Catal Lett (2009) 128:248–252
DOI 10.1007/s10562-008-9747-3

Synthesis of Cu/Fe/Ti/Al_2O_3 Composite Granules for SO_3 Decomposition in SI Cycle

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Received: 17 August 2008 / Accepted: 22 October 2008 / Published online: 11 November 2008

Abstract The present paper deals with the catalytic decomposition of SO_3 reaction. Cu/Fe/Ti/Al_2O_3 composite granule catalysts prepared by a combination of Yoldas process and oil-drop method were studied in an attempt to find some suitable catalysts for the decomposition of sulfur trioxide as the oxygen-generating reaction in the thermo-chemical water splitting process. CuFe/Ti:Al-1:2 shows high SO_3 conversion (69%) at 800 °C compared with other catalysts because of the high surface area and the support permitted a better dispersion of Ti.

Keywords SO_3 decomposition · Composite granules · Cu/Fe/Ti/Al_2O_3

1 Introduction

The most important fossil fuel is hydrogen that is estimated to become the energy carrier of the future because hydrogen as a fuel will allow sustainable development from the perspective of zero emission energy production systems. Thermo-chemical splitting of water has been proposed as a clean method for hydrogen production. Such hydrogen would be obtained by decomposition of water by using heat energy through a chemical cycle process that consists of several reactions. Among the thermo-chemical cycles, the sulfur–iodine (SI) process [1] has received attention as one of the reliable candidates that exhibits a great potential for the industrialization of hydrogen production by the water splitting.

The SI cycle consists of the following reactions: (1) The first step is decomposition of sulphuric acid to form gaseous H_2O, SO_3 and oxygen at temperature >600 °C, (2) second step is also known as Bunsen reaction proceeds exothermically in liquid phase and produces two immiscible aqueous acid phase viz., sulfuric acid and hydroiodic acid produce in the temperature range 70–120 °C and (3) HI decomposition is slightly endothermic, produces hydrogen and take place in the temperature range of 300–450 °C.

The iodine–sulfur cycle shows the following reaction.

$$H_2SO_4 \rightarrow H_2O + SO_2 + 1/2O_2 \tag{1}$$

$$I_2 + SO_2 + 2H_2O \rightarrow 2HI + H_2SO_4 \tag{2}$$

$$2HI \rightarrow H_2 + I_2 \tag{3}$$

The decomposition of sulfuric acid consists of two reactions in series:

$$H_2SO_4 \rightarrow H_2O + SO_3 \tag{4}$$

$$SO_3 \rightarrow SO_2 + 1/2O_2 \tag{5}$$

Sulfuric acid can be decomposed with a catalyst or without a catalyst, while the decomposition of SO_3 has been known to be a catalytic reaction.

Most metal oxides are considered as active catalysts for the sulfuric acid decomposition in the temperature range 600–1,000 °C. Noble metals are reliable as highly active catalysts for decomposition reactions, but non-noble metal catalysts should be developed from the economic point of

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view [2]. In order to decrease the operating temperature, transition metals or their oxides seem to be interesting candidates as sulfuric anhydride decomposition catalysts [3]. The preparation of catalyst, metal precursors and supports play an important role for SO_3 decomposition. In addition, catalysts were found to fail due to formation of volatile acid salts [4], support poisoning [4]. Kim et al. [2] reported the catalytic decomposition SO_3 on the binary metal oxide catalysts. Ginosar et al. [5] reported SO_3 decomposition using platinum supported Al, Zr and Ti at higher temperature. Although a few catalysts appeared promising under ideal conditions, primarily platinum supported on porous metal oxides, their long-term stability has not been reported [5]. Abimanyu et al. [6] reported Fe/Cu/Al_2O_3-composite granules catalysts were prepared by a combination of Yoldas sol–gel process and oil-drop method for SO_3 decomposition to assist hydrogen production. Catalytic decomposition of sulfuric acid on mixed Cr/Fe oxide samples and its application in sulfur–iodine cycle for hydrogen production was reported by Banerjee et al. [7].

In this research work, we have prepared copper, iron and titanium oxide insulated in Al_2O_3 (boehmite solution) matrices to disperse and stabilize the active component of copper and iron will acts as promoter in this reaction. The composite granules were prepared by a combination of the Yolda's sol–gel method. The catalytic activity was measured using pure SO_3, which was introduced into the fixed-bed reactor.

2 Experimental

The CuFeTi/Al_2O_3 composite granules of 1–2 mm in diameter were prepared by a combination of the Yoldas sol–gel process and the oil-drop method, as described in the literature [8–13]. The starting materials for preparing the composite granules were 2 M boehmite sol (colloidal suspension in aqueous medium was prepared containing small γ-AlOOH crystallites), 0.17 M of $Cu(NO_3)_2 \cdot 3H_2O$, 0.33 M of $Fe(NO_3)_3 \cdot 9H2O$ and Ti $[OCH\ (CH_3)_2]_{4,}$ the copper and iron wt% was 4:3. 2 M boehmite sol was synthesized by hydrolysis and condensation of 260 mL aluminum tri-sec-butoxide (ALTSB, 97%, Acros Organics) in 500 mL distilled water, followed by peptization with an appropriate amount of HNO_3 to give $H^+/Al^{3+} = 0.07$. In preparation, the addition of copper and iron precursors kept constant, 4 wt% and 3 wt%, respectively, varying titanium and alumina precursors to keep 120 mL of the total amount of solution.

For preparing the CuFeTi/Al_2O_3 composite granules, we mixed 2 M boehmite sol with $Cu(NO_3)_2$, $Fe(NO_3)_3$ and Ti $[OCH\ (CH_3)_2]_4$ solution (with various concentrations) in the volume ratio of 6:1. After aging at 70 °C for half an hour under vigorous stirring, the mixture became viscous and was transferred to droppers for granulation process. The granulation process included generating sol droplets by the droppers, shaping and partially gelating the droplets into spherical wet-gel granules in paraffin oil layer, and consolidating the structure of the wet-gel granules in an 8 wt% ammonia solution layer. For preparing CuFeTi/Al_2O_3 granules, we added $Cu(NO_3)_2$ to the ammonia solution at the concentration identical to that in the Cu-doped boehmite sol to prevent $Cu(NO_3)_2$ from being leached out of the wet-gel particles. After aging in the ammonia for 1 h, the spherical wet-gel particles were removed from the ammonia solution, carefully washed sequentially with water and ethanol, dried at 40 °C for 48 h, and finally calcined in air at 900 °C for 4 h.

The XRD patterns of CuFe/Ti:Al_2O_3 were recorded on (M/S. Shimadzu Instruments, Japan) diffractometer with Ni filtered Cu K_α as a radiation source and at a 2θ scan speed of 2°/min. The N_2 adsorption–desorption measurements were performed at 77 K using automated gas sorption system (M/S. Micromeritics ASAP 2000) utilized with Brunner–Emmett–Teller (BET) calculation for the surface area and Barrett–Joyner–Halanda (BJH) method for pore size distribution. The sample has been pre-treated at 200 °C for 2 h before analyzing the sample. The shape and size of the composite granules were observed using an optical microscope (Nikon C-PS). Elemental analysis of the composite granules was performed by means of AAS (Atomic absorption spectroscopy) and ICP (Inductively coupled plasma). The UV–vis diffuse reflectance spectra measurements were taken on a cary 5,000 spectrophotometer (Varian company) equipped with an intergrating sphere. The sample was analyzed under ambient conditions. The reflection in percentage was measured and presented by the normalized Kubelka–Munk function.

The catalytic activity for the SO_3 decomposition was measured in a fixed bed quartz reactor and the reaction was carried out with atmospheric pressure. The mixture of SO_3 (20 cm^3/min) and N_2 (40 cm^3/min) was fed into the reactor and the gas hourly space velocity (GHSV) in the catalyst bed was maintained 72,000 cm^3/(g cat. h). The product gases were analyzed by titration and absorption methods for SO_2 and SO_3 reported by Kim et al. [2]. The reaction was carried out in the temperature range of 700 °C to 1000 °C at atmospheric pressure over a 0.050 g of catalyst loaded in a fixed bed reactor.

3 Results and Discussion

The BET surface area of CuFe/Ti:Al_2O_3 composite granules of dried and calcined catalysts are shown in Table 1.

Table 1 BET Surface area of dried and calcined CuFe/Ti:Al_2O_3 composite granules prepared Yoldas process and oil-drop method

Sl. No.	Catalysts	BET surface area (m^2/g)		
		Dried	Calcined	
			500 °C	900 °C
1.	CuFe/Ti:Al-1:1	298.7	270.72	9.34
2.	CuFe/Ti:Al-1:2	325.47	267.76	9.71
3.	CuFe/Ti:Al-1:3	370.03	239.06	3.21
4.	CuFe/Ti:Al-1.5:1	315.21	255.65	5.78
5.	CuFe/Ti:Al-2:1	330.41	233.43	10.15

The composition of copper and iron oxide kept constant and varying titania and alumina content. The specific surface area was decreased dramatically with an increase of alumina or titania content after calcination. The surface area of CuFe/Ti:Al-2:1 catalyst at room temperature was 330.41 $m^2\ g^{-1}$ and it reaches 10.15 $m^2\ g^{-1}$ at 900 °C. The specific surface area of CuFe/Ti:Al-1:2 dried catalyst was 325 $m^2\ g^{-1}$ and after calcination at 500 and 900 °C the surface area was 268 and 10 $m^2\ g^{-1}$ respectively. This indicates that easy decomposition of titanium isopropoxide in boehmite solution took place resulted in the generation of smaller granules with a diameter in the range of 1–2 mm.

The composition of metals such as copper and iron were analyzed by atomic absorption (AAS) spectroscopy, titanium and alumina were analyzed by inductive coupled (ICP) plasma. These data along with the pore volume and pore size are summarized in Table 2. The ratios of metal to Al are in line with the theoretical values. With increase in aluminum content, decrease in the pore volume and slight increase in the pore diameter was observed. This indicates that the pore structure of the composite could be maintained by copper in the alumina matrix.

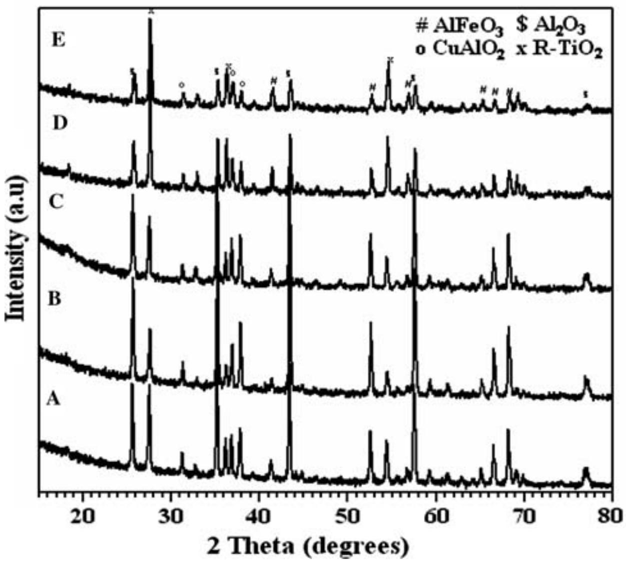

Fig. 1 XRD patterns of CuFe/Ti:Al_2O_3 composite granules calcined at 900 °C prepared by Yoldas process. **a** CuFe/Ti:Al-1:1, **b** CuFe/Ti:Al-1:2, **c** CuFe/Ti:Al-1:1, **d** CuFe/Ti:Al-1.5:1 and **e** CuFe/Ti:Al-2:1

Figure 1 shows the XRD patterns of CuFe/Ti:Al_2O_3 composite granules prepared by Yoldas sol–gel method calcined at 900 °C. The composite granules are prepared by varying the mole ratio of titanium isopropoxide and boehimite solution. The d-values of Al_2O_3 are 2.55_x, $2.09_{9.5}$ and $1.60_{9.1}$, $3.48_{6.8}$ and $1.23_{0.9}$ (ICDD No.82-1468), d-values of rutile TiO_2 are 2.37_x, $2.45_{4.3}$ and $2.82_{3.3}$ (ICDD No. 76-2398), d-values of $CuAlO_2$ are 2.37_x, $2.45_{4.3}$ and $2.82_{3.3}$ (ICDD No. 76-2398) and the d-values of $AlFeO_3$ are 2.65_x, 1.48_4, 1.43_3, 1.42_1, 1.38_1, 1.35_1 (ICDD No. 30-0024). The characteristic peak of Al_2O_3 was observed with peaks for $AlFeO_3$ with low intensities. This could be a reason of good dispersing of iron components in alumina matrix. In spectrum, no peaks of copper and iron were observed. This indicates that iron and copper were well dispersed on the grain surface of Al_2O_3 according to monolayer loading theory [14, 15]. This shows that crystallization of iron is more complete than that of Al_2O_3. It is reported that the reductions of iron oxide to Fe was observed at temperature of 720 °C and 850 °C, respectively, from pure Fe_2O_3 and pure Fe_3O_4 [16].

Table 2 Ratio of metal to aluminum, pore volume and pore size of CuFe/Ti:Al_2O_3 composite granular catalysts

Catalysts	Metal wt%[a]			M/Al[b] (wt%/wt%)	Pore volume (cm^3/g)[c]	Pore size (Å)[c]
	Cu	Fe	Ti			
CuFe/Ti:Al-1:1	3.36	2.37	9.06	0.317	0.2282	97.16
CuFe/Ti:Al-1:2	3.23	2.34	5.17	0.231	0.0214	108.45
CuFe/Ti:Al-1:3	3.75	2.75	3.01	0.204	0.0109	136.57
CuFe/Ti:Al-1.5:1	3.68	2.72	12.9	0.412	0.0366	270.87
CuFe/Ti:Al-2:1	3.63	2.82	17.2	0.509	0.0296	204.81

[a] Modified from analysis results of AAS and ICP

[b] M = CuFeTi/Al (Al content 46.60 wt%)

[c] After calcination at 900 °C for 4 h

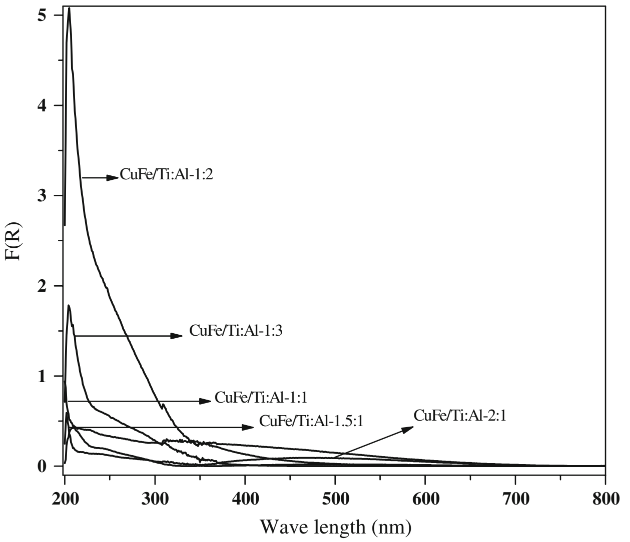

Fig. 2 UV–Visible spectra of CuFe/Ti:Al_2O_3 composite granules at room temperature

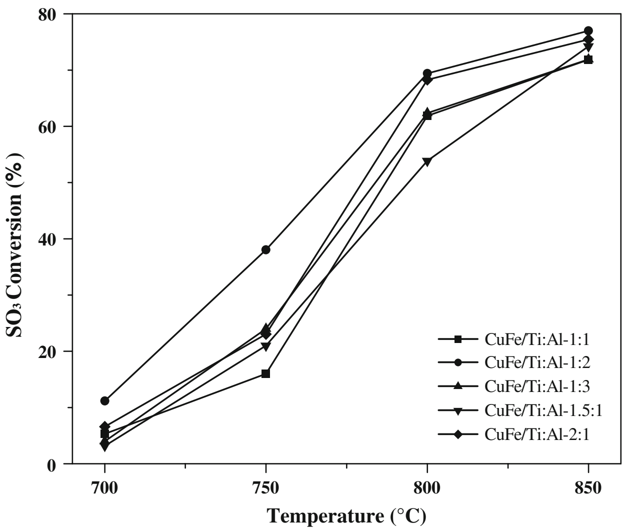

Fig. 3 Activity of CuFe/Ti:Al_2O_3 composite granules prepared by Yoldas oil-drop method for SO_3 decomposition. Reaction conditions: catalyst, 0.050 g; GHSV, 72,000 cm^3/(g.cat. h); Temperature effect: 700, 750, 800, 850, 900, 950 and 1,000 °C

UV–Visible spectroscopy is an important characterization technique for analyzing the electronic environment of Ti centre. Figure 2 shows the room temperature UV/Vis spectra of CuFe/Ti:Al_2O_3 samples used in this work. All the samples record an absorption band below 250 nm, accounting for the high dispersion of Ti achieved by the grafting procedure. The electronic spectra show an absorption associated with the ligand-to-metal charge transfer (LMCT) from the oxygen to the Ti^{IV} ion, namely $Ti^{4+}O^{2-} \rightarrow Ti^{3+}O^{-}$ reported by de la Peña-O'Shea VA et al. [17]. The wavelength at which this transition occurs is highly sensitive to the coordination of titanium sites, and this peculiarity has been proposed as a probe to test the coordination environment around a titanium center [18–21]. As a general rule, LMCT in titanium compounds containing octahedral coordinated Ti^{IV} takes place at higher wavelengths ($k > 300$ nm) than in compounds in which the titanium ions exhibit only a tetrahedral coordination (200–250 nm) [17, 18]. The shift of the adsorption band to higher wavelengths generally indicates the presence of polymeric rather than isolated Ti species [19]. The CuFe/Ti:Al-1:2 sample registers a maximum centered around 205 nm, which indicates a high proportion of isolated tetrahedral Ti centers. The other samples such as CuFe/Ti:Al-1:3, 1.5:1 and 2:1 shows weak intensity spectrum and broad absorption band of this catalyst accounts for the presence of different kinds of Ti species and polymeric Ti–O–Ti are probably present on this sample [22]. The CuFe/Ti:Al-1:2 sample shows an high intense absorption band shifted towards shorter wavelength, indicating that the high surface area and α-Al_2O_3 groups of the support permitted a better dispersion of Ti. The selective grafting of other sample had weak intensity spectrum with a maximum of around 245 nm. The dispersion and isolation of Ti centres on this sample is optimum.

The catalytic activity measurements were performed on the CuFe/Ti:Al_2O_3 catalysts in the range 700–1000 °C in a fixed bed reactor. Figure 3 shows the conversion of SO_3 to SO_2 at different reaction temperatures, where the intial SO_3 concentration in the inlet gas mixture is 33.33 mol%, and a GHSV of 72,000 cm^3/g.cat. h was maintained. The SO_3 conversion of CuFe/Ti:Al-1:1, 1:2, 1:3, 1.5:1 and 2:1 were 62, 69, 62, 54 and 68% at 800 °C. Kim et al. [2] reported the catalytic decomposition of SO_3 on the binary metal oxide catalysts of Fe/Al and Fe/Ti was ~20% conversion at 750 °C. Abimanyu et al. [6] reported 46% SO_3 conversion at 800 °C on Cu/Al_2O_3, Fe/Al_2O_3 and Cu/Fe/Al_2O_3 granules prepared by Yolda's sol–gel method. In the present study, CuFe/Ti:Al-1:2 catalyst shows high SO_3 conversion (69%) at 800 °C which is due to the easy decomposition of titanium isopropoxide resulting in well dispersion on alumina matrix. The UV–Vis pattern of this catalyst shows signal at shorter wavelengths with high intensity indicating that the high surface area and Al_2O_3 groups of the support permitted a better dispersion of Ti.

4 Conclusions

All CuFe/Ti:Al_2O_3 composite granules were prepared by a combination of the Yoldas sol–gel process and the oil-drop method. The CuFe/Ti:Al_2O_3 composite granules facilitated the thermal decomposition of sulfur trioxide to sulfur dioxide and oxygen in temperature range of 700–1000 °C at GHSV 72,000 cm^3/g.cat. h. The CuFe/Ti:Al-1:2 composite granules shows high SO_3 conversion (69%) at 800 °C compared with other catalysts. The UV/Visible spectroscopy of CuFe/Ti:Al-1:2 sample shows an absorption band shifted towards shorter wavelengths (205 nm) and high intensity spectrum, indicating that the Al_2O_3 groups of the support permitted a better dispersion of titanium. This suggest that sulfate formation rate as well as the metal sulfate decomposition can also be important for the higher rate and that metal sulfate decomposition should be considered as the necessary condition for the SO_3 decomposition.

Acknowledgment The authors wish to thank the financial support form MOST of Korea and KAERI. This work has been carried out under the Nuclear Hydrogen Development and Demonstration Project (NHDD).

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