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CATALYTIC OXIDATION OF CYCLOHEXANE OVER Cu-Zn-Cr TERNARY SPINEL SYSTEMS

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Abstract

Spinel systems with the composition of $\text{Cu}_{1-x}\text{Zn}_x\text{Cr}_2\text{O}_4$ [$x = 0$ CCr, $x = 0.25$ CZCr-1, $x = 0.5$ CZCr-2, $x = 0.75$ CZCr-3 and $x = 1$ ZCr] were prepared by homogeneous co-precipitation method and were characterized by X-ray diffraction (XRD) and FT-IR spectroscopy. Elemental analysis was done by EDX, and surface area measurements by the BET method. The redox behavior of these catalysts in cyclohexane oxidation at 243 K using TBHP as oxidant was examined. Cyclohexanone was the major product over all catalysts with some cyclohexanol. 69.2% selectivity to cyclohexanol and cyclohexanone at 23% conversion of cyclohexane was realized over zinc chromite spinels in 10 h.

Keywords: Spinel chromites, cyclohexane oxidation

INTRODUCTION

Oxidation of cyclohexane is one of the important bulk processes for the production of polyamide fibers and plastics, such as nylon-6 and nylon- 6, 6.

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More than 10^6 tonnes of cyclohexanone and cyclohexanol (K/A oil) are produced world wide per annum [1]. Industrially, the process for cyclohexane oxidation is carried out at 423-433K in the presence of cobalt-based homogeneous catalysts, resulting in about 4% conversion and 70-80% selectivity to K/A oil [2]. This process generates a plenty of big-products and waste. Also, this process is low in energy efficiency. Due to environmental and economic concerns, the development of highly efficient catalytic processes minimizing the formation of side-products and residues, is quite desirable. An interesting approach is the supporting of catalytically active metals on molecular sieves or related systems, thus enhancing the selectivity, because of the well defined porous system [3]. Co_3O_4 nanocrystals, bis-(maltolato) oxovanadium complexes, silicates containing cerium, V_2O_5 - TiO_2 mixed oxides and rare earth exchanged zeolites have been successfully applied as heterogeneous oxidation catalyst in the liquid phase [4-8]. Furthermore, various transition metals, *e.g.* Co, Sn, Zn, Cr, Fe, Mn and Cu have been incorporated into zeolites, silicates, SAPO's, AlPO's and metal doped MCM-41 and MCM-48 are used in oxidation reactions [9-16]. However, the use of these materials as oxidation catalyst is restricted because of the relatively low activity, or metal leaching from the molecular sieves. In this paper we wish to report the preparation of some zinc-substituted copper chromite spinels, and the application of these materials as catalysts in the oxidation of cyclohexane.

EXPERIMENTAL

Preparation of catalysts

A mixture consisting of 10% solutions of copper nitrate, zinc nitrate and chromium nitrate for $\text{Cu}_{1-x}\text{Zn}_x\text{Cr}_2\text{O}_4$ ($x = 0, 0.25, 0.5, 0.75$ and 1) series were taken in appropriate mole ratios and the mixture was heated to 343-353 K. To this hot mixture a 15 % ammonia solution was added dropwise with constant and uniform stirring to maintain a constant pH of 7. The mixture was digested for another two hours at the same temperature for the completion of precipitation. The precipitate was filtered, washed and dried at 353 K for 24 h and calcined at 923 K for 8 h. The samples prepared were designated as follows:

Catalyst composition	Designation
CuCr_2O_4 ($x = 0$)	CCr
$\text{Cu}_{0.75}\text{Zn}_{0.25}\text{Cr}_2\text{O}_4$ ($x = 0.25$)	CZCr-1
$\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Cr}_2\text{O}_4$ ($x = 0.5$)	CZCr-2
$\text{Cu}_{0.25}\text{Zn}_{0.75}\text{Cr}_2\text{O}_4$ ($x = 0.75$)	CZCr-3
ZnCr_2O_4 ($x = 1$)	ZCr

Catalyst characterizations

Elemental analysis of the catalysts was carried out by EDX analysis on a Stereoscan 440 (Cambridge, UK) energy dispersive X-ray analyzer used in conjunction with a scanning electron microscope (SEM).

X-ray powder diffraction patterns of the catalysts were recorded on a Rigaku D-max C X-ray diffractometer using Ni filtered Cu K_{α} radiation source ($\lambda=1.5406\text{\AA}$) in the region of $10\text{-}70^{\circ}$.

Surface area of the catalysts was calculated by measuring the adsorption of nitrogen at liquid nitrogen temperature in a conventional BET system.

2 to 4 mg of each substance was pressed with 200 mg of KBr. The spectra were recorded in an AVATAR 370 Thermo-Nicolet FT-IR spectrometer in the region of $400\text{-}4000\text{ cm}^{-1}$.

Catalytic activity

Cyclohexane oxidation was carried out in a 50 mL, two-necked round bottom flask provided with a magnetic bead for stirring and a water condenser. 1 mL of cyclohexane, 10 mL of acetonitrile and 0.1 g of the catalyst were added successively into the flask. The round bottom glass flask with the reaction mixture containing the catalyst was then immersed in a thermostated oil bath at 343 K. Then 2.4 mL of 70% TBHP (Cyclohexane: TBHP = 1:2) is added dropwise to the reaction mixture after attaining a constant temperature. The reaction was run for 10 h. The course of the reaction was followed by analyzing the liquid samples on a GC.

Catalyst reusability experiments were carried out with the CZCr-3 catalyst at 343K. After 10 h reaction times, the catalyst was recovered by hot filtration, washed several times with acetone, dried at 353 K and calcined for 8 h at 923 K. The recovered catalysts were reused for cyclohexane oxidation under the same reaction conditions up to four cycles.

RESULTS AND DISCUSSION

Surface characterization

The X-ray diffraction data for the entire series of compounds show an interesting crystal structure and zinc modification behavior. An inspection of all XRD patterns demonstrates some reflections for separate phases of chromium and copper oxides [17]. Figure 1 illustrates the XRD patterns for the spinel series. The standard JCPDS reflections and intensities for CuCr_2O_4 and

ZnCr_2O_4 were compared. The crystallite size of the samples was calculated using the Scherrer equation from the broadening of the most intense peak of the (311) plane, and the results show particles in the nano range with zinc chromite of the lowest size of 9.8 nm.

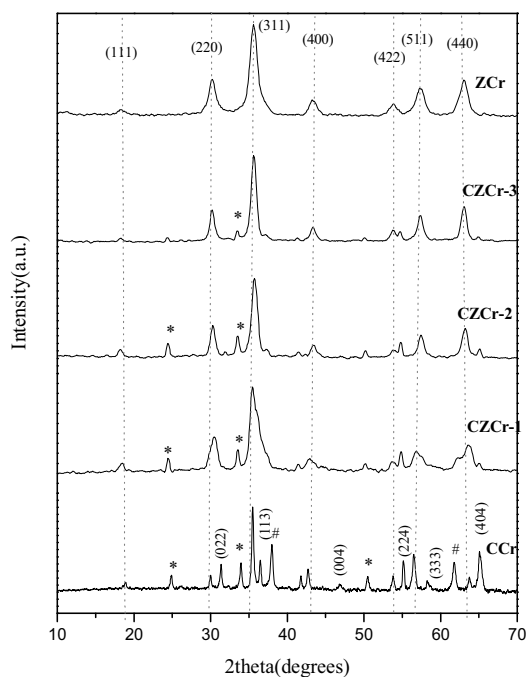


Fig. 1. XRD profiles of the catalysts. Reference lines for the cubic chromite spinels are given as dotted lines. Asterisk and hash indicate the most intense lines of Cr_2O_3 and CuO

The FTIR spectra of the samples are given in Fig. 2. The two strong absorption bands observed in the spectra of the samples are at 630 and 525 cm^{-1} . The bands at higher and lower wavelength regions are assigned by Yur'eva *et al.* [18] to the vibrations of tetrahedral metal-oxygen bond, and the octahedral metal-oxygen bond, respectively. The bands at 1640 and 3420 cm^{-1} indicate the presence of surface hydroxyl groups and coordinated water.

Results of the chemical analysis and surface area of this series of catalysts are presented in Table 1. It can be seen that the experimental and theoretical values of Cu, Zn and Cr agreed well. The BET surface area of the catalysts was found to be increased by zinc substitution, and the maximum surface area is shown by zinc chromite.

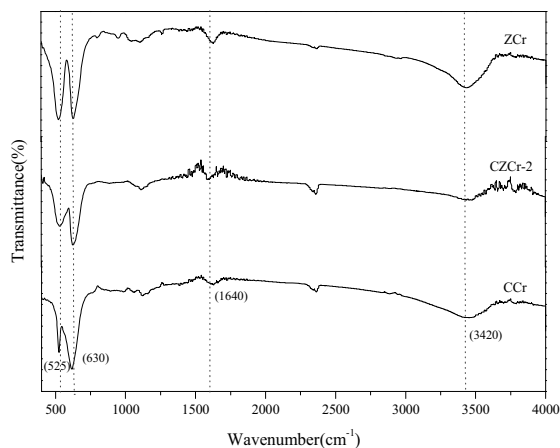


Fig. 2. FT-IR Spectra of the catalysts

Table 1

Elemental composition, surface area and crystallite size of the catalysts

Catalyst	Atom percentage			BET surface area (m ² /g)	Langmuir surface area (m ² /g)	Crystallite size (nm)
	Cu	Zn	Cr			
CCr	34.41	0.00	65.59	5.98	8.68	38.8
CZCr-1	24.47	7.71	67.62	16.04	23.58	8.3
CZCr-2	14.09	21.22	64.69	21.82	31.87	9.2
CZCr-3	7.49	23.74	68.76	35.32	52.25	15.5
ZCr	0.00	32.40	67.60	74.44	112.89	9.8

Cyclohexane oxidation

The catalytic activity of zinc substituted copper chromite spinels had been studied in cyclohexane oxidation using TBHP as oxidant. Table 2 presents the oxidation results. All the catalysts showed catalytic activity towards cyclohexane oxidation. Cyclohexane conversion was found to increase with zinc substitution. Copper chromite gave the lowest activity among the catalysts, whereas zinc chromite exhibited the best activity. Cyclohexanone was found to be the major product for all the catalysts. Cyclohexene is formed as a side

product in this reaction. The decrease in selectivity to cyclohexanol can be explained as follows. The catalyst is active, and promotes well the reaction with cyclohexanol, possibly to form cyclohexanone. Cyclohexanol is also dehydrated to form cyclohexene. The activity of these materials in liquid phase oxidations has generally been correlated with the redox properties of chromium.

Table 2
Catalytic activity towards cyclohexane oxidation

Catalyst	Cyclohexane conversion (%)	Cyclohexanol (%)	Cyclohexanone (%)
CCr	12.2	28.9	44.7
CZCr-1	14.4	25.6	50.8
CZCr-2	16.6	23.9	43.2
CZCr-3	16.8	23.6	46.9
ZC	23.3	12.3	50.9

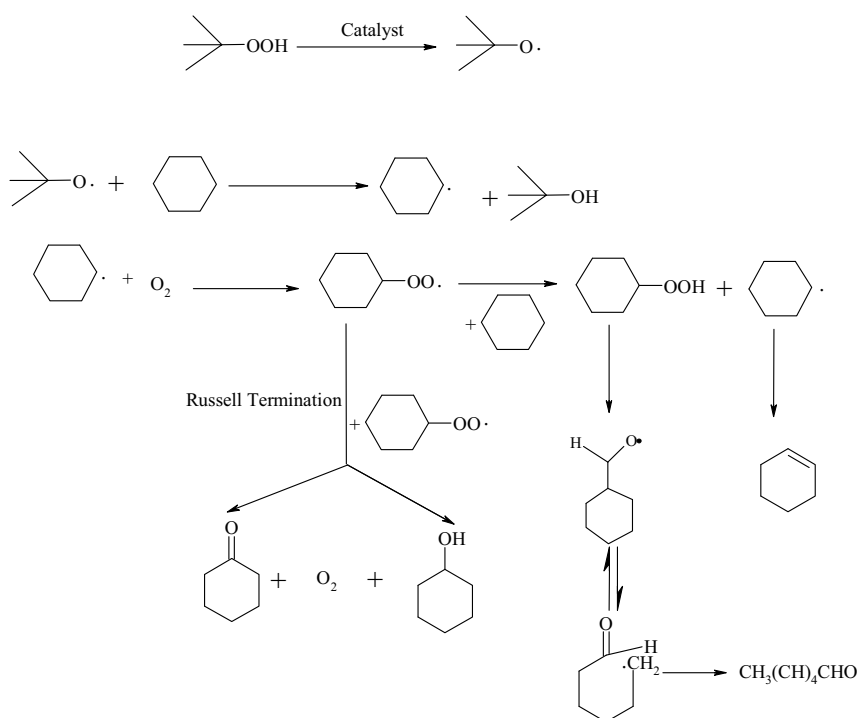
Temperature: 343 K, Reaction time: 10 h, Catalyst weight: 0.1g,
Cyclohexane: TBHP- 1:2 molar, Solvent: 10 mL Acetonitrile

Table 3
Recycling study of the catalyst CZCr-3

Cycle	Cyclohexane conversion (%)	Cyclohexanol (%)	Cyclohexanone (%)
1	16.8	23.6	46.9
2	18.8	22.9	45.3
3	17.9	21.4	43.7
4	18.4	20.1	41.7

The catalytic stability of CZCr-3 was further investigated, since a good catalyst should have a long life. As shown in Table 3, the activity of CZCr-3 (after the first reaction, it was washed with acetone three times and used for the subsequent run, and then, it was repeated for the third run) did not decrease during the three runs. The catalytic performance remains stable as proved by the similar conversion of cyclohexane and product selectivity for the second, third and fourth runs. This shows that CZCr-3 is a highly active, selective and stable heterogeneous catalyst for the oxidation of cyclohexane.

A proposed reaction mechanism for spinel catalyzed cyclohexane oxidation is depicted in scheme 1. TBHP is decomposed on the catalyst surface forming *t*-butoxy radicals with the oxidized catalyst. These radicals abstract hydrogen from cyclohexane forming thereby cyclohexyl radicals, which reacts with molecular oxygen from air. The cyclohexyl peroxy radicals thus formed can suffer a bimolecular Russell termination [19] to form cyclohexanone and cyclohexanol or abstract hydrogen from cyclohexane to form cyclohexyl hydroperoxide. Cyclohexyl hydroperoxide can undergo a bimolecular Russell termination to form cyclohexanone and cyclohexanol or abstract hydrogen from cyclohexane to form cyclohexyl hydroperoxide. Hydroxy radical abstraction from cyclohexyl hydroperoxide by the catalysts forms cyclohexyloxy radicals, which are in equilibrium with the open chain isomer, thus forming *n*-hexanal. The cyclohexyl radicals may suffer dehydrogenation to cyclohexene by reduction of the catalyst formed by the decomposition of TBHP, regenerating thus the active catalyst.



Scheme 1. Proposed mechanism for the oxidation of cyclohexane

CONCLUSIONS

Spinel chromites of copper substituted with zinc are prepared by a homogeneous co-precipitation method. These types of spinels are found to be highly active for the oxidation of cyclohexane with TBHP oxidant to the cyclohexanol and cyclohexanone. A good conversion is achieved with all the catalysts, and a maximum of 23% conversion with zinc chromite.

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