

Synthesis and Investigation the Catalytic Behavior of Cr₂O₃ Nanoparticles

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Abstract

The use of an inorganic phase in water-in-oil (w/o) microemulsion has recently received considerable attention for preparing metal oxide nanoparticles. This is a technique, which allows preparation of ultrafine metal oxide nanoparticles within the size range 40 to 80 nm. Preparation of nano chromium (III) oxide studied investigated in the inverse microemulsion system. Therefore the nucleation of metal particles proceeds in the water capsules of the microemulsion. the main advantage of this method is easily controllable conditions with using low cost chromium source is merit to be considered for scaling up by industrial researchers. Besides we mainly focus on the catalytic property nano chromium (III) oxide. Oxidation of aromatic aldehyde/alcohol to the corresponding carboxylic acids can be performed highly efficiently in the presence of a catalytic amount of nano chromium (III) oxide in THF as solvent under mild conditions.

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1. Introduction

Among inorganic nanoparticles, chromium (III) oxide (Cr₂O₃) nanoparticles have received great attention due to its numerous application domains, including green pigments [1], heterogeneous catalysts [2-4], coating materials for thermal protection [5-6], hydrogen storage [7-9], digital recording system [10], photonic and electronic devices [11-12]. Various techniques have been developed to synthesize Cr₂O₃ nanoparticles such as hydrothermal [13], solid thermal decomposition

[14], combustion [15], sol-gel [16], precipitation-gelation [17], oxidation of chromium in oxygen [18], laser induced deposition [19], mechanochemical reaction and subsequent heat treatment [20] and sonochemical methods [21]. The basic and traditional process used by the manufacturers consists of reducing an alkali dichromate by sulphur, carbon, wood or ammonium chloride [20]. But since either these processes are complex or their reaction apparatus are expensive, most of them have difficulties in

being industrialized. Some new methods of preparation should be explored.

In the present study, a simple and original method for the synthesis of nanosized Cr_2O_3 chromium oxide by sol-gel technique in nano and micro micelles is described. The surface properties, size, morphology and crystallographic structure of Cr_2O_3 particles are characterized by means of X-ray diffraction (XRD), transmission electron microscope (TEM) and scanning electron microscope (SEM) which will give much valuable information about these materials. In addition oxidation properties of chromium (III) oxide (Cr_2O_3) nanoparticles will be compared with Cr_2O_3 powder. Catalytic behavior of Cr^{+3} oxide-based nanocatalysts, on the oxidation of aldehydes and alcohols are reported.

2. Experimental procedure

Preparation of nanoparticle

All reagents were purchased from Aldrich or Merck and were used without further purification. Experimental procedure for the chromium (III) oxide (Cr_2O_3) nanoparticles are briefly summarized in Fig.1. CrCl_3 , NaOH, purified soybean oil, Tween 80 and distilled water were used in the experiments.

Nanoparticles were synthesized by the following steps: CrCl_3 (0.30 g) in water (1 mL) and 4% Tween 80 (2 mL) were added into purified soybean oil (30 ml) under mechanical stirrer with 2000 rpm until obtaining a nearly clear emulsion. This solution was referred to as solution A. NaOH(0.16 g) was dissolved into 1.5 ml of water was added into solution A under mechanical stirrer with 2000 rpm for 2 h at room temperature and then the reaction mixture was filtrated. The precipitate was washed with absolute water (300 ml) for 3 times.

This material was calcinated in electronic oven at $200\text{ }^\circ\text{C}$ for 1 h. the obtained powder was green.

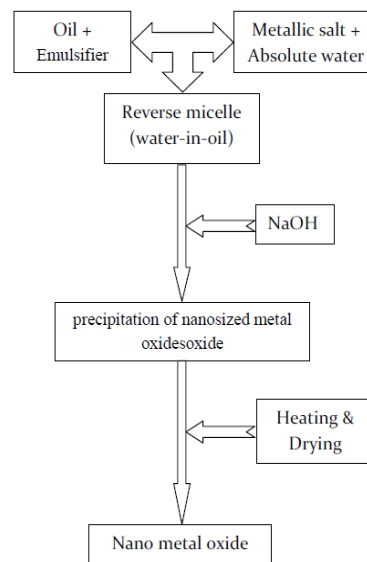


Fig. 1. Experimental procedure for the formation of nano metal oxide by the emulsion approach

The resulting powder X-ray diffraction was conducted on a Philips Analytical XPERT diffractometer using a $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056\text{ \AA}$) with a MINIPROP detector and operating at 40 kV and 40 mA. X-ray diffraction patterns were recorded between $2\theta = 5^\circ$ and 79° with a step of 0.04° and a time of 0.8 s by step. The crystallographic data of the resulting Cr_2O_3 powders were collected by using the PC-APD, Diffraction software. Surface morphologies of the specimens were observed with a scanning electron microscope (SEM, Philips XL-30). The ordered nano structures of Cr_2O_3 can be further confirmed by transmission electron microscope (TEM, Philips KV-120).

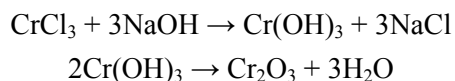
Oxidation of aldehydes

Aldehyde/alcohol (1 mmol) was slowly added dropwise to the mixture of nano Cr_2O_3 (100 mg) and

H₂O₂ (0.6 ml, 5 mmol, 30%) and THF (5 ml) at 50 °C. The mixture was stirred for a specified period (Table 1). The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction was quenched with aqueous potassium carbonate and then the reaction mixture was extracted with 20 ml diethyl Ether. The organic layer acidified with HCl (2N, 20 ml), dried over anhydrous MgSO₄ the solvent was evaporated to give the carboxylic acid. All the products gave satisfactory spectral data.

3. Results and discussion

The synthesis of nano chromium (III) oxide (Cr₂O₃) were carried out with the concurrent addition of sodium hydroxide and increasing the stirring time, to prevent excessive grain growth and aggregation of nanoparticles. The overall reaction scheme is shown below:



This is a multi step process that involves the transformation of the salt of metal to an metal hydroxide Cr(OH)₃ followed by the dehydration to form an oxo-hydroxide intermediate, that will constitute the precursor in the sol-gel process. In this study, when the mixture of CrCl₃, soybean oil (containing Tween 80) and water were mixed with mechanical stirrer, water solution was dispersed in the oil phase and Tween 80 assembled at the water/oil interface, acting as the emulsifier for the formation and stabilization of emulsion. The water solution was in the droplets and the oil solution became the continuous phase, hydroxyl groups in the droplets of water emulsion diffused to the water/oil interface, a part of which reacted with CrCl₃ to form chromium (III) oxide. In order to

characterize the nature of the Cr₂O₃ nanoparticles, SEM, TEM and XRD measurements were carried out. Fig. 2 shows SEM images of the Cr₂O₃ powder. The Cr₂O₃ powder shows agglomeration of particles, with diameters ranging from 40 to 80 nm.

The morphology of the prepared Cr₂O₃ nanoparticles was characterized by SEM and TEM images as shown in Figures 2-4. From images results, we can observe a large quantity of uniform nanoparticles (NPs) with average particle size of 40-80 nm, indicates that our synthesis process is an easy method for the preparation Cr₂O₃ nanoparticles. The corresponding diffraction patterns are shown in the insets. Fig. 5 shows the XRD patterns of Cr₂O₃ powders. Its average particle size was 50.78 nm. That calculated through the Scherrer's formula $D=0.89\lambda/B\cos\theta$. D, λ , B and θ were the average particle size, the X-ray wavelength, the angular line width of half maximum intensity and the Bragg's angle respectively. The FTIR spectrum of Cr₂O₃ NPs is shown in Figure 6. Two sharp peaks displayed at 705 and 760 cm⁻¹ attributed to Cr-O stretching modes, are clear evidence for the presence of the crystalline Cr₂O₃.

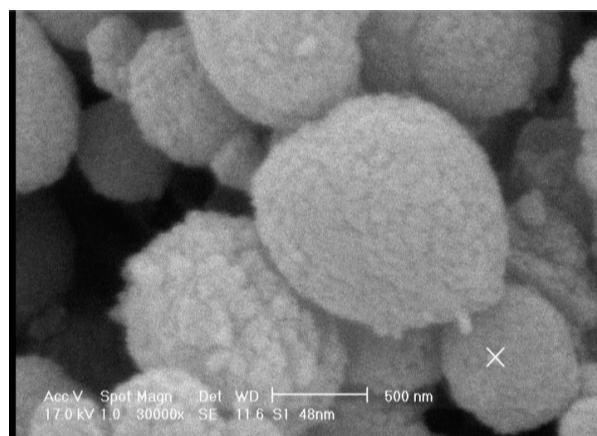


Fig. 2. SEM image of the Cr₂O₃ nanoparticles

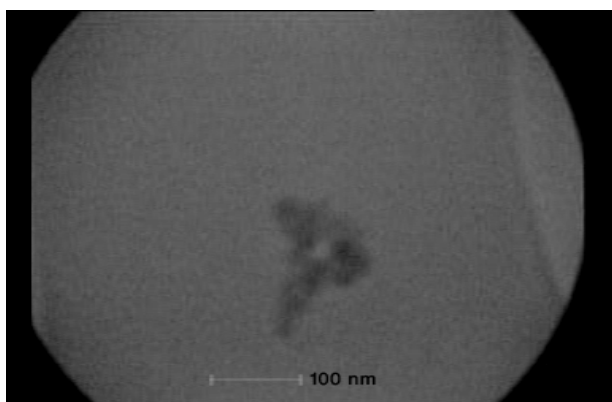
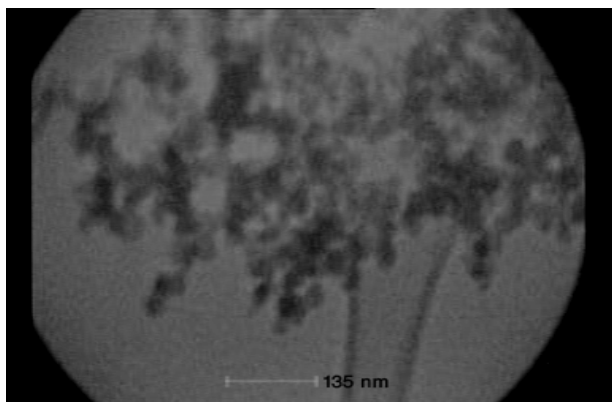


Fig. 3 & 4. TEM image of the Cr₂O₃ nanoparticles

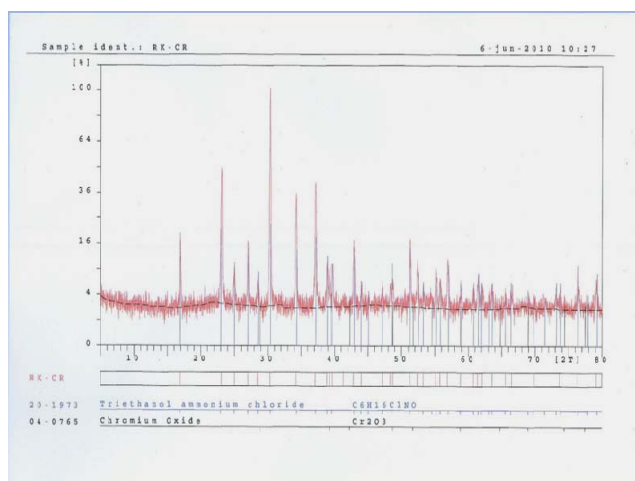


Fig. 5. XRD pattern of the Cr₂O₃ nanoparticles

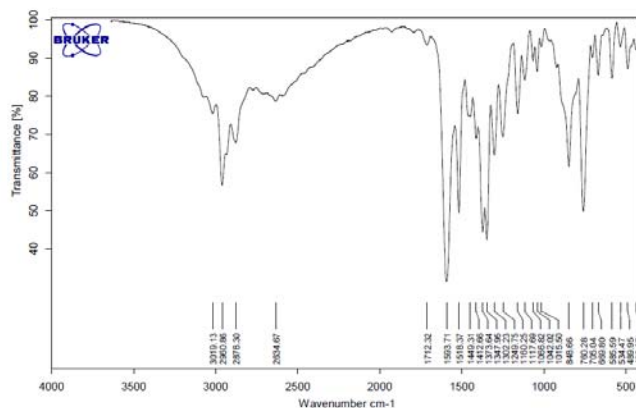
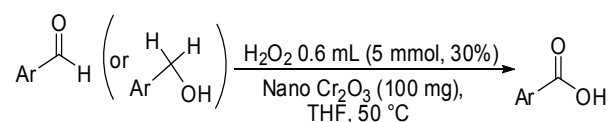


Fig. 6: FTIR spectrum of the nano-sized Cr₂O₃

In this paper, In the same conditions 50 mg of amorphous Cr₂O₃ and 50 mg of nano Cr₂O₃, catalyzed oxidation of benzaldehyde and compared to the results. Our results showed that nano Cr₂O₃ is superior to the amorphous Cr₂O₃. A series of experiments was conducted to investigate the effect of chromium (III) oxide (Cr₂O₃) on aldehyde and alcohol oxidation under constant conditions. All of the experiments were carried out at 50 °C, at room lighting with no other light source. The concentrations were (5 mmol, 0.6 ml) of hydrogen peroxide on nano catalysts (100 mg) and (1 mmol) of aldehyde or alcohol (scheme 1).



Scheme 1. Oxidation of aldehyde/alcohol with nano Cr₂O₃

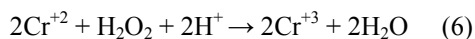
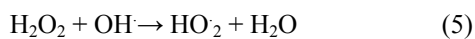
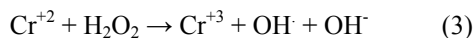
These results prompted us to investigate the scope and the generality of this new protocol for oxidation of various aromatic aldehydes under optimized conditions (Table 1).

Table 1. Oxidation of aldehyde/alcohol with Cr₂O₃ nanoparticles

Entry	Aldehyde/ Alcohol	Carboxylic Acid	Time (h)	Ran ^a (%)
1	PhCHO	PhCO ₂ H	2.50	98
2	4Me-PhCHO	4Me-PhCO ₂ H	1.50	92
3	4MeO-PhCHO	4MeO-PhCO ₂ H	1.50	92
4	4Br-PhCHO	4Br-PhCO ₂ H	2.35	98
5	4Cl-PhCHO	4Cl-PhCO ₂ H	3.10	89
6	4NO ₂ -PhCHO	4NO ₂ -PhCO ₂ H	4	92
7	3NO ₂ -PhCHO	3NO ₂ -PhCO ₂ H	4	89
8	PhCH ₂ OH	PhCO ₂ H	5.5	95
9	4Cl-PhCH ₂ OH	4Cl-PhCO ₂ H	6	85
10	4Me-PhCH ₂ OH	4Me-PhCO ₂ H	7.5	83

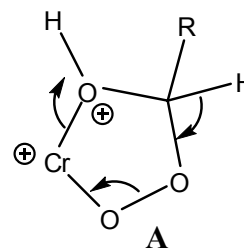
^a Yields refer to crude product (isolated product).

Because oxidation of aldehyde to carboxylic acid is elimination of aldehyde peaks (in C&H-NMR) and appearing carboxylic acid peaks. Results show a significant influence of Cr₂O₃ nanoparticles on aldehyde/alcohol oxidation rate. The mechanism for producing free hydroxyl radicals in (Cr⁺²/H₂O₂) and (Cr⁺³/H₂O₂) is very complex and thought to occur in the following stages.



The first three equations are responsible for the continuous production of the active radical the next two for the decay of this radical, and the final one for reducing the peroxide concentration. In addition increase in aldehyde oxidation reaction rate on Cr₂O₃

nanoparticles can be attributed to the complexation reactions of Cr-OOH⁺² by aldehyde Fig 7.

**Fig. 7.** Mechanism of the oxidation with Cr₂O₃ nanoparticles

The **A** complexes decompose efficiently and hence generate acid as oxidation Products. After the reaction, nano Cr₂O₃ can be easily separated (by centrifuge and filtration) and reused without decrease in its activity. For example, oxidation reaction of aldehydes and alcohols afforded the corresponding carboxylic acids over ten cycles.

4. Conclusion

We have described the use of an inorganic phase in water-in-oil (w/o) microemulsion has received considerable attention for preparing metal oxide nanoparticles. In addition, the main advantage of this method is easily controllable conditions with using low cost chromium source is merit to be considered for scaling up by industrial researchers. At the similar condition, the bulk (70 mg) and nano Cr₂O₃ (70 mg) catalyzed oxidation of aldehyde/alcohol. Particularly significant in this research is the enhanced catalytic activity observed for nano-sized Cr₂O₃ in comparison to that of bulk sample in the oxidation of aldehyde and alcohols. Besides oxidation of aromatic aldehyde/alcohol to the corresponding carboxylic acids can be performed

highly efficiently in the presence of a catalytic amount of nano chromium (III) oxide in THF as solvent under mild conditions.

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