

Short Communication

Selective oxidation of gas phase ammonia over copper chromites catalysts prepared by the sol–gel process

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ABSTRACT

Selective gas phase oxidation of ammonia at atmospheric pressure was studied over a series of undoped and doped (Mn, Ag) copper chromites prepared by sol–gel process (SG). The catalysts were characterized by elemental analysis, X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and by adsorption microcalorimetry (AMC). A comparative study was made with a commercial copper chromite catalyst. The surface of the sol–gel undoped catalyst was found to be enriched in high valence chromium species with respect to the commercial one ($\text{Cr}^{6+}/\text{Cr}^{3+} = 0.56$ versus 0.39 for commercial catalyst). From XPS, the $\text{Cu}^{2+}/(\text{Cu}^0 + \text{Cu}^+)$ ratio was the same (*ca.* 5) in both catalysts but the sol–gel sample, contained twice more surface copper species (8.3 at.%) than the commercial one (17.6 at.%). Ammonia AMC experiments showed both a higher ammonia uptake and a wider strength distribution of adsorption sites on the sol–gel-prepared sample than on the commercial one. Improved catalytic performance in selective oxidation of ammonia at low temperature was obtained by simultaneous addition of silver and manganese to the sol–gel-prepared copper chromite.

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1. Introduction

Among renewable energy sources, biogas is of great importance for energy production but it might contain significant amounts of ammonia (200 to 4000 ppm) [1,2] in addition to its main two components, CH_4 and CO_2 . Biogas valorization can be made through dry or steam reforming [3–5] and catalytic combustion [6]. In order to prevent harmful emissions of NO_x , biogas needs to be purified from ammonia before use. Previous studies showed that supported noble metals catalysts are more active for selective ammonia oxidation [7–9] but less selective than metal oxides catalysts [10–12]. The latter catalysts have also the advantage to be much cheaper, which allows higher loadings to improve catalytic activity. There are several reports [13–15] concerning the variation of the reducibility of supported metal oxide species with loading or dispersion, and relating catalytic activity and reducibility. Particularly, supported copper oxide catalysts were found to be the most reactive for ammonia oxidation due to their higher reducibility, thus providing additional sites for oxygen activation. Although the reducibility and the precise oxidation state of copper species in these catalysts are still under debate in literature, XPS characterization indicates that lower oxidation states are favored [16,17]. This may indicate a partial reduction of supported copper oxides species. Based on previous studies, copper oxide species exhibit a superior ability to oxidize

ammonia into nitrogen and nitrogen oxides but the effect of both oxidation state and acidity of copper based oxides with spinel structure on ammonia oxidation is not yet studied.

In the present study, we report the catalytic activity of $\text{CuO}/\text{CuCr}_2\text{O}_4$ and CuCrO_2 compounds in which copper species are both dispersed on and inserted into the crystal lattice of the solid. This is expected to prevent copper species from agglomeration and promote their dispersion, resulting in an enhancement of catalytic activity and stability.

The catalytic properties of a sol–gel-prepared copper chromite in selective NH_3 oxidation are compared to that of a commercial one in order to elucidate the effect of both the amount and the valence of surface copper and chromium species on catalytic activity. The oxidation state of Cu and Cr are studied by XPS and the acid–base properties by microcalorimetry of NH_3 adsorption. The influence of doping by Mn and Ag on catalytic properties of sol–gel samples is also addressed.

2. Experimental

2.1. Catalysts preparation

The catalyst was prepared (Fig. 1) by dissolving separately under constant stirring in liquid propionic acid (Aldrich 99%) at 85 °C, copper nitrate pentahydrate (Alpha Aesar 98%) and ammonium bichromate (SIGMA-Aldrich >97%). For some preparations, manganese acetate (Alpha Aesar 99%) or both silver nitrate (SIGMA-Aldrich 99%) and manganese acetate were also added to the solution.

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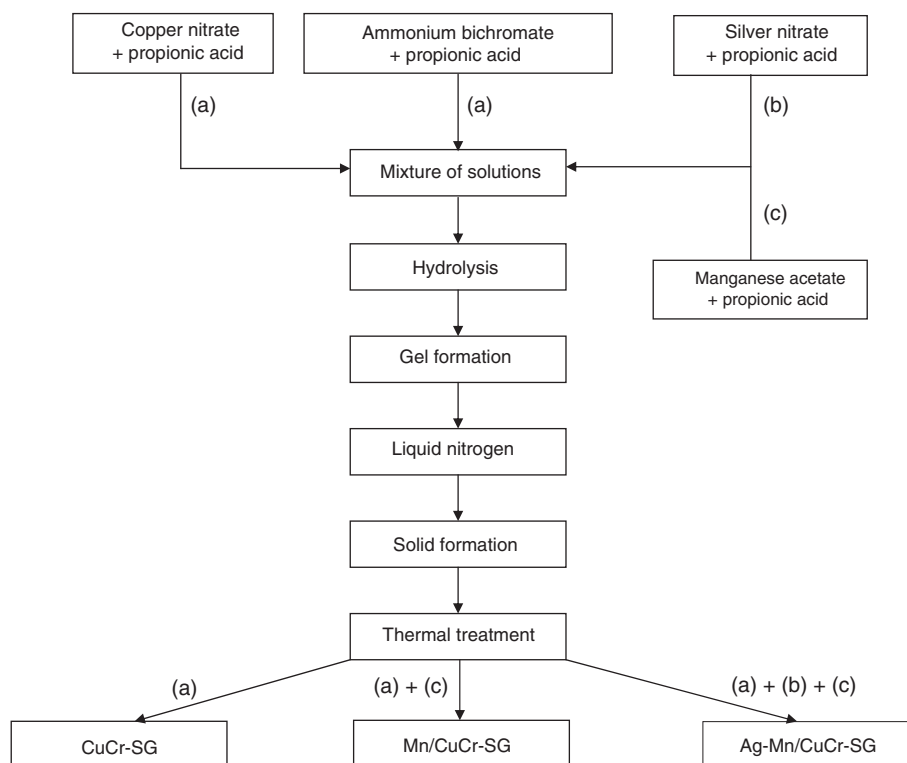


Fig. 1. Synthesis scheme of undoped and Ag and/or Mn-doped CuCr-SG precursors.

Ammonium bichromate dissolution was made separately and stepwise by addition of small quantities of the salt to the propionic acid solution under stirring. When the dissolution of all the components led to a transparent solution, the solution of Cr precursor was mixed under stirring with the solution of Cu (and Ag and/or Mn for doped samples). Then the transparent mixture was hydrolyzed by a few drops of distilled water and evaporated slowly (using a rotary evaporator) till obtaining a viscous colored gel containing a homogeneous mixture of Cr and Cu species (and Mn or Ag + Mn for promoted samples). The obtained polymer, composed of M–O–M or M–(μOH)–M bonds, was then reduced to a powder by treatment with liquid nitrogen. The resulting solids were crushed and heated in nitrogen at 450 °C/3 h. A slow heating ramp *ca.* 1 °C min^{−1} was used in order to avoid excessive heat flow and even explosive reactions.

2.2. Catalysts characterization

X-ray diffraction patterns of the samples were recorded using a Siemens D 5000 diffractometer with filtered CuKα radiation (count time of 1 s in the range 2θ of 5–70°).

The adsorption microcalorimetry experiments were performed at 80 °C in a heat-flow microcalorimeter (Tian-Calvet type, C80 from Setaram) linked to a conventional volumetric apparatus and equipped with a Barocel capacitance gauge (Datametries) for pressure measurements. The catalysts, *ca.* 100 mg, were outgassed at 350 °C overnight then cooled at 80 °C prior to ammonia adsorption. The differential heats of adsorption were measured as a function of coverage by repeatedly contacting the sample with small doses of NH₃ and waiting for the equilibrium to be reached each time.

XPS analyses were carried out using a surface Science Instruments M-probe. The system was equipped with a reaction chamber where the sample can be activated before analysis. A monochromatic AlKα radiation source (1486.6 eV) was used. XPS signals were recorded with a spot size of 200 × 750 μm and a pass energy of 25 eV (resolution equal to 0.74 eV). An argon ion gun (VG EX05, 5 keV) to clean the

metal foils and an electron flood gun (electron Energy 3 eV) have been used to compensate the accumulation of positive charges.

The binding energy scale was calibrated using the 2p_{3/2} level (932.47 ± 0.07 eV) and the 3 s level (122.39 ± 0.15 eV) of a sputtered copper foil and the 4f_{7/2} level of a freshly evaporated gold film (84.00 ± 0.10 eV). The 1 s level of carbon (284.6 eV) in hydrocarbon contaminants always present in the samples was taken as internal reference. The binding energy values and the atomic percentages were determined within ± 0.2 eV and ± 3% respectively.

Catalytic activity in gas phase ammonia oxidation was measured between 120 and 400 °C using 200 mg sample (2–3 μm), a reaction mixture containing 1000 ppm NH₃, 10% O₂ in He balance at a flow rate of 6.5 L · h^{−1} (GHSV = 26,000 h^{−1}).

The reactor was a quartz U-tube, 30 cm long and 0.5 cm i.d. at the catalytic bed section, mounted vertically in a tubular furnace. The temperature was measured using a thermocouple introduced into the reactor and in contact with the catalytic bed.

Preliminary tests have been carried out to verify the absence of diffusion limitations. Several runs have thus been performed by varying both the flow rate and the catalyst weight while maintaining the same contact time. Tests have also been carried out using different particle sizes of the same catalyst.

The reactor effluents were periodically sampled and analyzed by using an Agilent micro-chromatograph equipped with high sensitivity (5 ppm) thermal conductivity detectors. NO_x composition of the effluents was determined using a Rosemount Analytical NGA 2000 instrument.

3. Results and discussion

Transition metal oxides are considered of great interest for ammonia oxidation. However, these materials usually possess particularly low specific surface areas, which greatly compromise their practical use. Copper chromites considerably improve their catalytic performances when prepared as nanostructured materials [18]. This study focuses on an alternative synthesis method based on sol–gel process, using

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