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Supporting Information

Study on the Catalytic Performance of ZnCrAl Co-precipitated Oxides Washed with Ammonium Carbonate Solution in the Synthesis of Light Olefins from Syngas

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Experimental section

Catalyst preparation

(1) Preparation of oxides by coprecipitation

To prepare the water-washed oxide, combined $Zn(NO_3)_2 \cdot 6H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ to create a 100 mL metal salt solution. Then, combined $(NH_4)_2CO_3$ in the appropriate ratio to create a 100 mL precipitant solution. Two prepared solutions were added dropwise simultaneously in a water bath with constant speed stirring. After dropwise addition, the solution was aged for 3 h. The aged suspension was washed with water, filtered to neutral, and then dried in an oven at 110 °C for 6 hours. Finally, the precursor was calcined in an air environment in a muffle furnace at 2 °C/min up to 500°C for 1 h to obtain water-washed $ZnCrAlO_x$, denoted as ZCA-W.

Steps to prepare ammonium-washed oxides: First, prepare the metal salt solution and ammonium carbonate solution as described above. Similarly, two solutions were added dropwise simultaneously under stirring in a water bath at a constant temperature. The solution then was aged at a constant temperature for 3 h. After aging, the suspension was filtered to obtain a filter cake. Subsequently, the filter cake was soaked in 1 mol/L ammonium carbonate solution for one hour and filtered to obtain an ammonium-washed filter cake. The cake was dried in an oven at 110 °C for 6 hours. Finally, the precursor was calcined at the same temperature and time in the air atmosphere of a muffle furnace to give ammonium-washed $ZnCrAlO_x$, denoted as ZCA-A.

(2) Preparation of oxides by sol-gel method

Preparation: Weigh a certain proportion of $Zn(NO_3)_2 \cdot 6H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$, and $Al(NO_3)_3 \cdot 9H_2O$ to make 30 mL metal salt solution. Prepare 10 mL citric acid solution by weighing the appropriate proportion of anhydrous citric acid. The metal salt solution was then stirred in a water bath at 50 °C until completely dissolved. The citric acid solution was slowly added to the metal salt solution, and the mixing continued with stirring for one hour. The solution was then kept at 80 °C with continuous stirring to evaporate water until a sol was formed. The sol was dried in an oven at 110 °C for 10 h to produce a gel. The gel was then calcined in the air atmosphere of a muffle furnace to obtain the sol-gel $ZnCrAlO_x$, named ZCA-R. The heating process consisted of pre-calcining at 250 °C for 2 h and calcining at 500 °C for 1 h.

The oxides prepared by all three methods used the same elemental feed ratios, i.e., zinc, chromium, and aluminum, in a molar ratio of 2.5:1.2:0.8.

The SAPO-34 molecular sieves utilized in this study were prepared by fellow members of our research team, with no modifications made to their preparation conditions. Additionally, to ensure consistency, the SAPO-34 molecular sieves employed across the same experimental series were prepared from a single batch.

Characterization of catalysts

Crystal and textural properties were evaluated using X-ray diffraction (XRD) and low-temperature N_2 adsorption and desorption. The acid strength of the oxide surfaces and their acid centers were identified using NH_3-TPD, and the reducibility of ZnCrAl oxides was assessed using H_2 programmed temperature rise reduction (TPR). Oxides were examined using X-ray photoelectron spectroscopy (XPS) for their chemical composition and elemental chemical states.

A Cu Kα radiation source (λ= 1.5418 Å)-equipped PANalytical X'pert PPR diffractometer

was used for the measurements. The XRD patterns were captured in steps of 0.02° in the 2θ = 5-80° range while operating at 40 mA and 40 kV.

Tests on N_2 adsorption-desorption were carried out on a Micromeritics ASAP 2460 apparatus. The catalyst was degassed under vacuum for 6 hours at 300 °C before testing. Then, at 77.35 K, the adsorption and desorption curves were captured. The Brunauer-Emmett-Teller (BET) equation was used to get the total specific surface area of the oxides.

A programmed warming desorption of ammonia (NH_3-TPD) experiment was run on a chemisorption analyzer. Under the stream of Ar gas, a 100-mg sample was heated to 600 °C and kept there for an hour. After cooling to 100 °C, the sample was exposed to a 5% NH_3/Ar mixture for 30 min, and helium was used to purge the sample of any NH_3 that had physically adhered to it. The signal of NH_3 desorption was collected using a thermal conductivity detector (TCD), while the NH_3-TPD measurements were completed by heating to 600 °C at 10 °C/min.

The sample was analyzed for surface microzone elements using a Thermo Fischer ESCALAB X-ray photoelectron spectrometer. The instrument uses Al Kα-rays as the excitation source (hν = 1486.6 eV), with a test voltage and current of 15 kV and 10 mA, respectively, and a C 1s orbital binding energy of 284.8 eV as a reference for calibrating the binding energy.

H_2 temperature programmed reduction (H_2-TPR) curves were recorded using a Micromeritics Auto Chem 2920 instrument equipped with a TCD detector. The samples were heated from room temperature to 300 °C under Ar atmosphere and then cooled to 50 °C. The sample was purged by passing a 10% H_2/Ar mixture until the baseline was smooth, and then the program was started to increase the temperature to 800 °C for sample analysis, and the H_2 depletion was monitored by the TCD method.

Inductively coupled plasma emission spectroscopy (ICP-OES) was used to determine the metal element distribution.

The morphology and microstructure of the catalysts were examined using a JEOL JEM-2100 electron microscope at 200 kV. Before shooting, the powdered sample was ultrasonicated in anhydrous ethanol for 20 minutes and then distributed on ultrathin copper mesh. The electron microscope images were recorded on a Zeiss SUPRA 40 and operated at 5 kV.

Catalyst activity evaluation

A high-pressure fixed-bed microreactor built in-house by our group was used to test the catalyst activity. The output of the reaction was connected to an external gas chromatograph for immediate analysis of all products. Experiments were performed using 400 mg of catalyst in quartz-lined, high-pressure resistant stainless steel reaction tubes. The molecular sieves were made into 40-60 mesh particles and physically combined with the powdered oxides in a 1:1 mass ratio to make the catalyst. To retain the catalyst in the middle of the reactor, it was placed in a quartz tube, the top and bottom ends of which were held in place by 1 cm high quartz wool. Prior to the reaction, the catalyst was reduced in situ in H_2 at 310°C for 1 hour. Then H_2 was evacuated, syngas (H_2:CO=2) was added, and the catalytic reaction was carried out at 3 MPa, 400 °C, 20 mL/min. An external online gas chromatograph (Agilent 8890) with a flame ionization detector (FID) and thermal conductivity detector (TCD) was used to evaluate the reaction products. The following equations were used to determine CO conversion, product selectivity, and internal standardization using Ar.

$$n_{Ar} = F_{in} \times C_{Ar,in} = F_{out} \times C_{Ar,out}$$

$$Conv._{CO} = 1 - \frac{n_{CO,out}}{n_{CO,in}} = 1 - \frac{F_{out} \times C_{CO,out}}{F_{in} \times C_{CO,in}} = 1 - \frac{C_{Ar,in} \times C_{CO,out}}{C_{Ar,out} \times C_{CO,in}}$$

$$Conv._{CO} = \left[1 - \frac{\alpha \times C_{CO,out}}{C_{CO,in}}\right] \times 100\%$$

$$Sel._{CO_2} = \frac{\alpha \times CO_{2\,out}}{CO_{in} - \alpha \times CO_{out}} \times 100\%$$

$$Sel._{C_n H_m} = \frac{nC_n H_{m\,out}}{\sum_1^n C_n H_{m\,out}} \times 100\%$$

$$Y._{C_{2-4}^=} = \frac{\alpha \times C_{2-4}^=}{CO_{in} - \alpha \times CO_{out}} \times 100\%$$

Table S1. Percentage of the elemental composition of the three oxides.[a]

Sample	Zn(%)	Cr(%)	Al(%)
ZCA-W	64.73	26.23	9.04
ZCA-A	51.18	36.27	12.55
ZCA-R	62.93	25.2	11.87

[a] The metal element distribution was found by ICP-OES determination.

Table S2. Weaving properties of the three oxide samples.

Sample	BET (m²/g)	D[a] (nm)	Meso[b] (cm³/g)
ZCA-W	80.52	13.41	0.28
ZCA-A	91.04	9.77	0.24
ZCA-R	58.22	8.00	0.15

[a] The average pore size is derived from the BJH algorithm. [b] The mesopore pore volume was calculated by the t-plot method.
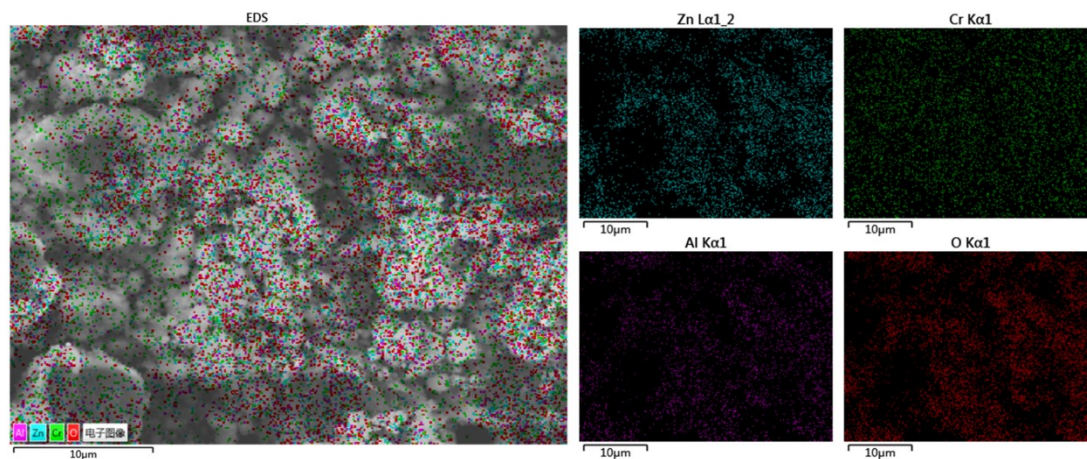
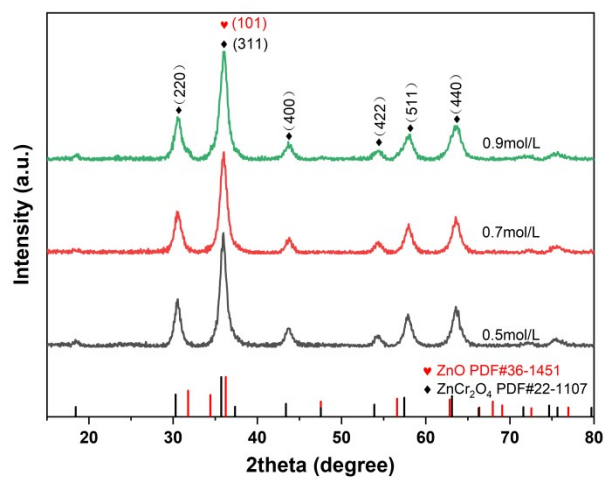**Figure S1.** SEM-EDX mapping images of ZCA-A oxide.

Figure S2. Different solution concentrations of ZCA-A oxides XRD spectra.

Table S3. Particle size of different solution concentrations of ZCA-A oxides.

Concentration (mol/L)	Particle size (nm)[a]	Particle size (nm)[b]
0.5	11.05	10.63
0.7	10.76	10.13
0.9	9.23	10.05

[a] The particle size of the oxides was calculated by using the Scherrer equation.

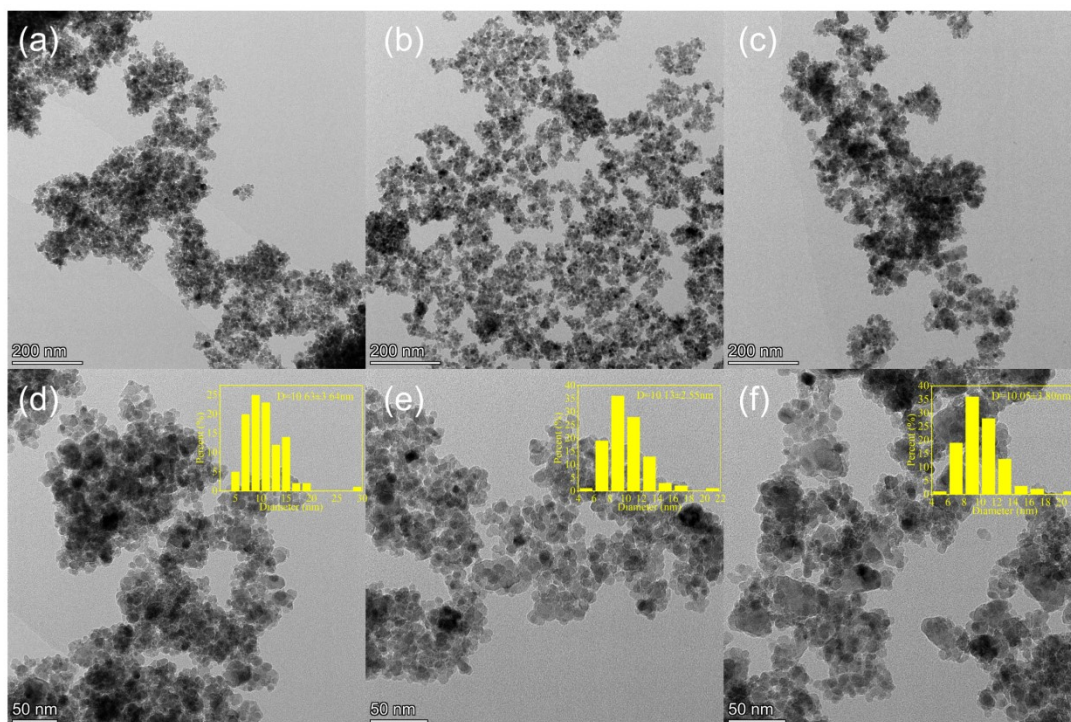[b] The particle size of the oxides was obtained by TEM statistics.

Figure S3. TEM images of ZCA-A oxides with different solution concentrations. (a)(d) 0.5 mol/L (b)(e) 0.7mol/L (c)(f) 0.9mol/L.
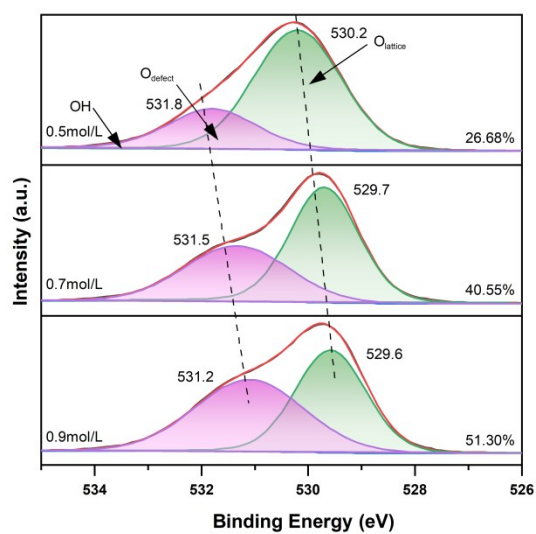

Figure S4. XPS spectra of ZCA-A oxides synthesized at different solution concentrations. (O1s orbital)
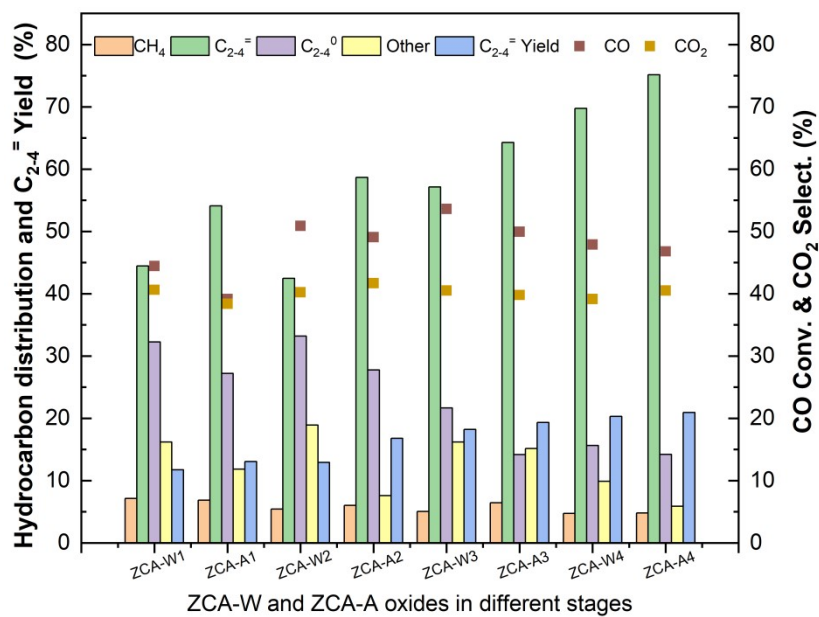
Figure S5. Catalytic properties of ZCA-A and ZCA-W oxides.

The use of the same number indicates that the oxides belong to the same batch, but various numbers indicate variations in the preparation time, method, and process conditions. Example: ZCA-W1 and ZCA-A1 are oxides prepared in the same batch, and catalytic experiments were carried out under the same process conditions.

Reaction conditions: ZCA-W1、ZCA-A1、ZCA-W2、ZCA-A2: 673 K, 2.0 MPa, 3000 mL·g_{cat}^{-1}·h^{-1}, H_2/CO = 2/1, weight ratio of OX/ZEO = 1/1. ZCA-W3、ZCA-A3、ZCA-W4、ZCA-A4: 673 K, 3.0 MPa, 3000 mL·g_{cat}^{-1}·h^{-1}, H_2/CO = 2/1, weight ratio of OX/ZEO = 1/1.