



Fluorinated Cu/Zn/Al/Zr hydrotalcites derived nanocatalysts for CO₂ hydrogenation to methanol



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ABSTRACT

A series of fluorinated Cu/Zn/Al/Zr hydrotalcite-like compounds are synthesized by incorporation of different amount of (AlF₆)³⁻ into hydrotalcite-like sheets. The fluorine-modified Cu/ZnO/Al₂O₃/ZrO₂ catalysts are then obtained by calcination and reduction of fluorinated precursors. With increasing of F/Al atomic ratios, the Cu particle size increases continuously and the Cu surface area and dispersion decrease gradually, as well as the amount of moderately and strongly basic sites first increases significantly and then decreases. The catalytic performance for the methanol synthesis from CO₂ hydrogenation is examined. The change of CO₂ conversion is small when F/Al ≤ 0.8, while the CO₂ conversion decreases remarkably with further increase of fluorine content. It is also found that the CH₃OH selectivity is closely related to the distribution of basic sites and the selectivity of CH₃OH takes a volcanic trend with increased fluorine content. The introduction of suitable amount of (AlF₆)³⁻ into the hydrotalcite-like structure can enhance the methanol yield markedly and the fluorine-modified catalysts with F/Al = 0.83 affords the substantial stability and the best catalytic performance.

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1. Introduction

One of the promising approaches to mitigate and solve the important environmental and energy issues is to convert CO₂ into useful chemicals and fuels. Thermocatalytic hydrogenation of CO₂ to methanol has been widely explored as one of the key processes for anthropogenic chemical carbon cycle, because methanol is a starting material for many industrial chemicals such as formaldehyde, dimethyl terephthalate, and acetic acid, as well as high-octane gasoline, aromatics, and ethylene or can be directly utilized as a fuel [1–4]. Moreover, renewable sources such as solar energy, wind, hydroelectric, and biomass may support such a green integrated process.

Commercially, the synthesis of methanol is accomplished by conversion of CO₂-containing syngas over coprecipitated Cu/ZnO/Al₂O₃ catalysts [5,6]. Furthermore, Cu/ZnO/Al₂O₃ catalysts with

promoter zirconia have demonstrated high performance in methanol synthesis from CO₂ hydrogenation due to the high copper dispersion and surface basicity [7–9]. However, the major competitive pathway of methanol synthesis is reverse water gas shift (RWGS) reaction, which leads to loss of methanol production [10,11]. A dual-site mechanism of CO₂ hydrogenation is widely accepted for the Cu/ZnO/Al₂O₃/ZrO₂ catalyst, which assumes that the atomic hydrogen transports from the surface of Cu onto the surface of ZnO-ZrO₂ sites via spillover and hydrogenates the adsorbed carbon-containing species to form methanol [7,12,13]. On the Cu/ZnO-based catalyst, most researchers are likely to favor the direct hydrogenation of CO₂ via a formate intermediate [10,14,15]. Some reports proposed that both methanol and CO were produced mainly via same intermediate species and the selectivity of CH₃OH was related to the fraction of strongly basic sites on the catalyst surface [12,16,17]. Therefore, appropriate adsorption amount and adsorption strength of CO₂ are beneficial for the production of methanol, which give a guideline for the design of high effective and efficient catalysts.

Recently, considerable attention has been focused on hydrotalcite-like compounds (HTLcs) as catalyst precursors, because the nanocatalysts derived from HTLcs possess homogeneous

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dispersion of metal cations at an atomic level, high stability against sintering, high specific surface area and strongly basic properties [18–20]. The general formula of HTLcs is $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$, where M^{2+} and M^{3+} are the di- and trivalent cation in the octahedral positions within the hydroxide layers, and A^{n-} represents an exchangeable interlayer anion that can vary. The acid-base properties of HTLcs can be tuned by the variation of interlayer anions. As a basic anion, fluorine ion can promote many base-catalytic reactions [21,22]. In our previous work, it was found that the introduction of fluorine ions into Cu-based catalysts could enhance the surface basicity, and then increased the CH₃OH selectivity [16,23]. The fluorine ions were incorporated between the HTL layers based on the so called “memory effect”, and the calcined material can be reformed to an HTL structure upon treatment with aqueous solutions containing the fluorine anions under protection of N₂ [22,24,25]. However, this process is complex and time consuming, as well as the specific surface decrease dramatically after reconstruction of the material. In the HTL structure, the M^{3+} is surrounded by six oxygen atoms of the OH⁻ anions as first neighbors and the fluorine ions can be directly introduced into HTL layers using a novel preparation method with partial substitution of the $(Al(OH)_6)^{3-}$ octahedra by $(AlF_6)^{3-}$ [26,27]. Therefore, fluorinated HTLcs can be easily obtained with a wide range in fluorine content.

In the present work, the fluorine ions were incorporated as a part of the Cu/Zn/Al/Zr hydrotalcite-like layers with a large range of fluorine content. The fluorine-modified Cu/ZnO/Al₂O₃/ZrO₂ catalysts with different fluorine were prepared by calcination and reduction of the fluorinated Cu/Zn/Al/Zr HTLcs. The main focus is to study the effects of the fluorine content on the physicochemical properties of precursors and the final catalysts. In addition, the catalytic performances of the catalysts for methanol synthesis from CO₂ hydrogenation were discussed deeply in relation to the results of physicochemical characterizations.

2. Experimental

2.1. Preparation of catalysts

Cu/Zn/Al/Zr hydrotalcite-like compounds with atomic ratio of Cu:Zn:Al:Zr=2:1:0.7:0.3 were prepared by the co-precipitation method at room temperature. An aqueous solution containing appropriate amounts of Cu(NO₃)₂·3H₂O, Zn(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, Zr(NO₃)₄·2H₂O and Na₃AlF₆ were added dropwise to 200 mL of deionized water under vigorous stirring. A second aqueous solution containing NaOH and Na₂CO₃ was simultaneously fed. The pH during precipitation was kept at a constant value of 10.0 ± 0.2. The product was aged at 333 K for 15 h under stirring and then filtered and washed with deionized water. The filter cakes were dried overnight at 353 K. The HTLcs were calcined in air at 773 K for 4 h. The source of aluminum was either aluminum nitrate or a mixture of aluminum nitrate with sodium hexafluoroaluminate. The as-obtained HTLcs were denoted as HT-Fn (*n* is

the nominal F/Al atomic ratio in the synthesis mixture which was listed in Table 1), and corresponding calcined HTLcs were denoted as CHT-Fn.

2.2. Characterization of catalysts

The chemical compositions of calcined catalysts were analyzed by an inductively coupled plasma-optical emission spectroscopy (ICP-OES) using Thermo iCAP 6300. Besides, the content of fluorine in the samples was determined by ion-selective electrode analysis.

The Brunauer-Emmett-Teller (BET) surface area and pore volume of samples were determined by N₂ adsorption-desorption, using a Micromeritics Tristar 3000 set-up at liquid nitrogen temperature 77 K. Prior to the measurements, the samples (80–120 mg) were degassed at 473 K for 12 h. The specific surface area were calculated from the isotherms using the BET method, and the total pore volume was estimated by the Barrett-Joyner-Halenda (BJH) method from desorption isotherm branch of the nitrogen isotherms.

Analytical X'Pert Pro X-ray diffractometer was employed for phase analysis of samples with Cu K α radiation. The X-ray diffraction (XRD) data were measured in the step mode of 0.0167°, 12 s and in the range of 5° < 2 θ < 75°. The average crystallite sizes of the copper species, *d* was estimated adopting the Scherrer equation, $d = k\lambda / (FW \times \cos(\theta))$, where θ is the diffraction angle of the maximum intense peak and FW is the full width at half-maximum (FWHM) of the peak (in radians).

The single pulse solid-state ¹⁹F MAS NMR single excitation spectra were acquired on a Bruker Avance III spectrometer. The ¹⁹F MAS NMR spectra were measured by operating the spectrometer at 375.5 MHz, using $\pi/2$ pulses of 3 ms with a recycle delay of 1 s, and ¹⁹F chemical shifts were referenced to those of CFCl₃ at 0 ppm.

The thermo gravimetric analysis (TGA) measurement was performed on a NETZSCH TG209F1 Thermal Analyzer in a flow of synthetic air (30 mL min⁻¹) in the temperature range of 303–1023 K (heating rate: 10 K min⁻¹).

N₂O reactive frontal chromatography (RFC) was used to estimate the exposed Cu⁰ area (*S*_{Cu}) and the dispersion of Cu (*D*_{Cu}) in the as-reduced catalysts. The measurements were carried out on Micromeritics AutoChem 2920 instrument based on the procedure as it mentioned previously [28]. Prior to measurements, the samples (100 mg) were reduced at 553 K in 5% H₂/Ar (30 mL min⁻¹) for 2 h. Then, the samples were cooled down to 338 K and isothermally purged with Ar for 30 min, after which the sample was exposed to 5% N₂O/Ar atmosphere (85 mL min⁻¹) for 1 h to ensure complete oxidation of exposed Cu⁰ to Cu⁺. Finally, a pulse of pure H₂ was passed over the catalyst at 553 K and the surface Cu₂O were reduced to Cu. *D*_{Cu} and *S*_{Cu} were calculated according to the amount of H₂ consumption. In addition, the average Cu particle size (*d*_{Cu}) obtained from the Eq. (1)

$$d_{Cu}(nm) = \frac{104}{D_{Cu}(\%)} \quad (1)$$

assuming a spherical shape of Cu particles [29].

The morphology of the samples was investigated using a FET XL30 S-FEG scanning electron microscope (SEM) with an accelerating voltage of 10.0 kV.

X-ray photoelectron spectroscopy (XPS) measurements were studied on a Kratos AXIS ULTRA DLD spectrometer equipped with Al K α radiation (150 w, $h\nu = 1486.6$ eV) under ultrahigh vacuum (10⁻⁷ Pa). The binding energies were calibrated internally by adventitious carbon deposit C (1 s) with *E*_b = 284.8 eV.

The temperature program reduction (TPR) was carried out in a U-tube quartz reactor on a Micromeritics ChemiSorb 2920 with a

Table 1

Structure, composition and the weight loss of the fluorinated hydrotalcite-like precursors.

Sample	F/Al atomic ratio ^a	a (Å)	c (Å)	Weight Loss ^b (%)	
				Total	Second
HT-F0	0	3.084	22.92	27	12
HT-F0.3	0.3	3.084	22.90	26	11.5
HT-F0.9	0.9	3.084	22.86	25	11
HT-F1.5	1.5	3.084	22.78	24.5	10.5
HT-F2.1	2.1	3.080	22.78	23	10

^a The nominal atomic ratio in the synthesis mixture.

^b The weight losses measured in TG experiments for total and second steps.

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