Assignment-6
Experimental methods in Catalysis Assignment
Submitted by
Kundan Kumar (CA19M005)
Catalysis Technology

Study by situ electrical conductivity measurements of semiconductive and catalyst properties of copper ferrite.

Introduction

The in situ electrical properties and the catalytic activity of copper ferrite obtained by co-precipitation and thermal decomposition of polynuclear coordination compounds were studied in the propane oxidation reaction. The sample prepared by complexation had a better catalytic activity.

Catalytic oxidation is one of the most efficient processes for volatile organic compound (VOC) destruction because it takes place at lower temperatures than those required for thermal destruction. Most of the catalysts used for VOC destruction are noble metal based catalysts. In recent years, many efforts have been directed towards the design of catalytic materials based on transition-metal mixed oxides as a replacement for noble metal catalysts. These materials can offer a range of technical and commercial advantages that make them a valuable alternative to noble metals. Among them, ferrites widely used in other applications (computer peripherals, telecommunication equipments, permanent magnets, for electronic and microwave devices), have been used as active catalysts in various catalytic reactions, as hydrocarbon oxidation, oxidative dehydrogenation, decomposition of alcohols and peroxides and decarboxylation of some organic acids, electro-catalytic activity and resistance to corrosion Copper ferrite can be successfully used in catalysis for the water gas shift reaction , CO oxidation and NOx reduction.

The use of these ferrites as depolluting agents or as gas sensors has received increasing attention.

Experiment

The catalysts were prepared by non-conventional methods, i.e thermal decomposition of polynuclear coordination compounds. For the sample (Cu_II), a soft chemical method was applied, i.e. thermal decomposition of the corresponding tartrate as a precursor.
Copper and iron nitrate solutions (1:2 of cation ratio) were mixed with an aqueous solution of tartaric acid (1:4 ratio of cations/tartaric acid). Ethanol solution was added until a yellow green precipitate was formed. The pH was carefully controlled (5.5–6) by adding an NH4OH:ethanol (1:1) solution. Complete precipitation required 24 h and a repeated adjustment of pH. The polynuclear coordination compound obtained ((NH4)[Fe2Cu(C4H4O6)2(OH)5]_9H2O) was submitted to thermal treatment, 800 C for 2 h in order to obtain well crystallized copper spinel.

The specific surface and the pore size distribution of the samples were determined from the nitrogen adsorption/desorption isotherms at the boiling point of liquid nitrogen under atmospheric pressure (77 K) on samples outgases at 378 K using Micromeritics ASAP 2000 equipment.

The electrical conductivity measurements were performed on the catalyst powder, under operando conditions, i.e. in gas flow, using the differential step technique (DST) and monitoring continuously the composition of the inlet/exit gas (on-line coupled gas chromatograph) at atmospheric pressure . A precision RLC Bridge (Hioki 3532-50 LCR HiTester), measuring the admittance Y at 1,592 Hz allowed the following of the evolution of conductance (G) in a specially designed conductivity cell filled with catalyst grains. The conductivity r (S/m) was calculated from the corresponding G values (for the cell, Go and for the cell-sample system G) by taking into account the special cylindrical geometry of the sample.

$$\sigma = (G - G_o) \times \frac{\ln \frac{r_2}{r_1}}{2\pi x}$$

where r1 and r2 represent the electrodes radius in the cell and x represents the fraction of the volume occupied by the sample in the annular space.

For the testing of the catalytic properties, experiments were done on the same batch of sample that was previously used in electrical conductivity measurements. Catalytic tests were performed in a fixed-bed flow reactor at atmospheric pressure, between room temperature and 450 _C, with 0.5 cm3 (*500 mg) of catalyst grains (size fraction between 0.2–0.5 mm), for propane:oxygen (from air) molar ratios between 1:0.9 and 1:6, at different contact times 1 and 2 s. The conversion data reported at each reaction temperature were the average of at least two steady-state measurements. The effluent composition was analyzed on-line by gas chromatography.

The propane conversion C (%) was calculated as follows:

$$C(\%) = \frac{C_3H_{8_{in}} - C_3H_{8_{out}}}{C_3H_{8_{in}}} \times 100$$

In the sample of the Cu_II, the changes induced by the catalytic tests are much more evident, a considerable amount of CuFeO2 (*47%) appears in the sample.
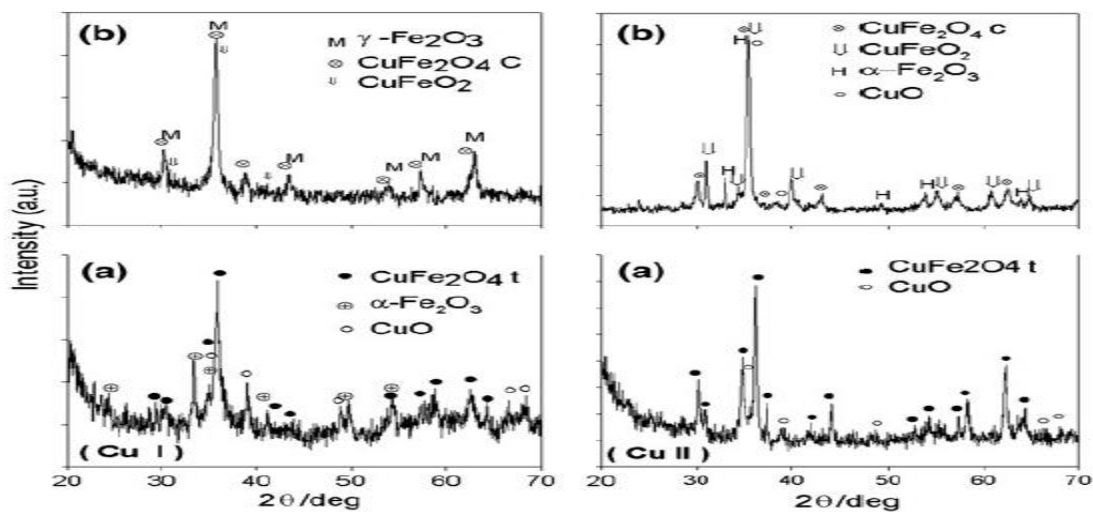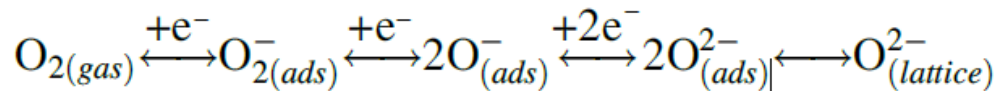

XRD spectra of CuFe2O4 (a fresh samples; b tested samples)

we observed a slight increase of the specific surface area. This effect is probably related to the severe phase transformation and reconstruction phenomena that occur in the sample after the catalytic tests. The electrical conductivity measurements on sample show that the copper ferrite behaves generally like an n-type semiconductor: lower conductivity after treatment in oxygen, higher conductivity in inert or reductive atmosphere.

The peculiarities of the surface interaction with a certain atmosphere can be evidenced by comparing the temperature dependence of the conductivity in a specific cycle with the previous and the subsequent runs, and by correlating the changes with the composition of the exit gas, as for instance the reaction products in catalytic tests. The decrease of conductivity r, by oxygen treatment is a result of oxygen ion adsorption, as follows:
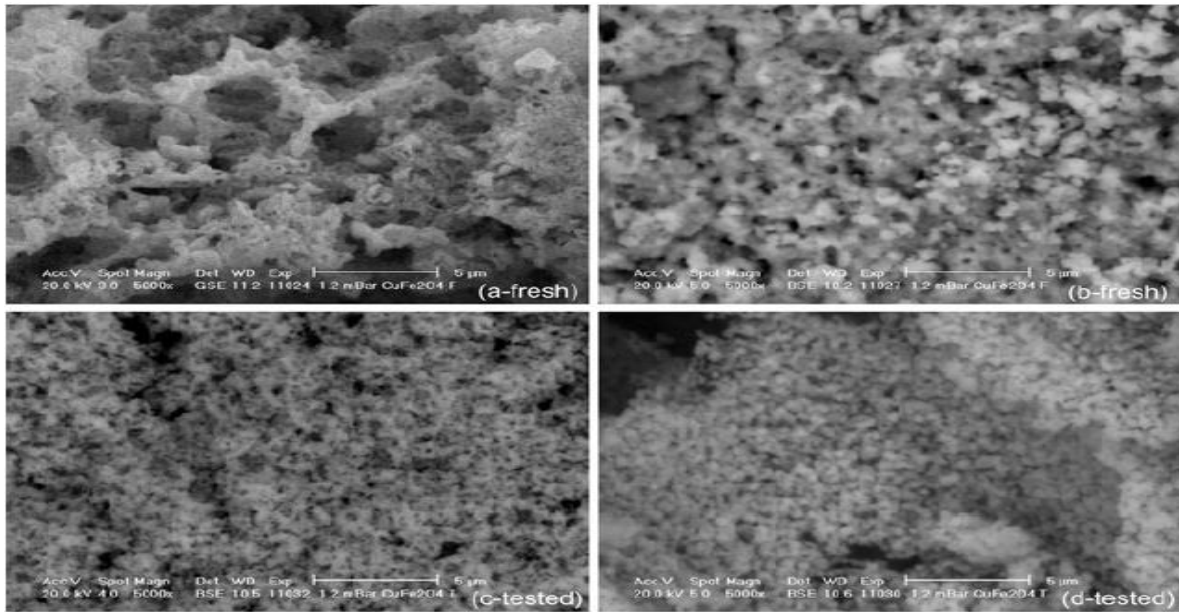

SEM micrographs of the investigated samples (a and c, Cu_I; b and d, Cu_II)

$$O_{2(gas)} \xrightarrow{+e^-} O_{2(ads)}^- \xrightarrow{+e^-} 2O_{(ads)}^- \xrightarrow{+2e^-} 2O_{(ads)}^{2-} \longleftrightarrow O_{(lattice)}^{2-}$$

The oxide surface provides the electrons that are trapped by the adsorbed oxygen species . The changes in slope indicate an increase of lattice mobility connected

with a possible phase transition for both samples. In a hydrocarbon-containing atmosphere, the absolute values for the conductivity were higher indicating the surface reduction of the samples. The higher values of the electrical conductivity in a reductive environment compared to those obtained in inert gas can be explained by the fact that the catalyst in contact with the hydrocarbon (n-type semiconductor) is enriched in free electrons. Interaction with a reducing gas, such as a hydrocarbon (i.e., propane), results in the formation of anion vacancies (redox type mechanism) acting as electron donors.

The conductivity pattern observed in the presence of hydrocarbons looks rather complex indicating possible multiple phase transitions. This behavior is certified by the XRD data presented on the used samples, one can observe the appearance of a reduced phase, CuFeO2. The values for the apparent activation energies Ea of conductivity, evaluated from the linear sections of lnr versus 1/T plots, also indicate different type of electrical behavior on samples. The changes can be ascribed to different conductivity mechanisms with different activation energies depending on the environment. The Cu_I sample shows higher energy values than the Cu_II sample. This behavior can be correlated with the phase composition as the Cu_I sample contains the individual oxides beside spinel structure; the activation energies of the materials are also larger than the copperm ferrite band gap of *0.4 eV.
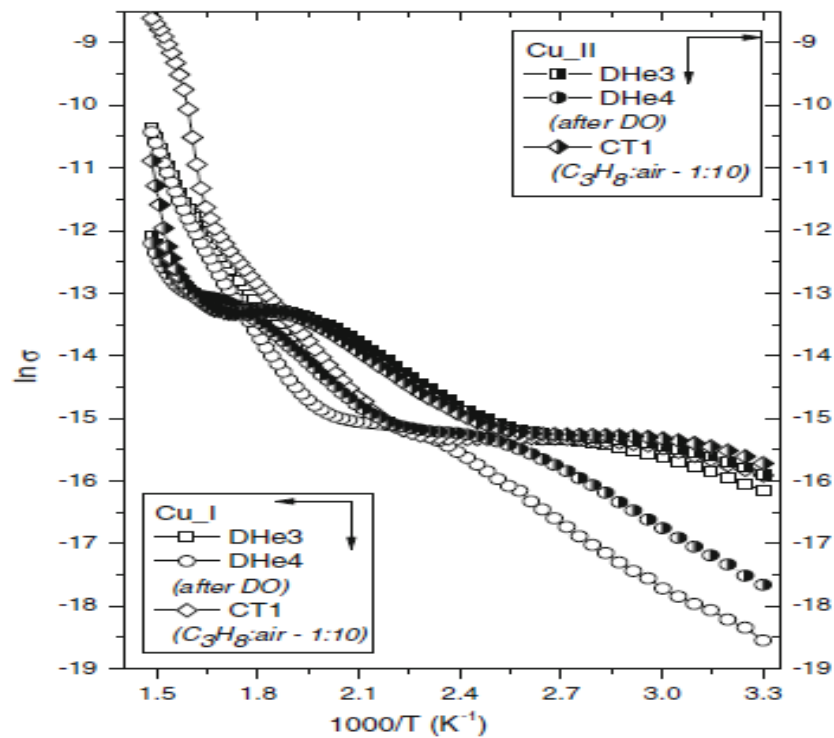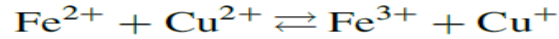

Arrhenius plots of conductivity in reductive atmospheres

It was reported that copper ferrite could act both as n- and p-type semiconductors. The electrical carriers can be generated by the following redox reactions.

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-_{(electron)}|$$

$$Cu^{2+} \rightleftharpoons Cu^+ + e^+_{(hole)}$$
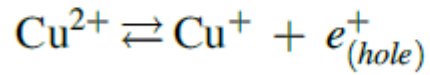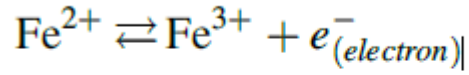
From above equation;

$$Fe^{2+} + Cu^{2+} \rightleftharpoons Fe^{3+} + Cu^+$$

The type of carriers and their concentrations depends on the reaction kinetics. The higher conductivity values obtained for the Cu_I sample in the presence of hydrocarbon containing atmosphere are due to the increasing number of Fe2+ centres, which act according to the electron-hopping model   The electron hopping occurs by electron transfer between adjacent octahedral sites in the spinel lattice.

After the treatment in humid oxygen(c %), the conductivity values were higher at low temperature indicating that the water adsorption increases the surface conductivity due to proton conduction by vehicle type mechanism . We can assume that the water adsorption at intergrain area is screening the oxygen adsorption in this temperature range.
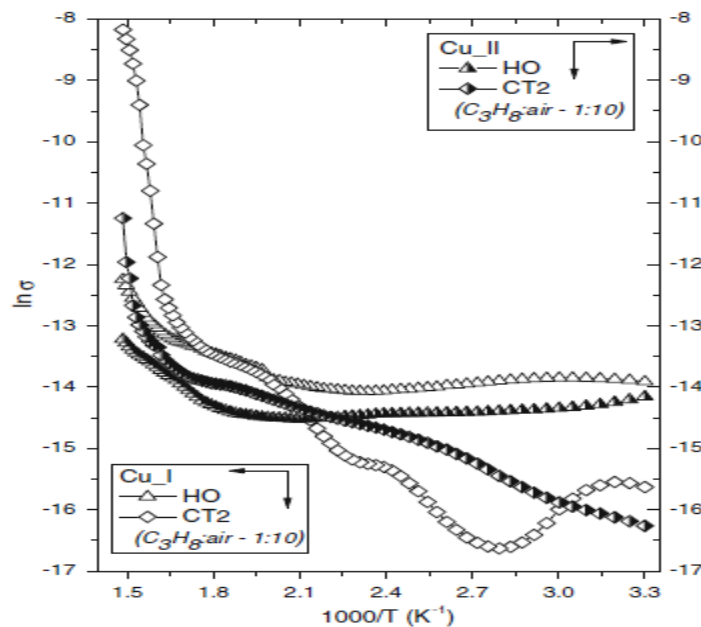
Arrhenius plots of conductivity—the influence of humidity

The sample prepared by the thermal decomposition of the tartrate complex (Cu_II) is the most active one, reaching 100% conversion of propane at 673k for propane/oxygen molar ratio of 1:4 with total selectivity to CO.

Conclusion

Two non-conventional synthesis routes, co-precipitation and thermal decomposition of polynuclear coordination compounds were successfully utilized to synthesized copper ferrites (CuFe2O4) samples. The catalytic properties of the obtained copper ferrites and in situ AC electrical conductivity measurements were investigated in propane total oxidation reaction. These materials show good catalytic properties in propane total oxidation. The sample prepared by the complexation method is the most active one, reaching 100% conversion of propane at temperatures below 673k.
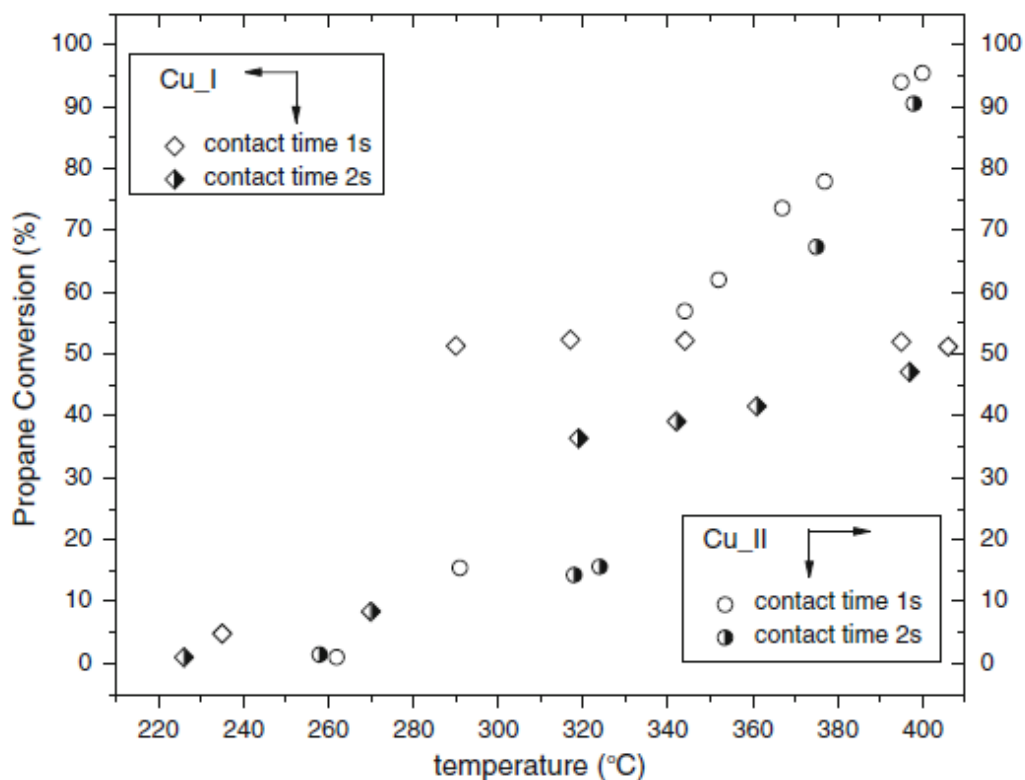
Propane conversion on CuFe2O4 (propane/oxygen ratio—1:2)

The presence of CuFeO2 after the catalytic tests suggests that propane oxidation on copper ferrite occurs via a redox-type process. This finding is also supported by the

analysis of residuals during electrical conductivity measurements, particularly in the absence of the oxygen in the feed.