyst (Fig. 10(a)), several bands at 3100–3500, 2800–3000, and 2300–2400 cm^{−1} are observed, assigned to the surface hydroxyl groups or gaseous water, δ_{C–H}, in the gaseous C₃H₈ and gaseous CO₂, respectively. The band intensity of the gaseous C₃H₈ species (2970 cm^{−1}) is relatively constant at 50–250 °C, although it gradually declines at higher temperatures, which is due to its consumption owing to the reaction between C₃H₈ and O₂. Accordingly, the formation of CO₂ on the catalyst is initiated at 200 °C, and the intensity (bands at 2300 and 2380 cm^{−1}) grows at elevated temperatures. In the region of 1000–1800 cm^{−1}, various surface carbonate species are observed. These species mainly include bi-

Table 4

Kinetic parameters on the 2Co1Cr, 1Co2Cr, and 1Co5Cr catalysts.

$r = k_{\text{app}} [\text{C}_3\text{H}_8]^a [\text{O}_2]^b$				
Catalyst	$k_{\text{app}} / \times 10^{-8}$	A	b	E _a / kJ mol ^{−1}
2Co1Cr	7.32	0.77 ± 0.02	0.98 ± 0.16	161.3 ± 12.5
1Co2Cr	42.60	0.58 ± 0.03	0.34 ± 0.05	128.5 ± 11.6
1Co5Cr	9.49	0.66 ± 0.05	1.30 ± 0.11	161.3 ± 12.7

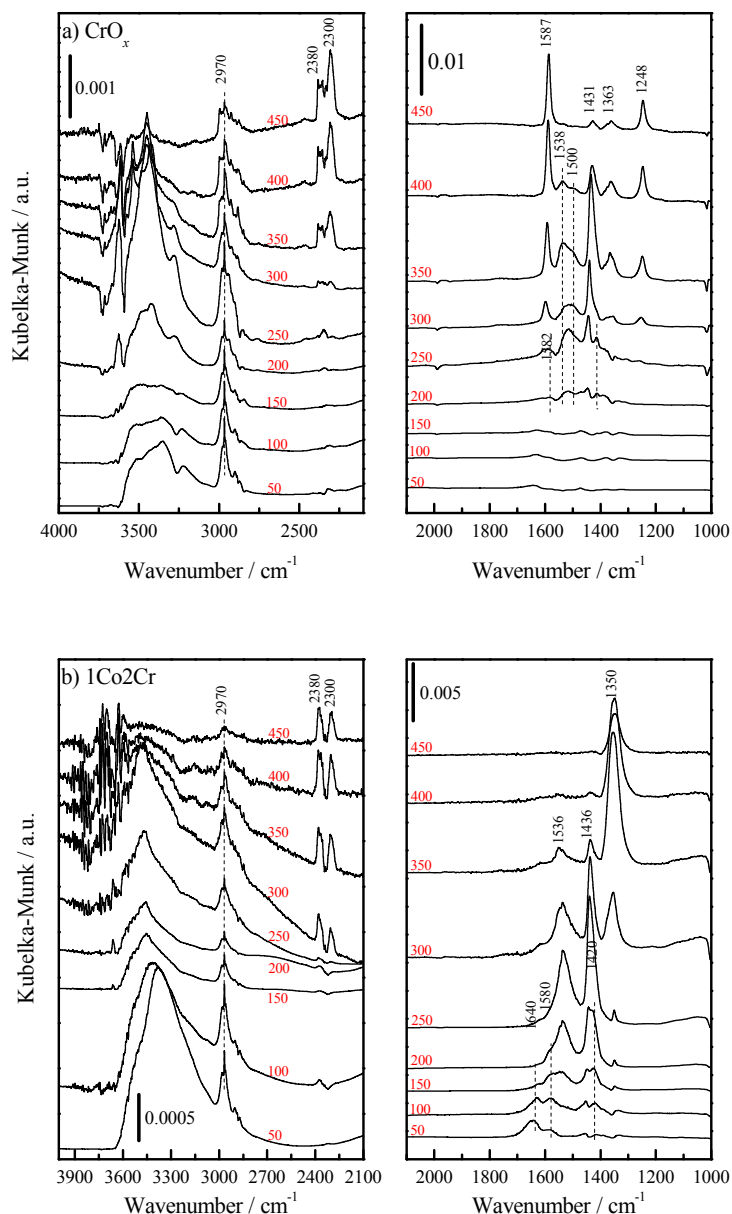


Fig. 10. In-situ DRIFT spectra of propane oxidation over the CrO_x (a) and $1\text{Co}_2\text{Cr}$ (b) catalysts at elevated temperatures.

dentate carbonate (1587 cm^{-1}), polydentate carbonate (1538 , 1500 , 1431 , and 1363 cm^{-1}), and bicarbonate (1248 cm^{-1}) [52,53], which emerge from $200\text{ }^\circ\text{C}$. It is also found that the intensities of the bidentate carbonate and bicarbonate continuously grow with increasing temperature. However, that of the polydentate carbonate reaches the maximum at $350\text{ }^\circ\text{C}$ and then declines up to $450\text{ }^\circ\text{C}$, indicating the decomposition of such species at high temperatures.

For the $1\text{Co}_2\text{Cr}$ catalyst (Fig. 10(b)), the band evolutions at $2100\text{--}3800\text{ cm}^{-1}$ are similar to those for CrO_x (Fig. 10(a)), which illustrates the consumption of C_3H_8 and the formation of CO_2 (starts from $200\text{ }^\circ\text{C}$). However, in the $1000\text{--}1800\text{ cm}^{-1}$ region, the bands are very different from those for CrO_x . The intensity of the bidentate carbonate (1580 cm^{-1}) is very weak

and quickly decomposes up to $350\text{ }^\circ\text{C}$. The dominant surface carbonate is polydentate (1536 , 1436 , and 1350 cm^{-1}), which could accumulate at low temperatures (up to $250\text{ }^\circ\text{C}$) and further decompose at elevated temperatures (up to $450\text{ }^\circ\text{C}$). The presence of polydentate carbonate on the $1\text{Co}_2\text{Cr}$ catalyst as the major species might be due to the interactions between the surface unidentate or bidentate carbonate owing to the abundant surface sites of $1\text{Co}_2\text{Cr}$ attributed to its high surface area and high surface acidity.

Therefore, the in-situ DRIFT spectra allow us to differentiate the surface species on various catalysts during the reaction, which are closely related to their surface properties. Moreover, the DRIFTS results reveal that the main surface species are various carbonates, which implies that these species might be

the reaction intermediates and could be further decomposed to the final product (CO_2). However, other species such as C_3H_7^* (as described in the reaction mechanism, Eq. (3)) are not observed, which requires a more detailed spectroscopic investigation in the future.

4. Conclusions

In this work, Co–Cr–O mixed oxides with different Co/Cr molar ratios are tested for the total oxidation of propane. The reaction behaviors are closely related to the surface properties of the mixed oxides. The 1Co2Cr catalyst with a spinel structure exhibits the best performance because it has the highest surface acidity and best low-temperature reducibility, which are two crucial parameters governing the performance. The detailed kinetic investigations on some catalysts further verify that the surface acid sites may provide adsorption/activation centers for C_3H_8 molecules, while the adsorption/activation of oxygen molecules is related to the low-temperature reducibility of the catalyst. Moreover, in-situ DRIFTS results reveal the main surface species (surface carbonates) during the reaction.

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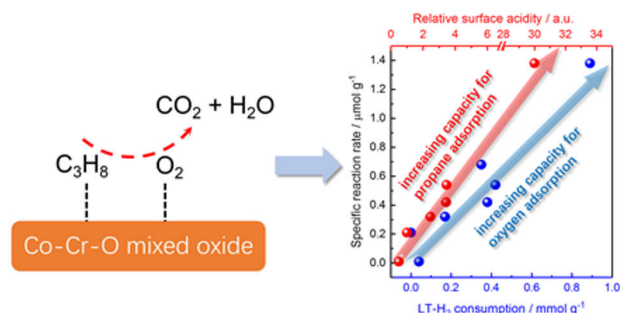
Graphical Abstract

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Co–Cr–O mixed oxides for low-temperature total oxidation of propane: Structural effects, kinetics, and spectroscopic investigation

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The performance of the Co–Cr–O mixed oxides for propane combustion is related to their surface acidity and low-temperature reducibility, which account for the adsorption of propane and the activation of oxygen, respectively.



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Co-Cr-O复合氧化物上丙烷低温完全氧化：结构效应、反应动力学和原位光谱研究

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摘要: 低碳烷烃是一类主要的挥发性有机污染物(VOCs), 广泛生成于汽车尾气以及各种工业过程如煤处理、石油精炼以及天然气处理等。随着对环保要求的日益提高, 对高效VOCs消除技术的需求愈加迫切。催化完全氧化(催化燃烧)技术具有起燃温度低、能耗低、净化效果好(无二次污染)等优点, 因而极具应用潜力。对于低碳烷烃的催化燃烧, 贵金属催化剂如Pt和Pd等具有很高的反应活性, 但存在价格昂贵并易中毒等缺陷限制了其商业应用。另一方面, 过渡金属氧化物由于其价格低廉、抗中毒性能优异及热稳定性好等特点受到广泛关注。Cu, Mn, Co, Fe等氧化物都具有良好的催化活性, 其中Co氧化物由于其在丙烷催化燃烧中的高活性受到关注。而在Co氧化物中添加第二金属更能促进其反应性能。因此本文制备了一系列不同Co/Cr比例的复合氧化物用于丙烷催化燃烧, 考察了催化剂结构和表面性质对其反应行为的影响, 并通过反应动力学和原位光谱技术对反应机理进行了探索。

实验结果表明, 随着Co/Cr比例的变化, 催化剂的晶相结构、颗粒尺寸、比表面积、表面酸性以及氧化还原性等特性均发生了明显变化, 进而影响了其反应行为。当Co/Cr比例为1/2时(1Co2Cr), 催化剂为尖晶石结构并具有最大的比表面积。该催化剂上具有最高的反应活性(250 °C时反应速率为 $1.38 \mu\text{mol g}^{-1} \text{s}^{-1}$), 可归因于其最高的表面酸性和低温氧化还原性能的协同作用。反应动力学结果表明, 1Co2Cr催化剂上丙烷和氧气的反应级数分别为 0.58 ± 0.03 和 0.34 ± 0.05 , 低于2Co1Cr(分别为 0.77 ± 0.02 和 0.98 ± 0.16)和1Co5Cr(分别为 0.66 ± 0.05 和 1.30 ± 0.11), 表明1122Cr催化剂相比后二者具有更高的丙烷和氧气表面覆盖度, 得益于其更高的表面酸性和更好的低温氧化还原性能。此外, 原位红外光谱表明, 在反应过程中, 1Co2Cr催化剂上的主要表面物种为多齿碳酸盐, 该物种在低温时(< 250 °C)在表面积聚, 但在高温时被分解。

关键词: 丙烷催化燃烧; Co-Cr复合氧化物; 氧化还原性能; 表面酸性; 反应动力学

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