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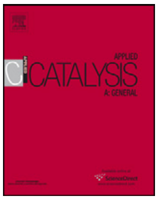

Highly active copper catalyst for low-temperature water-gas shift reaction prepared via a Cu-Mn spinel oxide precursor

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ABSTRACT

The effect of preparation method on structural properties and activity of Cu-Mn spinel oxide catalysts for the low-temperature water-gas shift reaction (LT-WGSR) has been studied. Single-step urea-combustion and coprecipitation procedures were used for synthesis of the catalysts. Catalyst characterization was performed by N_2 physisorption, XRD, HRTEM, CO-TPR, CO-TPD and FTIR spectroscopy. The WGS activity was evaluated in a conventional flow reactor in the temperature range of 140–240 °C. The influence of reaction gas mixture, including either idealized or realistic reformate, H_2O/CO ratio and contact time on activity were investigated. The catalytic activity tests carried out with both idealized and realistic reformate demonstrated the superior performance of the catalyst prepared by the single-step urea-combustion method. Moreover, comparison of the WGS activity of these catalysts with the one of a commercial CuO-ZnO-Al_2O_3 catalyst points out the potential application of Cu-Mn spinel oxide catalysts in LT-WGSR. The results revealed that the urea-combustion synthesis method is more appropriate than coprecipitation for the preparation of active and stable Cu-Mn spinel oxide catalysts for LT-WGSR.

1. Introduction

The water-gas shift reaction (WGSR) is a well-established industrial process for hydrogen generation through the conversion of CO present in reformate gas produced by steam reforming of hydrocarbons:

$$CO + H_2O \leftrightarrow CO_2 + H_2, \quad \Delta H_{298} = -41\ \text{kJ mol}^{-1}$$

During the last decades, WGSR has gained new research interest in relation to the production of pure hydrogen for fuel cell applications [1,2]. Two WGS reactors in series are employed industrially due to kinetic and thermodynamic constraints. The reactors operate in different temperature regimes with different catalysts: Fe_2O_3-Cr_2O_3 is employed as the high-temperature shift catalyst in the temperature range of 300–450 °C, while copper-based low-temperature shift catalysts are active at 200–250 °C. Among these, the CuO/ZnO/Al_2O_3 catalytic system is the state-of-the-art catalyst for LT-WGSR. However, it is not always applicable in fuel processors because of its sensitivity to poisons and deactivation after exposure to air or condensed water. Additionally, due to the pyrophoricity of this type of catalyst in reduced form, its reduction is complicated and needs careful temperature control. Currently, finely dispersed metallic copper supported on ZnO or ZnO–Al_2O_3 phases is considered to be the active phase. A good catalytic performance is related to the catalyst ability to restore the copper surface dispersion after reduction or oxidation pre-treatment [3,4]. The gradual recrystallization and sintering into larger copper aggregates influence negatively catalytic behavior [5–7].

Many research efforts are now directed to the development of cost effective catalysts with higher activity and stability compared to the conventional CuO/ZnO/Al_2O_3 catalytic system. The stability of the catalyst could be improved by applying novel preparation methods and also by using an appropriate support [8–10].

Copper-manganese spinel oxides have been found to show excellent WGS activity comparable to that of conventional CuO/ZnO/Al_2O_3 catalysts in spite of their low surface area [11–13]. Various synthesis procedures have been employed for the preparation of Cu-Mn spinel oxide catalysts for the WGSR: coprecipitation [8,11], organic acid complexation method [13], urea homogeneous coprecipitation method [13] and Pechini method [13]. The evaluation of WGS activity has shown that the use of citric acid as

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complexating agent leads to the preparation of catalysts with high activity. An additional advantage of the citric acid complexation method is the simple preparation route. Recently, some of us have demonstrated that the urea-nitrates combustion method is an attractive technique for the preparation of Cu-Mn catalysts with favorable characteristics and catalytic properties for steam or combined reforming of methanol [14,15]. In a recent work, Du et al. have studied the effect of the third metal on WGS activity and stability of Cu–Mn-M spinel catalysts (M = Ce, Zr, Zn, Fe, Al) [16]. These catalysts have been prepared by one-step urea-nitrates combustion method, similar to that described in [14,15] but at a fuel/oxidant ratio lower than the stoichiometric value.

In this study the emphasis is placed on the comparison of the effect of two preparation methods, namely coprecipitation and combustion, on the activity of Cu-Mn spinel oxides in the WGSR. Coprecipitation is one of the most frequently applied methods of catalyst preparation. It is very suitable either for the generation of a homogeneous distribution of catalyst components, or for the creation of precursors with a definite stoichiometry, which can be easily converted to the active catalyst [17]. However, the combustion synthesis offers several advantages over conventional preparation methods such as low processing cost and simple, solvent-free and quick preparation route, leading to homogeneous, high-surface-area materials without need of additional calcination steps. The catalytic behavior of Cu-Mn spinel oxides was studied under both idealized and realistic reformate gas mixtures and was compared with that of the commercial low-temperature WGS catalyst. Several characterization tools (XRD, HRTEM, TPR, TPD and FTIR spectroscopy) were used in order to gain new insight on the observed remarkable differences in catalytic performance.

2. Experimental

2.1. Catalyst preparation

Two different routes were used for the preparation of copper–manganese oxide catalysts with Cu/(Cu + Mn) atomic ratio of 0.30. The selection of this atomic ratio was based on the results reported in a recent study [15]. The combustion method (CB) was carried out as described previously [14]. It involves autoignition of a mixed solution of urea with manganese nitrate and copper nitrate (75% excess of urea) in an open muffle furnace (preheated at 400–500 °C). The resulting powder was further heated at 550 °C for 1 h in order to obtain the pure, well-crystallized Cu–Mn catalyst. The coprecipitation method (CP) takes place by mixing aqueous solutions of manganese and copper nitrate with Na_2CO_3 at 80 °C, keeping a constant pH value of 8.3 and aging the resulting precipitate at 80 °C for 6 h [18]. After aging, the precipitate is filtered and washed. Subsequently, the precipitate is dried at 100 °C and calcined at 700 °C for 7 h. The optimization of calcination temperature was carried out on the bases of XRD and catalytic measurements over samples, calcined at 600, 700 and 800 °C. The XRD patterns evidenced existence of cubic Mn_2O_3 phase and cubic non-stoichiometric spinel phase $Cu_{1.5}Mn_{1.5}O_4$ in all samples, but the best catalytic behavior was shown by the sample calcined at 700 °C.

The samples are labeled as CuMnCB (combustion method) or CuMnCP (coprecipitation method), respectively.

2.2. Catalyst characterization

The specific surface areas (S_{BET}) of the samples were determined by nitrogen adsorption-desorption at–196 °C using a Quantachrome Autosorb-1 instrument with the use of the BET (Brunauer–Emmett–Teller) method. Six relative pressures of nitrogen (p/p_0) in the range of 0.05–0.3 were employed.

Powder X-ray diffraction (XRD) patterns of the oxides were recorded with a Philips PW1830/40 powder diffractometer using nickel filtered CuKα radiation. The measurement was carried out in the 2θ angle range of 10–90°.

HRTEM analysis was performed using a side entry Jeol JEM 3010 (300 kV) microscope equipped with a LaB_6 filament. For analyses, the powdered samples were deposited on a copper grid, coated with a porous carbon film. All digital micrographs were acquired by an Ultrascan 1000 camera and the selected images were processed by Gatan digital micrograph. The Cu particle size distribution of the used CuMnCB sample (after reaction) was obtained by counting a statistically representative number of particles on 61 digital images.

Temperature-programmed reduction (TPR) experiments were performed in a conventional flow system [14] under a flow of a 1% CO/He mixture (50 $cm^3\,min^{-1}$) over 30 mg of catalyst using a heating rate of 10 °C min^{-1}. Prior to TPR, the catalysts were treated under air flow (20 $cm^3\,min^{-1}$) at 400 °C for 30 min. A mass spectrometer (Omnistar/Pfeiffer Vacuum) was used for online monitoring of TPR effluent gas. The curves in CO-TPR profiles correspond to CO consumption. These profiles correlate well with the corresponding profiles of CO_2 evolution. Adsorption of CO (CO-TPD) was carried out under a flow of 1% CO/He mixture. Following completion of the adsorption at room temperature, indicated by stable signal of CO in the mass spectrometer, the reactor was purged with pure He for 10 min. Then, the TPD run was started under a flow of 50 $cm^3\,min^{-1}$ He with a heating rate of 10 °C min^{-1}.

FTIR spectra were taken on a Perkin-Elmer 1760 spectrometer (equipped with a MCT detector) with the samples in self-supporting pellets introduced in a cell allowing thermal treatments in controlled atmospheres and spectrum scanning at controlled temperatures (CO adsorption was performed at −183 °C). Before the measurements, the samples were submitted to an oxidative pretreatment and a reductive one to mimic the effect of the reaction atmosphere. In particular, the oxidative treatment included heating from room temperature (r.t.) to 200 °C under outgassing; followed by an inlet of O_2 (20 mbar) and heating up to 400 °C; the O_2 was changed three times (20 mbar for 10 min. each one) at such temperature. The sample was then cooled down to r.t. in oxygen and finally outgassed at the same temperature. The reductive treatment was carried out (after oxidation) by heating from r.t. up to 200 °C in H_2 (10 mbar), keeping that temperature for 10 min. After that, the sample was cooled to r.t. under outgassing. The background, measured before introduction of CO, was subtracted from each spectrum. Band integration was carried out by “Curvefit”, in Spectra Calc (Galactic Industries Co.) by means of Lorentzian curves.

2.3. Catalytic activity measurements

WGS activity measurements were carried out in a flow reactor at atmospheric pressure. The following conditions were applied: catalyst bed volume = 0.5 cm^3 (0.63–0.80 mm pellets), space velocity = 4000 h^{-1}, partial pressure of water vapor = 31.1 kPa. The influence of the reaction gas mixture, including idealized (4.492 vol.% CO/Ar + H_2O) or realistic reformate (15 vol.% CO, 10 vol.% CO_2, 63 vol.% H_2, 12 vol. % $N_2 + H_2O$) was investigated. Before catalytic runs, the catalysts were subjected to a mild reduction under idealized reformate. Initially, the temperature was increased to 140 °C and kept for 2 h. Further on, the pre-treatment procedure included temperature increase in 20 °C steps (up to 240 °C) and soak for 2 h at each temperature.

Analysis of the reactor effluent gas was carried out on “URAS-3G” and “URAS-2T” (Hartmann & Braun AG) gas analyzers with respect to CO and CO_2 content at 40 °C intervals after steady-state