



Short Communication

Fluorine-modified Cu/Zn/Al/Zr catalysts via hydrotalcite-like precursors for CO₂ hydrogenation to methanol



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ABSTRACT

Fluorine-modified Cu/Zn/Al/Zr catalysts were prepared by calcination of the fluorine-containing Cu/Zn/Al/Zr hydrotalcite-like compounds and tested for CO₂ hydrogenation to methanol. The results revealed that the CH₃OH selectivity was greatly improved by the remarkable increase of the proportion of strongly basic sites, while the CO₂ conversion decreased slightly. It is also found that the activity of catalysts is closely related to the synergy between the Cu and basic sites. The CH₃OH yield for the fluorine-modified Cu/Zn/Al/Zr catalysts was higher than that for the fluorine-free catalysts; thus, the introduction of fluorine favored the methanol formation.

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1. Introduction

As a cheap, nontoxic and abundant C1 feedstock, chemical utilization of CO₂ is a challenge and an important topic. The catalytic hydrogenation of CO₂ to methanol is one of the most effective and economical ways to fix and utilize a large amount of anthropogenic CO₂ because methanol is a starting material for several important chemicals and can be used as a fuel additive or clean fuel [1,2]. However, the conventional Cu/Zn/Al catalysts that are highly effective for methanol synthesis from syngas exhibit a poor activity for the hydrogenation of CO₂ [3,4]. The addition of a suitable amount of Zr can enhance the copper dispersion and the surface basicity of catalysts, which in turn improves the catalytic performance [5]. In addition, the nature of catalyst precursor also plays an important role for the structure and catalytic performance. Very recently, the hydrotalcite-like compounds (HTLcs) have been used as catalyst precursors for their advantages of homogeneous dispersion of metal cations at an atomic level, high stability against sintering and strongly basic properties [6,7].

In order to better understand and design the highly active catalysts for CO₂ hydrogenation to methanol, the reaction mechanism has been widely investigated. For the Cu/Zn/Zr catalyst, a bi-functional mechanism

of CO₂ hydrogenation is currently accepted which assumes that the adsorption and dissociation of hydrogen occur on the Cu sites, while the adsorption of CO₂ takes place over the ZnO-ZrO₂ sites. 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 [5,8–11]. Therefore, a highly exposed Cu surface area and appropriate adsorption amount and adsorption strength of CO₂ are favorable for the hydrogenation of CO₂. In our previous work, the introduction of fluorine into Cu/Zn/Al catalyst could enhance the surface basicity, and then increased the CH₃OH selectivity significantly [12]. Experimentally, the fluorine anions can be introduced into the interlayer region of HTLcs based on the so called memory effect [13,14]. As a result, it could be expected that the introduction of fluoride into Cu/Zn/Al/Zr catalysts via hydrotalcite-like (HTI) precursors will further improve the catalytic performance.

In this study, the fluorine-modified Cu/Zn/Al/Zr mixed oxides with $Zr^{4+}/(Al^{3+} + Zr^{4+}) = 0.08$ and 0.24 were prepared by calcination of the fluorine-containing Cu/Zn/Al/Zr HTLcs and tested for CO₂ hydrogenation to methanol. The effect of the introduction of fluorine on the properties of the precursors and the catalysts was discussed.

2. Experimental

2.1. Preparation of catalysts

The Cu/Zn/Al/Zr hydrotalcite-like compounds with $Cu^{2+}:Zn^{2+}:(Al^{3+} + Zr^{4+}) = 2:1:1$ were synthesized by a co-precipitation method

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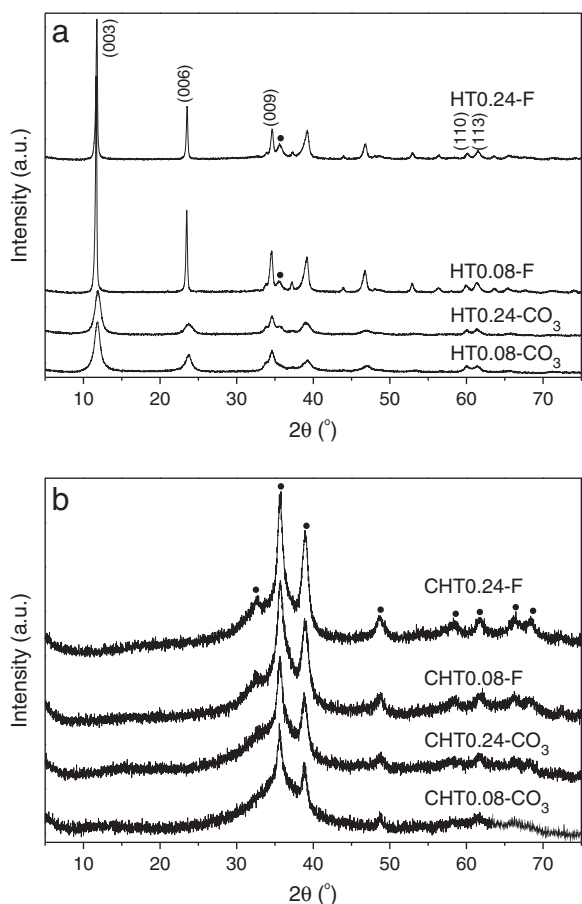


Fig. 1. XRD patterns of the (a) precursors and (b) calcined samples, (●) CuO.

according to the literature [5]. Synthesized HTICs were denoted as HTx-CO₃, where x means the Zr⁴⁺/(Al³⁺+Zr⁴⁺) atomic ratio in the synthesis mixture and x = 0.08, 0.24, and corresponding calcined samples were denoted as CHTx-CO₃.

The reconstructed forms of Cu/Zn/Al/Zr HTICs with fluorine anions in the interlayer region were prepared according to the literature [14]. Briefly, the mixed metal oxides (CHTx-CO₃) were treated separately with an aqueous solution of NaF under N₂ atmosphere for 48 h. To prevent CO₂ from contaminating the aqueous solution, the deionized decarbonated (DD) water was used. Then the resulting products were filtered, washed many times with the DD water and dried at 353 K under N₂ atmosphere. In this way, the fluorine-containing Cu/Zn/Al/Zr HTICs were prepared and denoted as HTx-F. The obtained HTx-F samples were further calcined in an oven at 773 K for 4 h under flowing stream of pure N₂. Then the fluorine-modified samples (CHTx-F) were obtained.

2.2. Characterization of catalysts

The weight of fluorine in the samples was determined by ion-selective electrode analysis. XRD patterns were recorded on a Panalytical X'Pert Pro X-ray diffractometer with Cu K α radiation. The surface area of catalysts was determined by N₂ adsorption–desorption at liquid nitrogen temperature 77.30 K. The morphology of the samples was investigated using a Hitachi S-4800 scanning electron microscope (SEM) with an accelerating voltage of 20.0 kV. The dispersion of Cu (D_{Cu}) and Cu surface area (S_{Cu}) were determined by dissociative N₂O adsorption and carried out on Micromeritics AutoChem 2920 instrument using the procedure described in our previous work [15]. X-ray photoelectron spectroscopy (XPS) measurements were performed over a Kratos XSAM800 spectrometer equipped with Al K α radiation under ultrahigh vacuum (10⁻⁷ Pa). The binding energies were calibrated internally by adventitious carbon deposit C (1s) with $E_b = 284.6$ eV. The basicity of the catalyst was measured by CO₂-TPD. The catalyst was first reduced at 603 K in H₂ flow for 2 h. After cooling to room temperature, the catalyst was saturated with pure CO₂ at 323 K for 1 h, and then flushed with Ar flow to remove all physical adsorbed molecules. Afterward, the TPD experiment was started with a heating rate of 10 K min⁻¹ under Ar flow (40 mL min⁻¹), and the desorbed CO₂ was detected by an AMETEK mass spectrometer.

2.3. Evaluation of catalysts

Catalytic performance for hydrogenation of CO₂ was carried out in a fixed-bed reactor. Catalyst (1.5 mL, 40–60 mesh) diluted with 1.5 mL quartz sand was placed in a stainless steel tube reactor. Prior to reaction, the catalyst was reduced in pure H₂ at 603 K for 8 h under atmospheric pressure. After reduction, CO₂ hydrogenation test was determined under reaction conditions of 523 K, 5.0 MPa, n(H₂):n(CO₂) = 3:1, GHSV = 4000 h⁻¹. Products were quantitative analyzed with gas chromatograph. The CO₂ conversion and the carbon-based selectivity were calculated by an internal normalization method.

3. Results and discussion

3.1. Textural and structural properties

As shown in Fig. 1a, the XRD patterns of all precursors were typical for hydrothermalite-like structures, indicating that the HTx-CO₃ and HTx-F were successfully prepared. The patterns of the reconstructed HTx-F samples displayed much higher and sharper basal peaks compared to that of HTx-CO₃. The apparent increase of the crystallinity upon reconstruction could be explained by a partial recrystallization of the amorphous phase existing in the mixed oxides forms [16]. For HTx-F, some extent of the CuO-like phase was also detected, indicating that some Cu²⁺ ions did not enter the layered structures during the reconstruction process. The crystallographic parameters a and c were calculated by assuming a hexagonal crystal system for samples and the results were listed in Table 1. In comparison with HTx-CO₃, HTx-F showed an increase in c with slight decrease in a . The increase in c value could be ascribed to the less

Table 1
Physicochemical properties and XPS results of the calcined samples.

Sample	a^a (Å)	c^a (Å)	F content (g/100g)	S_{BET} (m ² g ⁻¹)	S_{Cu} (m ² g ⁻¹)	D_{Cu} (%)	Binding energy (eV)					
							Cu 2p _{3/2}	Zn 2p _{3/2}	Al 2p	Zr 3d _{3/2}	Zr 3d _{5/2}	F 1s
CHT0.08-CO ₃	3.082	22.75	0	61	30.4	9.86	933.8	1021.2	73.8	183.7	181.4	–
CHT0.24-CO ₃	3.086	22.76	0	69	35.1	12.17	933.8	1021.2	73.7	183.8	181.5	–
CHT0.08-F	3.081	22.92	0.77	29	19.4	6.33	933.7	1021.4	74.1	184.1	181.7	684.4
CHT0.24-F	3.082	22.86	0.59	38	22.2	7.69	933.7	1021.4	74.1	184.0	181.7	684.3

^a As-prepared HTI precursors.

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