

Influence of Co on Ethylene Steam Reforming Over Co–Cr–O Spinel Catalysts

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Abstract

Two Co–Cr–O spinel catalysts with different stoichiometry were synthesized and characterized by X-ray diffraction, X-ray photoelectron spectroscopy, N₂ physisorption and temperature-programmed reduction in H₂. Excess Co in Co_{1.5}Cr_{1.5}O₄ existed as Co³⁺ that substituted for Cr³⁺ in the octahedral sites of the spinel lattice. High temperature treatment of the spinel catalysts in H₂ resulted in stepwise reduction of Co³⁺ to Co²⁺ and eventually to Co metal. Both CoCr₂O₄ and Co_{1.5}Cr_{1.5}O₄ catalysts were active and structurally stable in ethylene steam reforming under differential reaction conditions at 873 K, with the areal reforming rate over Co_{1.5}Cr_{1.5}O₄ being one order-of-magnitude greater than that over CoCr₂O₄. The steady state reforming rate after oxidation was comparable to that over the fresh catalyst for both CoCr₂O₄ and Co_{1.5}Cr_{1.5}O₄, indicating the stability of the spinel structure against reduction under steam reforming conditions.

Graphic Abstract



Keywords Heterogeneous catalysis · Steam reforming · X-ray photoelectron spectroscopy

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1 Introduction

Transition metal oxides have been widely studied as potential candidates for catalyzing oxidation of hazardous components from industries and automobile exhausts in light of their high stability and low cost [1, 2]. Among those, the remarkable performance of Cr_2O_3 was identified in the oxidation of various compounds, including CO [3], CH_4 [4] and heavier hydrocarbons [5]. The application of Cr_2O_3 catalysts remains limited due to concerns about gradually forming Cr^{6+} species (e.g., CrO_3) that are significantly more volatile and poisonous [6]. Thus Cr-containing spinel catalysts have been explored given the improved stability of Cr^{3+} in the spinel lattice [7, 8]. In particular, the $CoCr_2O_4$ spinel catalyst exhibited promising performance in the catalytic oxidation of hydrocarbons [8, 9].

Despite extensive studies on the CoCr_2O_4 spinel in catalytic oxidation, the activity and stability of the CoCr_2O_4 spinel under reductive environments was rarely explored. Moreover, the reactivity of Co^{3+} , which was suggested to play an important role in the oxidation of CO [10] and hydrocarbons [11] over Co_3O_4 , is not favored in stoichiometric CoCr_2O_4 where Co predominantly exists as Co^{2+} . In our previous studies, the activity and stability of MnCr_2O_4 [12] and NiCr_2O_4 [13] were evaluated in ethylene steam reforming, where ethylene was oxidized to carbon oxides accompanied by H₂ production. Specifically, the following reactions occurred simultaneously:

Steam Reforming:

$$C_2H_4 + 2H_2O \rightarrow 2CO + 4H_2 \quad \Delta H_r = 210.1 \text{kJ mol}^{-1}$$
 (1)

Water Gas Shift:

 $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad \Delta \text{H}_r^\circ = -41.2 \text{kJ mol}^{-1}$ (2)

Methanation:

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad \Delta H_r^{\circ} = -205.9 \text{kJ mol}^{-1}$$
 (3)

Herein, we have extended our ethylene steam reforming studies to the Co-Cr–O spinel system. Two spinel catalysts, $CoCr_2O_4$ and $Co_{1.5}Cr_{1.5}O_4$, were synthesized and thoroughly characterized. The reforming rate over the catalysts and stability against reduction to Co metal were evaluated in catalytic steam reforming of ethylene under the same conditions to investigate the influence of excess Co^{3+} in the spinel as well as to compare performance to $MnCr_2O_4$ and $NiCr_2O_4$ spinel catalysts.

2.1 Catalyst Synthesis

The two Co-Cr-O spinel catalysts were synthesized from a conventional sol-gel method. Specifically, Co(NO₃)₂·6H₂O (98%, Sigma-Aldrich) and $Cr(NO_3)_3$ ·9H₂O (98%, Sigma–Aldrich) of the desired molar ratio (Cr/Co = 2.0)for $CoCr_2O_4$ and Cr/Co = 1.0 for $Co_{1.5}Cr_{1.5}O_4$) were dissolved in 100 cm³ distilled deionized water with a total metal concentration of 0.4 M at ambient temperature. A 50 cm³ aqueous solution containing 1.6 M citric acid (99.5%, Sigma-Aldrich) was then added under vigorous stirring. The mixed solution was stirred at 368 K until the formation of a viscous gel. The gel precursor was transferred to an oven and dried overnight at 393 K in air. The dried gel was then pulverized and thermally treated in 100 cm³·min⁻¹ air flow at 1273 K for 4 h based on the conditions reported for Co-Cr-O spinel formation [14]. The pretreatment conditions were identical to those in our previous studies on ethylene steam reforming over $MnCr_2O_4$ [12] and $NiCr_2O_4$ [13]. The resulting powders were denoted as fresh $CoCr_2O_4$ and fresh $Co_{1.5}Cr_{1.5}O_4$ catalyst depending on the starting stoichiometry.

2.2 Catalyst Characterization

Physisorption of N_2 at 77 K was conducted on a Micromeritics ASAP 2020 analyzer with a sample of 2 g catalyst for the measurement of specific surface area and porosity, using the Brunauer–Emmett–Teller (BET) and the Barrett–Joyner–Halenda (BJH) method of analysis, respectively. The sample was evacuated at 473 K for 4 h prior to N_2 physisorption.

Powder X-ray diffraction (XRD) patterns of the catalysts were recorded on a PANalytical Empyrean X-ray Diffractometer equipped with a Cu K α radiation source in Bragg–Brentano geometry. The sample was scanned at a constant rate of 5°·min⁻¹ within a 2 θ range from 15° to 80° under ambient conditions. The collected XRD patterns were refined using the Material Analysis Using Diffraction (MAUD) software package [15].

Temperature-programmed reduction in H₂ (H₂–TPR) of the catalysts was measured on a Micromeritics AutoChem II 2920 Analyzer. A sample of 300 mg catalyst was first pretreated in 20 cm³·min⁻¹ Ar flow at 773 K for 0.5 h and cooled down to 323 K in the Ar flow. Upon the introduction of 20 cm³·min⁻¹ flow of 5 vol % H₂ in Ar, the sample was heated to 1273 K at a constant ramp rate of 10 K·min⁻¹ with the consumption of H₂ monitored by a thermal conductivity detector (TCD).

X-ray photoelectron spectroscopy (XPS) was performed on a Phi VersaProbe III Scanning X-ray Photoelectron Spectrometer. The sample was excited by an incident X-ray of 100 µm beam size and 25 W power output from a monochromatic Al K α radiation source (1486.7 eV). Kinetic energy of the photoelectrons was analyzed by a hemispherical energy analyzer under a passing energy of 55 eV and a stepwise dwell time of 100 ms to ensure high energy resolution. The XPS depth profiles were acquired by etching the sample surface with a high-energy Ar ion beam (3 kV bias, $3 \mu m \times 3 \mu m$ beam size) during the intervals between the collections. The sample was etched while rotating horizontally for 30 s in each cycle. A dual charge compensation using a low-energy electron flood gun and a low-energy Ar ion beam was applied in all scans. The reported binding energy was calibrated with respect to C1s (284.8 eV) from the adventitious carbon on the surface.

Thermogravimetric analysis (TGA) of the spent catalysts was carried out using a TA Instruments SDT Q600 thermogravimetric analyzer. The weight change of the sample was recorded during a temperature-programmed oxidation procedure, in which 30 mg catalyst was heated to 973 K from ambient temperature at a constant ramp rate of 10 K·min⁻¹ in 40 cm³·min⁻¹ synthetic air (20 vol% O₂ in He) flow.

2.3 Ethylene Steam Reforming

The two Co-Cr-O spinel catalysts were evaluated in catalytic steam reforming of ethylene at 873 K under atmospheric total pressure. A typical feed flow of 100 cm³·min⁻¹ containing 25 vol % C2H4, 50 vol % H2O, 5 vol % N2 and 20 vol % Ar was directed to 1 g catalyst loaded in a vertical, down-flow, fixed-bed quartz reactor (10.5 mm $I.D. \times 12.75$ mm O.D.). The catalyst was sieved to 250–425 μ m for CoCr₂O₄ and 70–180 μ m for Co_{1.5}Cr_{1.5}O₄ prior to reaction. Although two different particle sizes were utilized in this study because of difficulty forming compressed pellets, reforming rates measured on both samples were not influenced by intraparticle mass transfer artifacts as confirmed by the Weisz–Prater criterion [16]. Liquid water with dissolved O₂ removed by a N₂ purge was introduced by a syringe pump (ISCO, 500D) into a steel evaporator maintained at 413 K, where steam was generated and mixed with other gas components supplied from mass flow controllers (Brooks, 5850E). Upon removal of unreacted H_2O in the effluent gas through condensation, the produced CO₂ was measured by an infrared gas analyzer (Fuji Electric ZPA) and the produced H₂, CO and CH₄ were measured by a gas chromatograph (Agilent 7890A) equipped with a CarboPlot P7 column and a TCD. To properly compare the intrinsic activity of the catalysts, reaction rates were normalized by the exposed surface area instead of catalyst mass. Assessed under an ethylene conversion below 10%, the characteristic

rate of steam reforming is defined on the basis of overall C_1 product formation (CO, CO₂ and CH₄) normalized by the BET surface area:

$$r_{C1} = \frac{F(CO) + F(CO_2) + F(CH_4)}{S_{BET}}$$
(4)

The product-based ethylene conversion is evaluated assuming 100% carbon recovery from the C_1 products:

$$C_2H_4 \text{ conversion (\%)} = \frac{F(CO) + F(CO_2) + F(CH_4)}{2F_0(C_2H_4)} \times 100\%$$
(5)

The product selectivity is defined as the mole fraction of a certain component with respect to all quantified steam reforming products (H_2 , CO, CO₂ and CH₄):

Selectivity of X (%) =
$$\frac{F(X)}{F(H_2) + F(CO) + F(CO_2) + F(CH_4)} \times 100\%$$
(6)

where F(X) denotes the molar flowrate of component X measured downstream of the reactor, $F_0(C_2H_4)$ denotes the molar flowrate of C_2H_4 in the feed gas and S_{BET} denotes the BET surface area of the catalyst from N_2 physisorption. Given the identical reaction conditions and similar ethylene conversion levels to our previous work [12], the ethylene reforming rates reported in the present study were not affected by mass and heat transfer artifacts.

3 Results and Discussion

3.1 Characterization of The CoCr₂O₄ and Co_{1.5}Cr_{1.5}O₄ Catalyst

The textural properties of the catalysts assessed from N₂ physisorption are summarized in Table 1. The BET surface area of both CoCr_2O_4 and $\text{Co}_{1.5}\text{Cr}_{1.5}\text{O}_4$ catalysts was very low (i.e., less than 10 m²·g⁻¹) as a result of the high temperature treatment. Similar to the case of MnCr₂O₄ and Mn_{1.5}Cr_{1.5}O₄ [12], the introduction of excess Co caused a substantial decrease in the BET surface area of Co_{1.5}Cr_{1.5}O₄ (0.58 m²·g⁻¹) compared to the stoichiometric CoCr₂O₄ (5.4

Table 1 Textural properties of the fresh CoCr_2O_4 and Co_{1.5}Cr_{1.5}O_4 catalysts assessed from N_2 physisorption

Catalyst	BET surface area $(m^2 \cdot g^{-1})$	Pore volume $(cm^3 \cdot g^{-1})^a$
CoCr ₂ O ₄	5.4	0.019
$Co_{1.5}Cr_{1.5}O_4$	0.58	0.0011

^aBJH cumulative pore volume

 $m^2 \cdot g^{-1}$). The low cumulative pore volume calculated from the BJH method suggested both catalysts were essentially non-porous. The estimated pore diameter (70–140 Å) was likely representative of the voids between the particle aggregates [17]. Therefore, the measured BET surface area of the catalysts was attributed solely to external surface area.

The phase composition of the catalysts was characterized by XRD. As shown in Fig. 1, the $CoCr_2O_4$ sample exhibited the typical diffraction patterns corresponding to a cubic spinel structure without detectable crystalline Cr2O3 impurities that appeared when Cr was in excess [18]. By analogy to our previously reported Mn-rich $Mn_1 Cr_1 O_4$ spinel [12], the diffraction features observed for the Co1.5Cr1.5O4 sample are attributed to a Co-rich spinel phase according to prior reports [19–22], in which the octahedrally coordinated Cr^{3+} cations are partially substituted by the Co³⁺ cations as a result of the introduction of excess Co. The lattice parameter of the spinel phase in CoCr_2O_4 (8.332 Å) and $\text{Co}_{1.5}\text{Cr}_{1.5}\text{O}_4$ (8.270 Å) was acquired from Rietveld refinement, which is in agreement with the respective range of values of 8.327-8.333 Å for CoCr₂O₄ and 8.267–8.273 Å for Co₁₅Cr₁₅O₄ from prior reports [19–21], while both being significantly larger than the range of values of 8.082–8.083 Å reported for the Co_3O_4 spinel phase [19-21]. The significant decrease in the lattice constant of Co_{1.5}Cr_{1.5}O₄ with respect to the stoichiometric $CoCr_2O_4$ spinel is consistent with the distortion resulting from the replacement of Cr^{3+} by smaller Co^{3+} [21]. The occupancy from Rietveld refinement for both tetrahedrally and octahedrally coordinated cations was unity for the two Co–Cr–O spinel catalysts.

The redox properties of the catalysts were probed by H_2 -TPR with the reduction profiles shown in Fig. 2a. The results indicated the Co cations in the Co-Cr-O spinels were substantially more stable against reduction compared to Co₃O₄, which underwent complete reduction to Co metal at much lower temperatures (i.e., below 823 K) [23, 24]. The very small H₂ consumption below 450 K observed for both samples (Fig. 2a, inset) was attributed to the reduction of surface Cr⁶⁺ species that occurred over various Cr-based spinel oxides [25]. The reduction feature initiated at about 900 K in the profile of $CoCr_2O_4$ was assigned to the reduction of tetrahedrally coordinated Co^{2+} in the spinel lattice to Co^0 metal [26]. Consistent with this assignment, the formation of a trace amount of Co metal particles was detected in the XRD pattern of the $CoCr_2O_4$ sample after reduction in H₂ (Fig. 2b). However, due to a low reduction degree of Co^{2+} (3.3%), the small amount of Cr_2O_3 formed was dispersed and not detectable by XRD. Comparatively, the $Co_{15}Cr_{15}O_{4}$ sample exhibited a reduction feature at 960 K followed by a rapid increase in H₂ uptake above 1100 K, which was assigned to the stepwise reduction of Co³⁺ to Co^{2+} and Co^{2+} to Co^{0} , respectively [27]. Unfortunately, the



Fig 1 Rietveld refinement of the XRD patterns of the fresh $CoCr_2O_4$ and $Co_{1.5}Cr_{1.5}O_4$ catalysts. The refined lattice parameter for $CoCr_2O_4$ and $Co_{1.5}Cr_{1.5}O_4$ is 8.332 Å and 8.270 Å, respectively



Fig 2 a Temperature-programed reduction of the fresh CoCr_2O_4 and $\text{Co}_{1.5}\text{Cr}_{1.5}\text{O}_4$ catalysts in H₂. A minor H₂ consumption peak at low T from the reduction of surface Cr⁶⁺ species is shown in the inset. **b** X-ray diffraction patterns of the CoCr₂O₄ and Co_{1.5}Cr_{1.5}O₄ catalysts

overall reduction degree of Co (6.5%) could not be separated into individual reduction events as multiple processes occurred simultaneously. While the appearance of CoO diffraction feature was in accordance with the reduction of Co^{3+} to Co^{2+} , the diffraction feature corresponding to Co metal was not observed in the reduced $Co_{1.5}Cr_{1.5}O_4$ sample (Fig. 2b). We speculate that the CoO formed upon reduction of Co^{3+} in the octahedral sites interacts strongly with the Cr-containing spinel lattice and therefore impedes continuous reduction of the spinel to Co metal by retarding the outward diffusion of Co^{2+} and Co^{3+} cations [24, 28, 29]. Moreover, very small Co metal particles exposed to air during collection of the XRD patterns will likely oxidize surface Co metal.

The chemical speciation of Co and Cr on the catalyst surface was investigated by XPS. Results from previous reports have shown that the 2p binding energy of Co^{2+} and Co^{3+} did not correlate explicitly with the oxidation state, so discrimination between Co^{2+} and Co^{3+} from the 2p binding energy can be ambiguous [24, 30, 31]. As shown in Fig. 3a, the spectra of Co $2p_{3/2}$ were deconvoluted into two peaks including the major $2p_{3/2}$ energy state and a satellite feature from Co^{2+} and Co^{3+} [32, 33] according to the report from Xie et al. [34]. The Co $2p_{3/2}$ binding energy of the $CoCr_2O_4$ sample (780.9 eV) was slightly higher than that of the $Co_{1.5}Cr_{1.5}O_4$ sample (780.4 eV). The predominant presence of Co^{2+} on the surface of $CoCr_2O_4$ was confirmed by the intense satellite feature at 786.4 eV [34, 35], whereas the weak satellite feature at 784.6 eV in $Co_{1.5}Cr_{1.5}O_4$ was

lysts after H₂–TPR to 1273 K. The remaining spinel structure in the reduced $Co_{1.5}Cr_{1.5}O_4$ was labelled as $Co_xCr_{3-x}O_4$ since the stoichiometry changed as a result of CoO formation

consistent with those seen in Co₃O₄ and Co-excess Co-Cr-O spinels, suggesting the presence of Co^{3+} on the surface of that sample [24, 36]. The Cr $2p_{3/2}$ spectra were deconvoluted into three peaks as described by Keturakis et al. [37] with one peak at *ca*. 578.9 eV assigned to Cr^{6+} and two peaks at ca. 576.6 and 575.6 eV assigned to Cr^{3+} to account for the multiplet splitting of Cr^{3+} [38]. As shown in Fig. 3b, the broad peak with the highest binding energy of 578.7 eV in CoCr₂O₄ and 578.2 eV in Co_{1.5}Cr_{1.5}O₄ suggested the presence of Cr⁶⁺ species on the surface of both samples, which was supported by the weak low temperature reduction features observed in H₂-TPR (Fig. 2a). The two peaks of lower binding energies in the CoCr₂O₄ (576.8 and 575.6 eV) and Co15Cr15O4 (576.5 and 575.4 eV) samples were associated with Cr^{3+} cations likely residing in the spinel lattice. The fraction of Cr⁶⁺ with respect to total surface Cr (Cr³⁺ and Cr^{6+}) estimated from the peak areas was 12% for $CoCr_2O_4$ and 15% for $Co_{15}Cr_{15}O_4$, respectively, indicating Cr^{3+} to be the predominant form of existence for surface Cr in both samples.

The elemental composition of the catalysts was analyzed by XPS depth profiling using Ar ion beam etching. As shown in Fig. 4, the Cr/Co ratio measured on the surface of the CoCr₂O₄ sample was 2.0, which was slightly higher than the range of values from 1.7 to 1.8 observed in the later four cycles with pre-sputtering before each measurement. The Cr/ Co ratios measured for the Co_{1.5}Cr_{1.5}O₄ sample appeared in a narrow range of 0.8–0.9 regardless of the measuring depth. Despite a minor enrichment of Cr possibly on the surface



Fig 3 X-ray photoelectron spectra at a Co $2p_{3/2}$ and b Cr $2p_{3/2}$ region on the surface of the fresh CoCr₂O₄ and Co_{1.5}Cr_{1.5}O₄ catalysts

of $CoCr_2O_4$, the depth profiles indicated a fairly uniform elemental distribution for both samples that was consistent with the desired stoichiometry. The spectra associated with the Co $2p_{3/2}$ and Cr $2p_{3/2}$ regions of the $Co_{1.5}Cr_{1.5}O_4$ sample during depth profiling are shown in Fig. 5. The chemical state of Co in the bulk spinel was unfortunately inaccessible from the current depth profiling since Co cations were rapidly reduced to Co^0 metal upon exposure to the Ar ion beam, as evident by the development of the peak at 778.2 eV corresponding to metallic Co. The chemical state of Cr did not change appreciably with the probing depth except the decline of the broad Cr^{6+} feature at 578.2 eV starting from the first cycle. A similar trend was observed in the XPS spectra during depth profiling of $CoCr_2O_4$ (not shown).

3.2 Rate and Stability of the CoCr₂O₄ and Co_{1.5}Cr_{1.5}O₄ Catalyst in Ethylene Steam Reforming

The catalytic performance of the CoCr_2O_4 and $\text{Co}_{1.5}\text{Cr}_{1.5}\text{O}_4$ catalysts was evaluated in ethylene steam reforming at 873 K, a temperature at which the background ethylene

conversion was negligible [12]. Since Cr₂O₃ was found to be nearly inactive for ethylene steam reforming under identical reaction conditions [12], the observed reforming activity for the Co-Cr-O spinel oxides was attributed to the Co sites. As shown in Fig. 6, a steady rate of formation for H₂ and C₁ molecules (CO, CO₂ and CH₄) was observed over both catalysts after introduction of the reactants. Both catalysts exhibited stable steam reforming activity without appreciable deactivation up to 7 h on stream, suggesting severe coke formation did not occur. As listed in Table 2, the product-based ethylene conversion over the $Co_{15}Cr_{15}O_4$ catalyst (2.0%) was slightly higher than that over the CoCr₂O₄ catalyst (1.3%) for an equivalent mass loading of catalyst in the reactor. The product distribution favoring H₂ and CO₂ was observed for both catalysts, which was attributed to the nearly equilibrated water-gas shift reaction that occurred simultaneously with ethylene steam reforming. The steady state rate of C_1 formation over $C_0Cr_2O_4$ $(0.093 \,\mu\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1})$ was comparable to the steady state rate over MnCr₂O₄ (0.13 μ mol·m⁻²·s⁻¹) [12] and the initial rate over NiCr₂O₄ $(0.20 \,\mu\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1})$ [13] under identical conditions (see Table 3). Along with the results from H_2 -TPR



Fig 4 Profiles of atomic Cr/Co ratio in the fresh $CoCr_2O_4$ and $Co_{1.5}Cr_{1.5}O_4$ catalysts measured by XPS. Cycle 0: as prepared; Cycle 1–4: etched with Ar ion beam prior to the measurement



Fig 5 X-ray photoelectron spectra during depth profiling at a Co $2p_{3/2}$ and b Cr $2p_{3/2}$ region of the fresh $Co_{1.5}Cr_{1.5}O_4$ catalyst. Cycle 0: as prepared; Cycles 1–4: etched with Ar ion beam prior to the measurement



Fig 6 Product formation rate during ethylene steam reforming over the fresh $CoCr_2O_4$ and $Co_{1.5}Cr_{1.5}O_4$ catalysts. Reaction conditions: 873 K, 1 g catalyst, 100 cm³·min⁻¹ total flow, 25% C₂H₄, 50% H₂O, 5% N₂ and 20% Ar

Table 2 Rate and product distribution of ethylene steam	Catalyst	C_2H_4 conversion	ion C_1 production rate	Product selectivity (%)			
reforming over the fresh $CoCr_2O_4$ and $Co_{1.5}Cr_{1.5}O_4$ catalysts	(%) ^a		(µmol·m ² ·s ⁻¹)	СО	CO ₂	CH_4	H ₂
	CoCr ₂ O ₄	1.3	0.093	2	28	14	56
	Co _{1.5} Cr _{1.5} O ₄	2.0	1.3	1	28	15	56

^aProduct-based conversion. Reaction conditions: 873 K, 1 g catalyst, 100 cm³·min⁻¹ total flow, 25% C_2H_4 , 50% H_2O , 5% N_2 and 20% Ar

Table 3 Comparison of ethylene steam reforming rates over the $MCr_{2}O_{4}$ spinel catalysts

Catalyst	C ₂ H ₄ conver- sion (%)	C_1 production rate (μ mol·m ⁻² ·s ⁻¹)	Source	
CoCr ₂ O ₄	1.3	0.093	This work	
MnCr ₂ O ₄	1.8	0.13	Ref [12]	
NiCr ₂ O ₄	2.1 ^b	0.20 ^b	Ref [13]	

^aProduct-based conversion. Reaction conditions: 873 K, 1 g catalyst, 100 cm³·min⁻¹total flow, 25% C_2H_4 , 50% H_2O , 5% N_2 and 20% Ar. ^bInitial results at t < 1 h.

(Fig. 2a), this comparison suggested the steam reforming activity was likely from the stable Co–Cr–O spinel surfaces without severe decomposition of the spinel structure to form Co metal particles. Interestingly, the steady state rate of C₁ formation over Co_{1.5}Cr_{1.5}O₄ (1.3 μ mol·m⁻²·s⁻¹) was an order-of-magnitude greater compared to CoCr₂O₄ (0.093 μ mol·m⁻²·s⁻¹), which potentially resulted from Co³⁺ on the surface that was proposed as the active site for the oxidation of hydrocarbons [39, 40]. The structure and oxidation state of Co in the octahedral Co sites during steam reforming conditions remain undetermined.

The spent CoCr₂O₄ and Co₁₅Cr₁₅O₄ catalysts were reoxidized and then evaluated in ethylene steam reforming for a second cycle to examine whether slow reduction of Co cations to Co^0 metal occurred during the first cycle. As shown in Fig. 7, the rate of C_1 formation over the reoxidized $CoCr_2O_4$ (0.086 µmol·m⁻²·s⁻¹, second cycle) was stable and nearly identical to that of the fresh catalyst $(0.093 \ \mu mol \cdot m^{-2} \cdot s^{-1})$, first cycle). This comparison suggests the reduction of Co^{2+} in the $CoCr_2O_4$ spinel lattice to Co⁰ metal was negligible under reaction conditions and did not contribute to the observed reforming activity. These results contrast the behavior of NiCr₂O₄ where the reforming rate increased substantially in the second cycle as a result of the formation of NiO agglomerates upon re-oxidation [13]. Interestingly, the re-oxidized $Co_{15}Cr_{15}O_4$ exhibited an induction period for about 1.5 h before reaching steady state during the second cycle, over which the C_1 formation rate gradually increased from 0.94 μ mol·m⁻²·s⁻¹ and plateaued at a rate of 1.3 μ mol·m⁻²·s⁻¹ that was comparable with the first cycle. Although the reason for the induction period was unclear, the consistency in the steady state rate between the two cycles nevertheless indicated the stability of the $Co_{1.5}Cr_{1.5}O_4$ catalyst against the formation of Co metal



Fig 7 Comparison of C_1 formation rate during ethylene steam reforming over the fresh and re-oxidized CoCr₂O₄ and Co_{1.5}Cr_{1.5}O₄ catalysts. Reaction conditions: 873 K, 1 g catalyst, 100 cm³·min⁻¹



Fig 8 Rietveld refinement of the XRD patterns of the CoCr_2O_4 and $\text{Co}_{1.5}\text{Cr}_{1.5}\text{O}_4$ catalysts after two ethylene steam reforming cycles. The refined lattice parameter for CoCr_2O_4 and $\text{Co}_{1.5}\text{Cr}_{1.5}\text{O}_4$ is 8.332 Å and 8.270 Å, respectively

particles. We speculate this phenomenon was related to the interconversion between Co^{3+} and Co^{2+} . In particular, the Co^{3+} on the surface was potentially reduced to Co^{2+} during steam reforming based on the H₂–TPR results (Fig. 2a), forming a CoO-like layer with octahedrally coordinated Co^{2+} . These octahedral Co^{2+} sites might be partially converted to the less reactive tetrahedral Co^{2+} sites when oxidized to Co_3O_4 during the re-oxidation [36, 39], whereas this process was perhaps reversible when the catalyst was

total flow, 25% C₂H₄, 50% H₂O, 5% N₂ and 20% Ar. The catalysts were re-oxidized at 873 K for 4 h under 100 cm³·min⁻¹ air flow in between the two cycles

exposed to the reductive environment during the second cycle of steam reforming.

The stability of the spinel structure in both catalysts was also evident from the XRD patterns after the second steam reforming cycle. As shown in Fig. 8, diffraction features corresponding to CoO or metallic Co resulting from the decomposition of the spinel structure were not detected in either of the two catalysts. The refined lattice parameter for the CoCr₂O₄ (8.332 Å) and Co_{1.5}Cr_{1.5}O₄ (8.270 Å) spent catalysts after the second cycle remained identical to the respective value of the fresh catalyst, suggesting most of the excess Co^{3+} cations in $Co_{1.5}Cr_{1.5}O_4$ were retained in the lattice under reaction conditions. The occupancy for both tetrahedrally and octahedrally coordinated cations in the two catalysts remained unity. As expected from the steady reforming rate observed over both catalysts (after 1.5 h on stream), the amount of coke deposited during the second reforming cycle measured by temperature-programmed oxidation (Fig. 9) was negligible over either $CoCr_2O_4$ or $Co_{15}Cr_{15}O_4$ (i.e., less than 0.5 wt%).

4 Conclusions

The synthesized $CoCr_2O_4$ and $Co_{1.5}Cr_{1.5}O_4$ catalysts both adopted a cubic spinel structure. The excess Co in $Co_{1.5}Cr_{1.5}O_4$ was attributed to octahedrally coordinated Co^{3+} that partially substituted for Cr^{3+} in the stoichiometric $CoCr_2O_4$ spinel lattice, resulting in a significant decrease in lattice constant. High temperature treatment in H₂ reduced the Co^{2+} in the $CoCr_2O_4$ spinel lattice to Co metal particles, whereas the reduction of Co^{3+} to Co^{2+} in $Co_{1.5}Cr_{1.5}O_4$



Fig 9 Thermogravimetric analysis profiles during temperature-programmed oxidation of the $CoCr_2O_4$ and $Co_{1.5}Cr_{1.5}O_4$ catalysts in synthetic air after two ethylene steam reforming cycles

occurred at lower temperatures. Both the $CoCr_2O_4$ and $Co_{1.5}Cr_{1.5}O_4$ catalyst were active and structurally stable for ethylene steam reforming at 873 K. The areal reforming rate over $Co_{1.5}Cr_{1.5}O_4$ was one order-of-magnitude greater than that over $CoCr_2O_4$, which was potentially related to the presence of Co^{3+} on the catalyst surface as evident by X-ray photoelectron spectroscopy. The steady state rate of ethylene steam reforming over both catalysts after re-oxidation was comparable to the respective rate from the fresh catalysts, suggesting an outstanding stability of the Co–Cr–O spinel structure against reduction to Co metal under steam reforming.

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Compliance with Ethical Standards

Conflict of interest The authors declare no conflict of interest.

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