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Physico-chemical studies and CO adsorption on zeolite-encapsulated Mn^{II}, Mn^{III}–hydrazone complexes

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Abstract

Complexes of Mn(II) and Mn(III) with N_2O_3 hydrazone ligand derived from salicylaldehyde and benzenesulphonylhydrazide have been encapsulated in zeolite Y- supercages by a diffusion method. The synthesized new materials have been characterized by combination of elemental analysis, FT-IR, UV–vis., magnetic measurements, XRD, thermal analysis (TG, DTG and DTA), as well as surface area measurements and nitrogen adsorption studies. Investigation of the stereochemistry of these incorporated chelates pointed out that, Mn(II) complex is tetrahedral with involvement of zeolite oxygen in coordination meanwhile Mn(III) complex has octahedral configuration without contribution of the lattice oxygen. The intrazeolitic hydrazone complexes are thermally stable up to 1000 °C without decomposition. Catalytic activity towards CO adsorption for these zeolite encapsulated complexes has been investigated and compared with Mn^{II}-Y using in situ FT-IR spectroscopy. The results revealed that, Mn^{II}(SBSH)/Y and Mn^{III}(SBSH)/Y give an elementary peak near 1728 cm^{-1} indicating a selectivity to form —COOH species while Mn^{II}-Y catalyst gives a broad band in the region of 1765–1560 cm^{-1} assigned to different (—COOH) and carbonates species. On the other hand, the in situ FT-IR data indicate that Mn^{II}(SBSH)/Y and Mn^{III}(SBSH)/Y can be used as reactive catalysts in water gas shift reaction (WGSR).

Keywords: Zeolite encapsulated Mn(II), Mn(III)-complexes; Diffusion method; Physico-chemical studies

1. Introduction

The encapsulation of metal complexes into zeolite has produced a growing number of heterogeneous hydrocarbon oxidation catalysts [1]. In many cases, the entrapment of the complex in the zeolite is crucial to promote the catalytic properties of the introduced complex [2] by two ways, first by dispersion of the complex and/or second by construction of new structure differs from that formed under ordinary condition owing to the zeolite restriction. Since the zeolite surfaces may be act as multidentate ligands for transition metal ions, the intrazeolite complexation is a competition between two chelates for one metal ion. So that, the zeolite oxygen may be involved in coordination. The synthetic faujasite (FAU) type zeolites (Y or X) have been the most widely studied host materials. The FAU structure involves large cavities about 1.2 nm in diameter but the openings to these supercages are only 0.74 nm in diameter. In some cases, zeolite inclusion is applied to avoid the formation of polynuclear aggregates and to strongly reduce the self-oxidation tendency of the complexes. In spite of major classes of ligands studied to date with Mn(II) and Mn(III) ions include schiff bases [3,4] and poly(pyridines) [5] in addition, Nakamura et.al. [6], and Chan and Wilson [7] reported the unique examples of Y-zeolite-encapsulated metalloprophyrins (iron and manganese tetramethyl- and tetraphenyl prophyrins) by using the template synthesis method, hydrazone type ligand was never used with manganese (II, III) ions through the encapsulation process. Virtually, much effort has been paid to immobilize Mn(II) and Mn(III) complexes homogenous catalyst, onto solid supports such as polymers [8] clays [3], zeolites [4,9,10] and

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MCM-41 [11] as such heterogenization of homogeneous catalysts may combine the ease of product separation with selectivity of the complexes.

Air pollutants released from automobiles, industries, and power generation unites strongly affected human health and the environment. Air pollutants create primary problems as well as secondary problems such as reactions with other atmospheric chemicals to produce acid rain or ozone. To reduce environmental pollution, catalytic systems are commonly utilized for the destruction of harmful compounds. Currently noble metal catalysts are used for the catalytic decomposition of these air pollutants. For reducing the increasing global air pollution problems, efforts are being made to obtain more effective and economical catalytic materials. Transition metal incorporated supported catalyst materials have shown potential as pollution control systems. However, the adsorption of carbon monoxide (which is considered an air pollutant, discarded product, and/or a key intermediate of many reactions) on MnO_x species was studied by FT-IR spectra [12], this adsorption on zeolite encapsulated Mn(II), Mn(III)-complexes had not carried out yet.

In the preliminary study, we wish to isolate and characterize of Y-zeolite-encapsulated Mn(II) and Mn(III)–hydrazone complexes by a flexible ligand method as heterogeneous catalysts. The structures of the intrazeolite complexes have been elucidated and the composites have been tested for CO adsorption. Furthers, the texture of these newest zeolites is described to show the possibility of using them in catalysis and in the same time to provide an evidence for the successful occlusion of the complexes within the zeolite matrix.

2. Experimental

2.1. Materials and physical measurements

All the chemicals and solvents used in this research were of Aldrich or AR quality and used without further purification. NaY zeolite (Lot No. D1-9915, HSZ-320N-NAA, Si/Al = 5.6) was obtained from Toyota Company Ltd., Japan and used as a host matrix. The elemental analysis for carbon and hydrogen was determined at Microanalytical Unit of Cairo University, Egypt, and the metal contents (%) were measured using GBC 932/933 atomic absorption spectrometer (Table 1). IR spectra were recorded as KBr pellet in the range 200–4000 cm^{-1} on a Mattson 5000 FT-IR spectrometer. Mass spectrum of the ligand was recorded on Shimadzu-GC.MS-QP 1000 EX using the direct inlet system at Cairo University, Egypt. UV–vis spectra of the materials in Nujol mull were measured in the range 200–1100 nm using a Perkin-Elmer lambda 35 UV–vis spectrophotometer. The mass susceptibility of the solid materials (χ_g) was measured with a magnetic susceptibility balance of models Johnson Metthey and Sherwood. X-ray diffractograms were recorded using a Philips PW1840 X-ray powder diffractometer with Cu Kα target ($\lambda = 1.54$ Å). The thermal analyses (TG, DTG, and DTA) under flowing dry nitrogen were carried out with a Shimadzu 50 H thermal analyzer. The surface texture characteristics obtained from nitrogen adsorption isotherms were measured at −196 °C using a conventional volumetric apparatus. The specific surface area was obtained using the BET method. The samples were thermally degassed at 200 °C prior to the adsorption measurements. The micropore volume and the external surface area were obtained from the *t*-plot method.

FT-IR spectra of CO adsorbed on modified zeolites were recorded by use of FT-IR instrument Bruker (Vector 22) single beam spectrometer with a resolution of 2 cm^{-1}. A self-supporting wafer of about 30 mg/cm^2 was placed in an in situ FT-IR quartz cell equipped with $CaCl_2$ windows and a built-in furnace. As a typical experiment the samples were thermally treated at 200 °C for 1 h under a reduced pressure of 10^{-5} Torr prior to admitting CO (50 Torr) gas at room temperature. At each step of measurements, the FT-IR spectrum was recorded after cooling down to room temperature and the spectrum recorded was subtracted from the background (the free CO spectrum) to evaluate the spectral changes due to CO adsorption.

2.2. Sample preparation

2.2.1. Preparation of ligand (SBSH)

The ligand used in this work is salicylidinebenzenesulphonylhydrazone (SBSH) having the chemical formula $C_{13}H_{12}N_2O_3S$ and was obtained using the procedure reported in literature [13] as follows. Benzenesulphonylhydrazine, BSH (50 mmol) dissolved in methanol (50 cm^3) was mixed with salicylaldehyde, sal. (50 mmol) in methanol (50 cm^3) and the reaction mixture was refluxed for 4 h in the presence of 2–3 drops glacial acetic acid. On cooling, white crystals of SBSH formed were washed with dilute ethanol, recrystalized from hot ethanol and finally dried at 80 °C for 2 h in furnace. The prepared crystals has a sharp melting at

Table 1
Physical and analytical data for SBSH and the prepared zeolites

Sample label	Colour	*M* (%)	Mp (°C)	M/C ratio found (calcd)	χ_g (c.g.s.)	S_{BET} (m^2/g)	S_t (m^2/g)	V_p (cm^3/g)
SBSH	White		155					
Mn^{II}-Y	White	2.90	>300		1.45×10^{-5}	787	782	0.74
Mn^{II}(SBSH)/Y	Yellow	3.95	>300	0.166(0.154)	1.365×10^{-5}	620	677	0.63
Mn^{III}(SBSH)/Y	Yellow	4.10	>300	0.200(0.154)	1.334×10^{-5}	660	683	0.64