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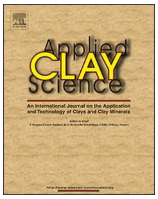

Research paper

Novel Cu-Zn-Al catalysts obtained from hydrotalcite-type precursors for middle-temperature water-gas shift applications

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ABSTRACT

Water gas shift (WGS) reaction is a key step in the steam reforming industrial processes, allowing to increase the H_2 production reducing the CO content in the exiting stream. Currently the WGS reaction is performed in two steps, at high and low temperature, but in recent years, the possibility to perform it in only one step using one reactor operating at middle temperature (about 300 °C) has received increasing interest. Cu/Zn/Al hydrotalcite-type (HT) compounds having a Cu-content lower than 30 wt% showed to be useful precursors of highly active and stable catalysts for the WGS reaction in the 250–350 °C temperature range. The best performances were observed for a catalyst containing 20 wt% of copper and a M(II)/M(III) atomic ratio equal to 2.0 that reached the equilibrium values of CO conversion in all the temperature range with a behaviour similar to one of the most widely employed commercial catalyst, associated to a very good stability with time-on-stream. The catalytic behaviour may be rationalized considering both the Cu^0 surface area and the Cu/ZnO interactions, which are promoted by the homogeneous distribution of the cations in the brucite-type layers of the HT precursors.

1. Introduction

The recent years have seen increasing interest towards the hydrogen production. In this context the water gas shift reaction (WGSr), $CO + H_2O \rightleftarrows H_2 + CO_2$, plays an important role when used as an upgrading step to adjust different syngas ($CO + H_2$) and to reduce the CO content (Twigg, 1989; Springer et al., 2001).

Currently, the WGSr is performed in 2 steps: i) immediately after the steam reforming reactor (SRR), operating at about 350 °C with Cr-rich Fe-based catalysts (HTS); ii) in the subsequent converter at about 220 °C using highly active Cu-based catalysts (LTS) (Twigg, 1989). In order to reduce the operational costs there is an increasing interest for new formulations able to operate in one step at middle (MTS) temperature (about 300 °C) with high activity, selectivity and stability with time-on-stream (TOS) (Fuentes et al., 2011, 2014). By this way it is possible to reduce the required inlet steam flow (that must to be high in HTS operating with Fe-based catalyst), allowing to work more efficiently in the previous SR reactor (Winter-Madsen and Olsson, 2007; Sehested et al., 2014). In order to increase the CO conversion obtained, it is sufficient to expand the Prox step, already present when the application of the H_2 stream is low temperature fuel cells.

In order to obtain active catalysts and avoid interferences due to structure dishomogeneity or phase segregation, it would be best to select multicomponent and flexible structures, such as hydrotalcite-type (HT) anionic clays, which are characterized by homogeneous cation distributions and are simple and relatively inexpensive to prepare on laboratory or industrial scale (Trifirò and Vaccari, 1996; Sehested et al., 2014).

HT anionic clays, also called layered double hydroxides (LDH), have the following general formula $[M^{2+}_{(1-x)}M^{3+}_{x}(OH)_2]^{x+}(A^{n-})_{x/n} * mH_2O$, with $0.20 \le x \le 0.33$ (Cavani et al., 1991). Cu-containing HT precursors may therefore be employed thanks to their capacity to cover broad composition ranges and form mixed oxides by calcination with high surface area values However, it is known that due to their preferential symmetry Cu^{2+} ions form pure HT compounds only when other bivalent cations are present (Busetto et al., 1984; Cavani et al., 1991; Trifirò and Vaccari, 1996; Basile and Vaccari, 2011).

HT-derived catalysts, containing carbonates as interlayer anions, have already been reported as effective catalysts in the production of syngas by catalytic partial oxidation (CPO) or SR of natural gas (Basile et al., 2009a, 2009b, 2010; Ballarini et al., 2013).

In LTS the performances of $Cu/ZnO/Al_2O_3$ catalysts are significantly affected by the Cu particle properties (Ginés et al., 1995; Souza et al., 2008) and synergetic interactions between Cu and ZnO (Herman et al.,

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1979; Frost, 1988; Shido and Iwasawa, 1991; Souza et al., 2008), depending on the Cu and Zn contents (Rodriguez et al., 2007; Souza et al., 2008; Park et al., 2010). High amounts of Cu promote the WGSr and CH_3OH synthesis at low temperature, while the increase of temperatures facilitates hydrocarbon synthesis and sintering phenomena (Gunawardana et al., 2009). On the other hand, supported catalysts with a Cu content lower than 30 wt% show high activity, selectivity and resistance to sintering (Sekizawa et al., 1998). A study has already been reported on the activity of catalysts derived from HT precursors in MT-WGSr (Fuentes et al., 2011, 2014), but test conditions were far different from industrial ones in terms of pressure and inlet composition; furthermore, deactivation tests were not performed.

In this study were prepared Cu-containing catalysts, starting from HT precursors, tested in MTS conditions (250–350 °C range), to achieve a high activity and stability with TOS. The effect of Cu-content on the WGS activity was studied maintaining the molar ratio (Cu + Zn)/Al = 3.0 and changing the amount of Cu. Furthermore, the role of Al content, that may affect the precursor structure and the active phase availability (Fu et al., 2011), was investigated decreasing M(II)/M(III) molar ratios from 3.0 to 2.0 and keeping constant the Cu-content considering that a value between 2.00 and 3.00 is required to obtain pure HT compounds (Cavani et al., 1991).

2. Experimental

2.1. Sample preparation

All the Cu/Zn/Al precursors, (HT-ZAC samples, see Table 1) contained carbonates as interlayer anions and were prepared by co-precipitation (Cavani et al., 1991; Sanfilippo, 1997); $Cu(NO_3)_2 * 2.5H_2O$ (Aldrich > 98%), $Zn(NO_3)_2 * 6H_2O$ (Aldrich > 98%) and $Al(NO_3)_3 * 9H_2O$ (Aldrich > 98%) were dissolved in deionised water. The solution (1 M) was dropped wise added in a 2 M $NaHCO_3$ solution at 60 °C under energetic stirring, maintaining the pH at 9.0 ± 0.1 by addition of drops of a 3 M NaOH solution. After 45 min of ageing under stirring, the precipitate was filtered under vacuum, washed with hot water (60 °C) until minimum Na^+ content, dried overnight at 70 °C and calcined at 550 °C for 6 h (ZAC samples). The powder was pressed, crushed and sieved to a 30–40 mesh size to optimize the radial gradient of temperature and concentration, avoiding diffusion phenomena and preferential by-pass (Sanfilippo, 1997).

2.2. Sample characterization

X-ray powder diffraction patterns were recorded on a Philips PW1050/81 diffractometer equipped with a graphite monochromator in the diffracted beam and controlled by a PW1710 unit (Cu Kα, $\lambda = 0.1541$ nm). The patterns were collected in the 2 θ range between 5 and 80° with a step size of 0.1° and a measuring time of 2 s per step. The diffraction patterns were identified by comparison with those included in the Joint Committee of Powder Diffraction Standards (JCPDS) data base (Klug and Alexander, 1974) and collected in a database X'Pert Highscore software. The crystallite size was calculated using the Debye-Scherrer's formula.

The BET surface area was determined in a Micromeritics ASAP 2020 instrument by N_2 physic adsorption at −196 °C (Gregg and Sing, 1982), pre-treating the sample (250 mg) in vacuum at 200 °C before the measurement. The porosity analysis was also measured in a Micromeritics ASAP 2020 instrument. A typical physic adsorption analysis started with degassing the calcined sample (250 mg) in vacuum at 150 °C for 30 min, then it was heat up to 250 °C for 30 min. The pore volume and size distribution were calculate applying the BJH equation (Gregg and Sing, 1982).

The specific Cu^0 surface area (MSA) and dispersion were determined by N_2O decomposition performed by Pulse Chromatography as reported in the literature (Scholten and Konvalinka, 1969; Narita et al., 1982; Evans et al., 1983), assuming a Cu^0 surface density of 1.46×10^{19} Cu atom/m^2 and a reaction stoichiometry of two Cu atoms per oxygen atom. The measurement was performed on 200 mg of calcined sample using a Perkin Elmer GC equipped with a TCD and a Porapak Q column to separate N_2 and N_2O at room pressure. Before the analysis, the samples were reduced with a 80 mL/min flow of H_2/N_2 (5:95 v/v) mixture from 40 to 220 °C (10 °C/min) and hold for 1 h, followed by cooling down to 60 °C for 20 min in He. The analysis was carry out at 60 °C by introducing successive pulses of 1.0 mL of N_2O into a He flow by a 6-port valve until the N_2O area remained constant.

TPR measurements were carried out in a ThermoQuest TPD/R/O 1100 Catalytic Surface Analyser, equipped with a TCD, using 50 mg of calcined sample. It was pre-treated under N_2 (20 mL/min) from room temperature to 150 °C (20 °C/min) and hold for 30 min at 150 °C, cooling it until 60 °C. Then it was heated up to 550 °C (10 °C/min) in 20 mL/min flow of H_2/Ar (5:95 v/v) mixture and held at this temperature for 60 min.

2.3. Catalytic evaluation

The catalytic tests were performed in a lab-scale plant, using a plug-flow reactor (i.d. 10 mm; bed length 30 mm) operating at 1.5 MPa and 250–350 °C, feeding a $CO:CH_4:CO_2:H_2 = 18.8:4.6:4.6:72.0$ (v/v %) gas mixture, typical of an exit stream from a SR reactor. Water was introduced in a pre-heater using a HPLC pump, maintaining the steam to dry gas (S/DG) values of 0.55 or 0.25 (v/v) and a contact time value (τ) between 0.25 and 1.00 s, higher than those used industrially, to stress possible deactivation phenomena. Before the catalytic tests, the samples were reduced by H_2/N_2 mixture by increasing H_2 concentration from 0.5 to 4.0 (v/v%), controlling the hot spot temperature at 230 °C, the pressure at 1.0 MPa and the GHSV value between 300 and 400 h^{-1}. The concentration of all components was measured both in inlet and exit dry gas (i.e. after water condensation) by means of a Perkin Elmer GC, equipped with TCD and FID with a methanizer and a Carbonsphere 80/100 packed columns (6 ft × 1/8 in.). The methanol (MeOH) concentration in the excess water condensed after reaction was measured offline using an Agilent 7890A GC, equipped with a FID and a CP-Volamine capillary column.

Table 1
Composition and physical-chemical properties of HT-ZAC precursors.

Sample	Cu (wt%)	(Cu + Zn)/Al (mol/mol)	Cu/Zn/Al (at. ratio %)	Phase detected by XRD	d_{HT} (nm)	BET surface area (m^2/g)
HT-ZAC13	10	3.0	11.6/63.4/25.0	HT, ZnO	24	26
HT-ZAC23	20	3.0	23.1/51.9/25.0	HT, ZnO	22	32
HT-ZAC33	30	3.0	34.5/40.5/25.0	HT, ZnO, malachite	18	42
HT-ZAC22	20	2.0	22.3/44.4/33.3	HT	20	36

HT = hydrotalcite-type phase.