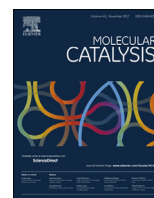




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Dispersion of nanosized ceria-terbia solid solutions over silica surface: Evaluation of structural characteristics and catalytic activity

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ABSTRACT

In this work, we investigated the dispersion effects of nanosized ceria-terbia solid solutions over silica surface in terms of structural characteristics and catalytic activity. The dispersion process was carried out via a soft chemical route using colloidal silica precursor and nitrate precursors of cerium and terbium. The structural features were elucidated by means of analytical techniques namely TGA, BET surface area, XRD, Raman Spectroscopy, UV-vis DRS, TEM, XPS, and TPR-TPO. The catalyst samples were subjected to thermal treatments at different temperatures ranging from 773 to 1073 K to understand the influence of silica support on dispersion, textural properties, and thermal stability. Catalytic activity was evaluated for selective dehydration of 4-methylpentan-2-ol to 4-methylpent-1-ene in the vapor phase at atmospheric pressure. The silica supported ceria-terbia catalyst exhibited better dehydration activity as well as selectivity in comparison to the unsupported catalyst. The catalytic properties were found to be dependent on structural features of the prepared catalyst samples.

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1. Introduction

Since its inception as the oxygen storage component in catalytic converters by Ford Motor Company, nanosized cerium oxide (ceria, CeO₂) has been known to be an unrivaled component in three-way-catalysts (TWCs) and is currently an attractive catalyst or a support for a variety of catalytic applications [1,2]. The unique property making ceria extraordinarily viable is its oxygen storage and release capacity via the Ce⁴⁺/Ce³⁺ redox shuttle under oxidizing and reducing environments, respectively [1–5]. Primarily, ceria was recognized as a promising material, because it maintains a cubic fluorite crystal structure even during the alternate storage and release of oxygen with small volume change. However, due to severe loss of its textural characteristics and oxygen storage capacity (OSC) at elevated temperatures, its use in controlling the emissions of toxic pollutants from automotive exhaust is restricted [3]. Two strategies are particularly effective for resolving this critical problem. One is modification of ceria by preparing its mixed oxides or solid solutions with transition metals and other rare-earth elements, and another is exploitation of thermally stable inert supports [1–3,4,6]. Captivatingly, both the strategies have come up with improved thermal/textural properties and catalytic activities for ceria nanostructures. For instance, prominent mixed

oxides of ceria such as CeO₂-ZrO₂, CeO₂-HfO₂, CeO₂-La₂O₃, CeO₂-TiO₂, CeO₂-TbO₂, CeO₂-PrO₂, etc. have been known in view of both structural characteristics and catalytic activities compared to pure ceria in different applications [3,6–10].

Due to chemical inertness, high specific surface area and high thermal stability, silica is widely exploited as a support for stabilizing different metal nanoparticles and metal oxides [11,12]. It is revealed that the dispersion of nanosized ceria and/or ceria-based mixed oxides over the surface of silica, transition alumina, or titania results in significant improvement of the physical as well as chemical properties without changing the thermal and mechanical properties of the mixed oxide material [11]. Mention worthy that amorphous silica outperforms the ability of alumina and titania towards the stabilization of the ceria-based mixed oxides against sintering during the high temperature operations [13]. Furthermore, compared to the bulk oxides, the silica supported ceria-based mixed oxides possesses more active surface area and stability due to better dispersion of the catalytically active ceria-based phases on the support surface. As a consequence, the oxygen exchange rate experiences an enhancement that leads to a remarkable increase in the reactivity [6,13]. These facts grow intense motivation towards using silica as the support material for other ceria-based materials.

Apart from the well-known redox behavior, acid-base property is another intriguing feature of ceria-based catalysts. Generally, different techniques employed to explore the acid-base properties of ceria suggest strong basicity and weak acidity caused by the highly mobile surface O²⁻ ions and cerium cations, respectively [11,14].

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Introduction of metal dopants into the CeO₂ lattice generates oxygen vacancy defects and increases the acidity or basicity of CeO₂ [4,10,15,16]. Finding an appropriate metal for doping is greatly important and a lot of attention should be focused on this issue. By making the use of acid-base as well as the redox properties, ceria and/or ceria-based materials can catalyze the transformation of diverse organic molecules. For instance, dehydration, dehydrogenation and dimerization of alcohols, condensation of aldehydes, ketonization of acids, hydrogenation of olefins, esterification of alcohols, and transesterification of esters were found to be effectively catalyzed by ceria-based catalysts [11,17–20].

Selective dehydration of 4-methylpentan-2-ol is technologically very important as the exclusive product 4-methylpent-1-ene is used as the starting material for manufacturing thermoplastic polymers [21]. However, the dehydration reaction often leads to the formation of undesired product, 4-methylpent-2-ene with trace amounts of C₆-alkenes [4,22]. Besides, the dehydration reaction may be simultaneously accompanied by dehydrogenation which produces 4-methylpentan-2-one along with higher ketones in negligible amounts [4,22]. Hence, product selectivity remains a fundamental issue particularly in alcohol dehydration and tremendous effort has been directed to achieve satisfactory selectivity. It is believed that the strength of acid- and base-sites govern the competition among products of 4-methylpentan-2-ol dehydration [17]. Pure ceria predominantly produces 2-alkene as the alcohol dehydration product. However, binary ceria-based mixed oxide solid solutions reveal good catalytic activity as well as high selectivity to 1-alkene in the dehydration of secondary alcohols [8,23,24]. It is reported that dispersion of ceria-based nano-oxide catalysts, namely, Ce_xZr_{1-x}O₂, Ce_{0.8}Hf_{0.2}O₂, and CeO₂-La₂O₃ over silica amazingly increase their catalytic activity in selective dehydration of 4-methylpentan-2-ol [4,24,25]. Reddy and co-workers reported the efficiency of alumina supported ceria-terbia solid solution in comparison to unsupported ceria-terbia toward enhancement of OSC and CO oxidation ability [3]. In view of this, investigation on ceria-terbia solid solutions supported on silica is vital for making a rational comparison to the previously reported work. To the best of our knowledge, very little research endeavor has been dedicated toward investigation of acid-base characteristics of ceria-based nanostructures correlating their catalytic activity, and particularly, no report could be found on SiO₂ supported CeO₂-TbO₂ composite oxides so far.

Against the abovementioned background, we have undertaken the present investigation to understand the dispersion effects of CeO₂-TbO₂ composite oxide over the surface of silica obtained from colloidal dispersion because of its certain advantages. First, the colloidal dispersion is much less reactive towards the catalytic material, and therefore, solid-state reactions are slightly less likely to occur with the colloidal materials than with the co-precipitated materials from soluble salts. Second, the particles of the colloid are larger than the particles of the co-precipitated salt. This has the feature of making larger pores and a more open structure for the final catalyst. In this work, we therefore aim to evaluate the physicochemical characteristics, nanostructural evolution, and catalytic activity of CeO₂-TbO₂/SiO₂ ternary oxide catalyst where ceria-terbia mixed oxide acts as a promoter and silica forms part of the substrate.

2. Experimental

2.1. Preparation of catalysts

The silica supported ceria-terbia (*i.e.*, CeO₂-TbO₂/SiO₂) catalyst (CTS; CeO₂:TbO₂:SiO₂ = 80:20:100 mol% based on oxides) was synthesized by a deposition co-precipitation method. Nitrate pre-

cursors, ammonium cerium(IV) nitrate (Himedia) and terbium(IV) nitrate (Himedia) in requisite quantities were dissolved separately in double distilled water under mild stirring conditions and mixed together. Upon complete mixing, required quantity of colloidal silica (Ludox 40 wt.%, Aldrich, AR grade) was added to the abovementioned mixture solution under vigorous stirring. Dilute aqueous ammonia solution was subsequently added dropwise until the precipitation was complete (pH ≈ 8.5). The resulting precipitate was carefully filtered off and washed with distilled water until it became free from anion impurities. The accumulated paste was left for overnight drying in a hood. Subsequently, the solid product was dried in an oven at 393 K for 12 h, and crushed it using an agate mortar to obtain fine powders. Finally, the dried sample was calcined at 773 K for 5 h in air atmosphere. Some portions of this sample were again heated at 873, 973, and 1073 K, respectively for 5 h in air atmosphere for investigating the thermal stability of the samples. A heating rate of 5 K/min was maintained during all the calcination processes. For comparison, unsupported CeO₂-TbO₂ (CT; 80:20 mol% based on oxides) was also prepared by same method, annealed at different temperatures, characterized and evaluated for catalytic usefulness.

2.2. Characterization of catalysts

The thermogravimetric measurements were carried out on a Mettler-Toledo TG-SDTA instrument. The catalyst sample was heated from ambient to 1273 K under nitrogen flow at the heating rate of 10 °C per minute. The BET surface areas were determined by N₂ physisorption at liquid N₂ temperature on a Micromeritics Gemini 2360 instrument using a thermal conductivity detector (TCD). Prior to analysis, the samples were oven dried at 393 K for 12 h to remove the surface adsorbed moisture contents and finally flushed with argon gas for 2 h. The powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Multiflex instrument using nickel-filtered CuKα (0.15418 nm) radiation source and a scintillation counter detector. The intensity data were collected over a 2θ range of 10–80° with a step size of 0.02° and a collection time of 2 s per step. Average particle sizes were calculated using Scherrer equation and the cell parameter 'a' of various catalysts was determined by a standard cubic indexation method using the most intense (111) peak. The Raman spectra were recorded on a DILOR XY spectrometer equipped with a confocal microscope and liquid N₂ cooled charge-coupled device (CCD) detector. Samples were excited with the emission line at 325 nm from He-Cd laser (Melles Griot Laser) under the microscope with the diameter of the analyzed spot being ~1 μm. The wavenumber values obtained from the spectra are precise to within 2 cm⁻¹. UV-vis diffuse reflectance spectra were collected on a UV-vis spectrophotometer, Model U-4100 spectrophotometer (solid). BaSO₄ was used as the reference material and the spectra were recorded in the wavelength range from 200 to 800 nm. XPS investigations were carried out on a Shimadzu (ESCA 3400) Spectrometer by using MgKα (1253.6 eV) radiation as the excitation source. The samples were dried and evacuated at high vacuum before analysis and then introduced into the analysis chamber. The recorded XPS spectra were charge corrected with respect to the binding energy of C 1s peak at 284.6 eV. Quantitative analysis of atomic ratios was accomplished by determining the elemental peak areas as reported in our previous literature [3]. Transmission electron microscopic (TEM) investigations were made on a JEM-2100 (JEOL) instrument equipped with a slow scan CCD camera and at an accelerating voltage of 200 kV. Samples were prepared by ultrasonic dispersion in ethanol and deposited onto carbon-coated copper grids. The TPR-TPO measurements were performed using a micro-reactor coupled to a TCD. Oxygen storage capacity (OSC) was measured from the oxygen release characteristics of the sample in the temperature

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