

Ce-containing Mordenites: Synthesis, structure and reactivity towards NO and CO gases

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Abstract

Aqueous solutions of cerium nitrate of increasing concentrations (2.5, 5 and 7.5 wt.% Ce) have been contacted with the components forming Mordenite zeolite; during forming the gel under hydrothermal conditions, for allowing the accessibility of Ce ions to proceed into compensating positions in Mordenite structure. These materials were characterized by the methods of FTIR, XRD, N₂ adsorption and UV–vis diffuse reflectance spectroscopy. The interaction of NO and CO adsorptions; at room temperature, on thermally pre-treated (300 °C, 10⁻⁵ Torr, 3 h) as well as pre-reduced (50 Torr, 500 °C, 1 h) samples were studied by in situ Fourier transform infrared spectroscopy. XRD and FTIR results indicate that the Ce atoms are mostly present in internal surfaces in Mordenites for 2.5 and 5CeMOR samples whereas for 7.5CeMOR, a decrease in diffusion of Ce to be in compensating positions is perceived; as conceived from lowering the lattice volume, pointing to the presence of discrete amounts of CeO₂ (582 cm⁻¹) and cerium silicate (Si–O–Ce; 797 cm⁻¹) species. All the samples indicate intra-crystalline mesopores as depicted from *V_t-t* plots particularly the 7.5CeMOR sample that showed the highest wide-pore volume (0.073 cm³/g), lowest pore radius (21 Å) and thus, revealed the highest *S_{BET}* between all samples (363 m²/g). UV–vis characterization of 7.5CeMOR sample shows octahedral Ce species (345, 360 and 390 nm) in small clusters inside zeolite channels and most probably originated from cerium silicates having different coordination with NaMOR along with discrete amounts of CeO₂ (420 nm) species. CO readily adsorbs on the Ce³⁺ sites of the pre-reduced 7.5CeMOR catalyst, rather than those on Ce⁴⁺, to display minor amounts of carboxylate and dominant amounts of monodentate carbonate that were amenable to decompose to produce CO₂ gas (2335 cm⁻¹). On the other hand, the in situ interaction of nitric oxide (NO) gas on the 7.5CeMOR catalyst led to the formation of a series of nitrosyl species: N₂O (2240 cm⁻¹), NO (1908 cm⁻¹), N₂O₃ (1880 cm⁻¹) and (NO)_{2s,as} (1844, 1734–1720 cm⁻¹). Such nitrosyl complexes were favorably formed on Ce³⁺ in 7.5CeMOR those exchanged Na ones.

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1. Introduction

Mordenite is one of high silica zeolites and has two pore channels, i.e. 6.7 × 7.0 Å which is parallel to the *c*-axis and 2.6 × 5.7 Å which is parallel to the *b*-axis. Owing to its unique properties in adsorption and catalysis, a lot of

articles and patents concerning the synthesis of Mordenite zeolite in presence of organics as templates are reported [1,2]. That growing demand of the synthesis of Mordenites specifically those of large pore and defined texturing has attracted a recent interest [3]. Mordenites have also been modified by isomorphous substitution of silicon and aluminum to prepare modified zeolites having new physicochemical and catalytic properties, which becomes an important research subject in the field of zeolitic chemistry [4]. The chemical composition, structure and extra-framework cations of the zeolite significantly affect the molecular

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adsorption–interaction with the zeolitic active sites, thus strongly influencing the catalytic properties of the zeolitic material [5–7].

Noble metals such as Rh, Pt and Pd are used for the catalytic decomposition of toxic gases like NO, CO and SO₂ released into the atmosphere from industrial and automobile exhaust sources. With an increase in global air pollution, efforts are being made to obtain more effective catalytic materials such as transition metal oxides in zeolites [8,9]. Actually the interaction of d-block transition metals with NO often involves a d-electron and/or an empty d-orbital, which leads to the formation of metal nitrosyls [10]. These species are supposed to be susceptible to decomposition depending on the mode of d-transition metals for NO coordination. Catalytic oxidation of CO, on the other hand, has acquired tremendous attraction lately particularly in connection with the worldwide endeavors to curb the detrimental impacts of automotive emissions on the atmosphere.

Cerium oxide, which is one of the important components of automotive and industrial exhaust catalyst, is active for NO_x removal and oxidation of CO since it acts as oxygen storage materials during performing reactions [11,12]. The surface area and the type of active sites/species, however, are important factors in deciding the catalytic activity of a material. Because of the limitations in the surface area of cerium oxide, a high surface cerium containing catalytic material using cerium-exchanged zeolites has been developed [13,14]. Yet, a little has been published on the application of Ce-zeolites as selective catalysts for the reduction of NO_x compounds and oxidation of CO gas. This was attributed to difficulties arisen due to a possible loss in the degree of crystallinity of Ce-exchanged zeolites during the exchange process [14,15], decreasing the thermal stability of zeolite, and the probability of forming CeO₂ segregates appear as clusters after calcination [15,16]. Thus, Ce was used most of the time to improve the catalytic properties of some other metal ions as a promoter; especially on oxides, rather than using it as main active species [17]. Consequently, it was mandatory for allowing Ce to be accessible in Mordenite channels as a result of substitution of Na by Ce. Cerium cation is known to show redox properties (Ce^{III}/Ce^{IV}) that can possibly account for a distinguished NO and CO oxidation capacity of Ce-zeolite at low temperatures [18,19]. The interaction of molecular species with active metal sites is usually studied with nitric oxide and carbon monoxide probe molecules using the FT-IR technique. In the present paper, the adsorption–interaction of NO and CO gases with the active cerium species in Mordenite catalysts was investigated at low temperatures. Physicochemical properties of the synthesized Ce/Mordenites have been characterized using N₂ adsorption, FT-IR, UV–vis diffuse reflectance and XRD measurements to have informations on cation positions and resulting changes could be caused by the replace of Na ions by Ce ions in the zeolite structure of Ce exchanged Mordenite type.

2. Experimental

2.1. Materials

The materials used were: silicic acid powder, sodium hydroxide pellets (AR 98%), aluminum sulfate [Merck, Al₂(SO₄)₃ · 16H₂O], *o*-phenylenediamine (Merck), Cerium nitrate [Ce(NO₃)₃ · 6H₂O 98%] and commercial H₂SO₄.

Details concerning methods of preparation of Mordenite and Ce-containing Mordenites have been illustrated elsewhere [20]. The amounts of encapsulated Ce in zeolitic substrates during their synthesis were 2.5, 5 and 7.5 wt.% and expressed as CeO₂. The samples were referred to as xCeMOR where *x* point to the amount of Ce in Mordenite.

2.1.1. Preparation of Mordenite

The hydrogels of the following oxide molar compositions were arranged for the synthesis of Mordenite zeolite: 3.12Na₂O:0.162Al₂O₃:6.185SiO₂:0.185Q:100H₂O where Q is *o*-phenylenediamine (OPDA) template. A known weight of NaOH was added to silicic acid in calculated amount of H₂O while stirring, followed by heating at 80 °C until clear solution was obtained. The OPDA was dissolved in small amounts of H₂O followed by heating at 50 °C for 20 min. Subsequently, the solution of OPDA was added to that of sodium silicate while stirring for 15 min. The aluminum sulfate, on the other hand, was dissolved in calculated amount of acidified H₂O via addition of 0.05 ml concentrated H₂SO₄. To the latter solution, the combined solution of sodium silicate and OPDA was added followed by stirring for 30 min. The pH of the mixture was adjusted at 11 by using NaOH (0.1 M) and H₂SO₄ (0.1 M) solutions. Finally, the mixture was hydrothermally treated at 160 °C in an oil bath, using stainless steel autoclaves, for 6 days. The autoclaves were removed at the pre-specified time from the oven and were quenched immediately with cold water. The solid product was filtered and washed with distilled water until the pH of the filtrate reached to 8. The products were dried at 110 °C for 10 h then calcined at 550 °C for 6 h in an air oven. This sample was referred as MOR.

2.1.2. Inclusion of CeO₂ in Mordenite zeolite

The synthesis procedure is described in molar compositions as follows: 3.12Na₂O:0.138Al₂O₃:6.185SiO₂:0.00343–0.0103CeO₂:0.185Q:100H₂O.

Aluminum sulfate was dissolved in a small amount of water followed by addition of 0.05 ml H₂SO₄ with gentle heating until reaching a clear solution. On the other hand, the soluble complex of sodium silicate was formed onto which the template (OPDA) was added. A calculated amount of cerium nitrate was dissolved in distilled water and this amount was taken in specific molar ratios relative to aluminum sulfate. A simultaneous addition of aluminum sulfate solution into mixture composed of cerium nitrate and sodium silicate was achieved; followed by stirring for 30 min. Sulfuric acid or sodium hydroxide adjusted the pH to 11. The amorphous gel formed was allowed to age

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