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Research Paper

Synthesis and Characterization of Magnesium Copper Chromite Spinels

Chemistry

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ABSTRACT

Various composition of copper magnesium chromite spinels (Cu1-x MgxCr2O4 with x=0, 0.25, 0.5, 0.75, 1.0) were synthesized by co-precipitation method. The catalysts were characterized by various Physico-chemical methods XRD, nitrogen adsorption studies, FT-IR spectroscopy, Thermogravimetric analysis (TG), UV-DRS and Temperature Programmed Desorption of NH3. Magnesium chromite posses large surface area and crystal size among the synthesized materials.

Introduction

Spinels show interesting catalytic properties. In these compounds electric and magnetic properties are controlled by the nature of the ions, their charge and their distribution among tetrahedral and octahedral sites. The catalytic activity of spinels containing transition metal ions is influenced by the redox properties and the acid base properties of these ions. Good correlation between catalytic activities and the electric and magnetic properties of spinels is often found. This is a direct consequence of the dependence of both properties on cation distribution between T and O sites.

Chromite spinels have general formula MCr_2O_4; where M is a bivalent metal ion. All MCr_2O_4 chromites have normal spinel structure with M in tetrahedral sites because of strong preference of Cr^{3+} ions for octahedral sites [1]. This was confirmed by thermodynamic and quantum chemical calculations .$MgCr_2O_4$ have normal spinel structure with space group Fd3m (Oh^7). The primitive rhombohedral unit cell contains two formula units, with oxygen ions forming ccp structure . The Cr and Mg ions in $MgCr_2O_4$ are octahedrally and tetragonally co-ordinated by oxygen ions. It has high melting point and low thermal conductivity and has some paramagnetic effect at 380-400°C [2]. It is used as refractory material [3-4].

2. Materials and Experimental procedures

2.1Materials

The materials used for the preparation and catalytic activity measurements are Cu $(NO_3)_2.3H_2O$, Mg $(NO_3)_2.6H_2O$, Cr $(NO_3)_3.9H_2O$, NaOH , Aniline and Methanol (Merck).

2.2 Synthesis of catalyst

Stoichiometric masses of the metal nitrates were accurately weighed out and dissolved in distilled water to get 10% solutions. To metal nitrate solution 10% NaOH solutions are added drop-by-drop and stirred well by using a mechanical stirrer. pH of the first series was adjusted between 9 and 10 while for the second series it was adjusted to 8.5.The precipitation is carried out at a temperature of 80°C.The precipitate was kept overnight for ageing and then washed several times with distilled water until free from nitrate ions and alkali .It was filtered, dried in an oven at 80°C for 24hrs and the dried materials were powdered and sieved below 75µm mesh. The powdered samples were calcined at 500°C for 6hrs to achieve complete spinel phase formation. When x=0, 0.25, 0.5, 0.75, 1.0 $Cu_{1-x}Mg_xCr_2O_4$ series were designated as CC, CMC 1, CMC 2, CMC 3, MC respectively.

2.3 Characterization of synthesized materials

The XRD pattern of catalyst was taken by using Philips diffractometer (PW 1710). A stationary Ni filtered Cu Kα radiation (λ=1.5404A°) and a movable detector, which measures the intensity of diffracted radiation, as a function of 2θ are the main parts of the instrument. Micromeritics Gemini surface area analyzer was used to determine the surface area with nitrogen as adsorbate. The TG analysis of the chromite samples were carried out using thermal analyzer with heating rate 10°Cmin^{-1}from Perkin Elmer, Pyris Diamond in nitrogen atmosphere. Electronic spectra of samples were recorded in a reflectance mode using solid samples. The spectra were recorded at room temperature between 200-1500nm using MgO as standard in the Ocean optics instrument, Inc.SD 2000, Fiber optic spectrometer with a charged coupled device (CCD) detector.

3. Results and discussion

3.1 XRD

A sharp peak observed at 35° is due to the spinel phase formed and characteristic of (311) plane [5]. By the addition of iron, lattice parameter decreases. This is due to the addition of Fe^{3+}ions into octahedral sites. The XRD peak for Mg substituted Cu-Cr spinels show the presence of spinel phase formation. It can be observed that, spinel phase was formed at 500°C hence it was taken as optimum calcination temperature for the prepared chromites. Table 1 shows XRD data for $Cu_{1-x}Mg_xCr_2O_4$ series. Fig.1 represents the X-ray diffractogram of $Cu_{1-x}Mg_xCr_2O_4$ series. The results confirm the crystal structure of the systems. MC has highest crystallite size in the $Cu_{1-x}Mg_xCr_2O_4$ series. Crystallite size is calculated by Scherrer equation [6, 7].

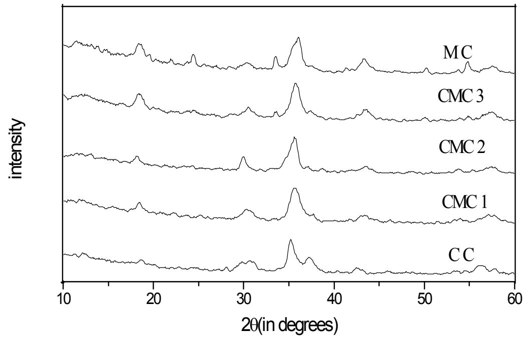

Fig.1 X-ray diffractogram of $Cu_{1-x}Mg_xCr_2O_4$ series.

Table 1 XRD data for $Cu_{1-x}Mg_xCr_2O_4$ series

CATALYST	d_{hkl} (d-spacing) (A°)	Lattice parameter (nm)	Unit cell volume (nm^3)	Crystal size (nm)
CC	2.5539	4.4234	86.5503	10.61
CMC1	2.51852	4.3621	83.0017	8.45
CMC2	2.51004	4.3474	82.1654	9.13
CMC3	2.47961	4.2947	79.2134	7.05
MC	2.48289	4.3004	79.5292	49.57

3.2 BET Surface area and pore volume measurements

The BET and Langmuir surface areas and total pore volume of the different compositions of the chromite samples calcined at 500°C were measured by nitrogen temperature (Micromeritics Gemini Analyzer). The data are shown in the Table 2. The different series of chromite spinels prepared by low temperature co-precipitation technique possess high surface area. It is observed that MC is having the highest surface area among the chromite spinels.

Table 2
Surface areas and total pore volume of different Magnesium chromite spinels

CATALYST	SURFACE AREA (m^2/g)		PORE VOLUME (cm^3/g)
	BET	LANGMUIR	
CC	26.8	39.2	0.09
CMC1	49.7	72.9	0.09
CMC2	58.8	86.7	0.10
CMC3	58.6	86.3	0.09
MC	82.2	121.4	0.21

3.3Thermal Analysis

TG analysis provides information about the stability of the catalyst upon thermal treatment. A small endothermic peak is observed around 100°C is due to the loss of residual water. A small exothermic peak near 450°C is due to the crystallization of spinel structure .The horizontal behavior of the curves indicated the stability of the sample. The chromite samples are stable from 500°C. (Figure is not given).

3.4 Ultraviolet-Visible Diffuse Reflectance Spectroscopy (UV-vis-DRS)

The UV-DRS spectrum is taken in the range 200-1500nm regions. Peaks observed in the region 230-300 nm are assigned to M-O bonds in tetrahedral sites. This is due to charge transfer transition.

3.5 Surface Acidity measurements by TPD –NH_3

Spinels have both Lewis and Bronsted acid sites [8]. The quantitative amount of acid site in the specified temperature range is characterized by TPD of ammonia . It allows the determination of both the protonic and cationic acid centers. In this method, the interaction of acid sites and basic ammonia molecule is studied to determine the amount and strength of acid sites . The acid site distribution pattern can be classified into weak (desorption at 100-200°C), medium (201-400°C) and strong (401-600°C) acid sites. Table 4 represents acidity values of $Cu_{1-x}Mg_xCr_2O_4$ series. It is observed that CMC 2 has high acidity value in $Cu_{1-x}Mg_xCr_2O_4$ series.

Table 3
Acidity values of different chromite spinels

CATALYST	NH_3 desorbed (m $molg^{-1}$)			
	Weak 100-200°C	Medium 201-400°C	Strong 401-600°C	Total 100-600°C
CC	0.12	0.13	0.02	0.27
CMC1	0.15	0.028	0	0.18
CMC2	0.15	0.11	0.06	0.32
CMC3	0.16	0.08	0.02	0.26
MC	0.11	0.06	0.05	0.22

Conclusions

Chromite samples were synthesized via co-precipitation method and XRD results confirm the spinel phase formation. BET surface area measurements reveal that there is considerable increase in surface area in Mg substituted Cu-Cr spinels and MC has highest surface area. UV-DR spectral analysis shows the presence of charge transition between tetrahedral metal and oxygen. Thermal analysis explains the thermal stability of samples. CMC-2 shows highest acidity

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