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Mesoporous CaO–ZrO_2 nano-oxides: A novel solid base with high activity and stability

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ABSTRACT

A new solid base, mesoporous CaO–ZrO_2 nano-oxides, was prepared via appropriate sol–gel process. It was found that such solid base showed high basicity and stability. Temperature programmed desorption of CO_2 confirmed that both weak and strong basic sites coexisted on the surface of CaO–ZrO_2 and the basicity could be modified by adjusting Ca/Zr molar ratio of the nano-oxides. The mesoporous CaO–ZrO_2 nano-oxides showed high thermal stability, since X-ray diffraction (XRD) and transmission electron microscopies (TEM) proved that the mesoporous network of this material preserved well even up to 700 °C. At the same time, XRD and Raman spectra indicated that Ca^{2+} incorporated into t-ZrO_2 lattice and the basic sites were firmly anchored to the substrate. As a result, this novel solid base showed remarkable activity and durability in the synthesis of dimethyl carbonate from methanol and propylene carbonate.

1. Introduction

In recent years, the fine-chemical industry has developed growing interest in the utilization of solid catalysts in base-catalyzed reactions. Replacement of currently used homogeneous alkaline bases by solid catalysts can result in catalyst reuse and waste stream reduction. Owing to the solid base catalysts are noncorrosive and easy to be separated from the products [1,2], they offer environmentally benign and more economical pathways for the industrial production. Moreover, taking into account that a large amount of fine chemicals were produced world-wide every year using homogeneous bases, which resulted in high cost for product purification and waste disposal [3–6], it is quite significant to develop and exploit solid base catalysts with more satisfactory quality for the industrial application. However, conventional solid bases such as single alkali earth metal oxide e.g. CaO and MgO possesses low specific area and vulnerability to water and carbon dioxide in the air, which to some extent limited the production efficiency in practical application [7–10]. In order to obtain solid base catalysts with high specific area, many approached were developed for fabricating porous alkali earth metal oxide [11–13]. However, single porous MgO or CaO still showed poor stability as employed in the solvent. Porous materials supported alkali was also extensively studied in the past decade. Davis et al. prepared CsNaX and CsNaY by impregnating NaX and NaY with cesium acetate followed by thermal decomposition of the acetate into the oxide [14]. The use of mesoporous silica e.g. MCM-41 and SBA-15 as carriers for basic guest species has also been proposed, which could overcome the drawback of zeolite supported basic catalysts wherein the small pore openings prevented bulky molecules from reaching the active sites [15,16].

Although microporous or mesoporous support materials provided relatively high specific area for solid base catalysts, some supporting materials would negatively influence the basicity and stability of the catalyst. Thus, selecting appropriate carrier for the solid base catalyst was quite significant. In exploring novel solid bases with high activity and durability, our group scanned alumina, silica and other oxides as the support of CaO or MgO based on many literatures. Recently, it was found that zirconia was an ideal candidate since Ca^{2+} could incorporate into the host lattice and led to the formation of solid solution structure [17,18]. This solid base was tested in the transesterification of methanol and propylene carbonate and exhibited remarkable stability. However, the specific surface area of CaO/ZrO_2 solid base was only $10 \sim 50$ $m^2\ g^{-1}$ and further effort was required to improve the structure of catalyst.

Since the discovery of mesostructured silica-based materials [19,20], synthesis of mesoporous zirconia and other metal oxides has attracted intensive attention [21–23]. Yang et al. developed a new way to synthesize mesostructured zirconia using tri-block copolymer as template in non-aqueous solvent. The so-called evaporation induced self-assembly (EISA) approach has been employed to prepare a wide range of transition metal oxides. In order to improve the thermal stability of mesoporous zirconia, Cassiers et al. [24] developed ammonia treatment and found this strategy

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can fairly enhance the thermal stability of mesoporous titania or zirconia. Based on the previous research, a sol–gel route was employed to prepare mesoporous $CaO–ZrO_2$ nano-oxides, and this new type of solid base was found to be highly active and stable.

2. Experimental

2.1. Preparation procedure

In preparation of mesoporous $CaO–ZrO_2$ nano-oxides, a delicate procedure was designed. Typically, 1 g of amphiphilic poly(alkylene oxide) block copolymers ($PEO_{20}PPO_{70}PEO_{20}$, Pluronic P123) was dissolved in a designed amount of absolute ethanol. As the surfactant was completely dissolved, calculated amount of calcium nitrate was added. To this solution, 4.45 g of zirconium(IV) n-propoxide (23–28% free alcohol, Strem Chemicals) mixed with 0.5 g of acetylactone (acac) was added with vigorous stirring, herein acetylactone acted as a stabilizer to prevent the zirconium(IV) n-propoxide from uncontrollable hydrolysis. Upon stirring at room temperature for 1 h, 1.8 g of deionized water was added dropwise. The mixture, with molar ratio of 1 Zr: 0.02 P123: 0.5 acac: 0 ~ 1.0 Ca: 80 EtOH: 10 H_2O, was gelled in a closed vessel at 40 ~ 60 °C for 24 h. Subsequently the obtained resin-like hybrid was crushed and refluxed in 0.1 ~ 0.5 mol L^{-1} Na_2CO_3 solution for another 24 h. Then, the products were thoroughly washed with deionized water and filtered to remove the residual Na^+. Finally, the samples were heated in flowing N_2 at a ramping rate of 5 °C min^{-1} to 700 °C. The samples were denoted as *r*$CaO–ZrO_2$, where *r* stands for the Ca/Zr molar ratio.

2.2. Characterization

The structure of the materials were characterized by a Rigaku D/max-A X-ray diffractometer (XRD) with $\lambda = 0.1541$ nm, Cu K_α radiation. High resolution transmission electron microscopy (HRTEM) images were obtained on a Philips EM 400 T transmission electron microscope operating at 100 kV. The specific surface area of the powder was measured with a Tristar 3000 analyzer using the multipoint Brunauer, Emmett and Teller (BET) adsorption. The basicity of the samples were measured by Temperature programmed desorption of CO_2 (CO_2-TPD), 0.2 g sample were heated in a flow of He (99.99%) at a rate of 10 °C min^{-1} to 700 °C and kept at 700 °C for 2 h. Prior to adsorption of CO_2 (99.999%) at 30 °C, blank TPD was carried out from 30 °C to 700 °C to confirm no desorption of CO_2 occurred. When the temperature elevated, the CO_2 desorbed was detected by a Balza Q-Mass spectrometer.

Raman spectra of the samples were recorded on a DILOR XY spectrometer equipped with a liquid-nitrogen cooled charge-coupled device (CCD) detector. Catalyst powder was put in the sample cup in the cell. This cell was connected to the high-pressure gas flow system. The emission line at 514.5 nm from Ar^+ ion laser (Spectra Physics) was focused on the sample under microscope, the width of the analyzed spot being ~1 μm. The power of the incident beam on the sample was 3 mW. The time of acquisition was adjusted according to the intensity of the Raman scattering. The wavenumber values reported from the spectra are accurate to within 2 cm^{-1}. For each sample, the spectra were recorded at several points to ascertain the homogeneity of the sample.

2.3. Catalytic test

In order to investigate the activity of the as-prepared solid base catalysts, synthesis of dimethyl carbonate (DMC) from propylene carbonate (PC) and methanol was employed as the model reaction. The catalytic test was conducted in a vertical fixed-bed stainless steel tube (8 mm i.d.) under pressure of 0.5 MPa. The mixture of propylene carbonate and methanol with PC:MeOH molar ratio of 1:2 was pumped into the reactor. The reaction products were collected by an ice cooler and were analyzed by a gas chromatograph with TCD. In all reactions, same amount of catalyst were used in the form of granules (20–40 mesh) prepared by palletizing the catalyst powder and crushing to the desired size.

3. Results and discussion

3.1. Structure of the solid base

The XRD patterns of $CaO–ZrO_2$ solid bases with different Ca/Zr molar ratio were shown in Fig. 1. The samples with Ca/Zr of 0 ~ 0.5 showed a distinct reflection peak at $2\theta = 1°$, which revealed the products possessed mesoporous framework. It was found that the structure of $CaO–ZrO_2$ solid bases was greatly influenced by the composition. With Ca/Zr increased, the diffraction peak became weaker and broader, which suggested the increase of Ca/Zr exerted a negative effect on the mesoporous framework of $CaO–ZrO_2$ solid bases. It is well-known that soluble salts could significantly affect the sol–gel process. In this work, the precursor of CaO (calcium nitrate) had a strong impact on the hydrolysis/condensation of zirconium n-propoxide and the self-assembly of the gel. Thus, excessive calcium salt added to the system could influence or even damage

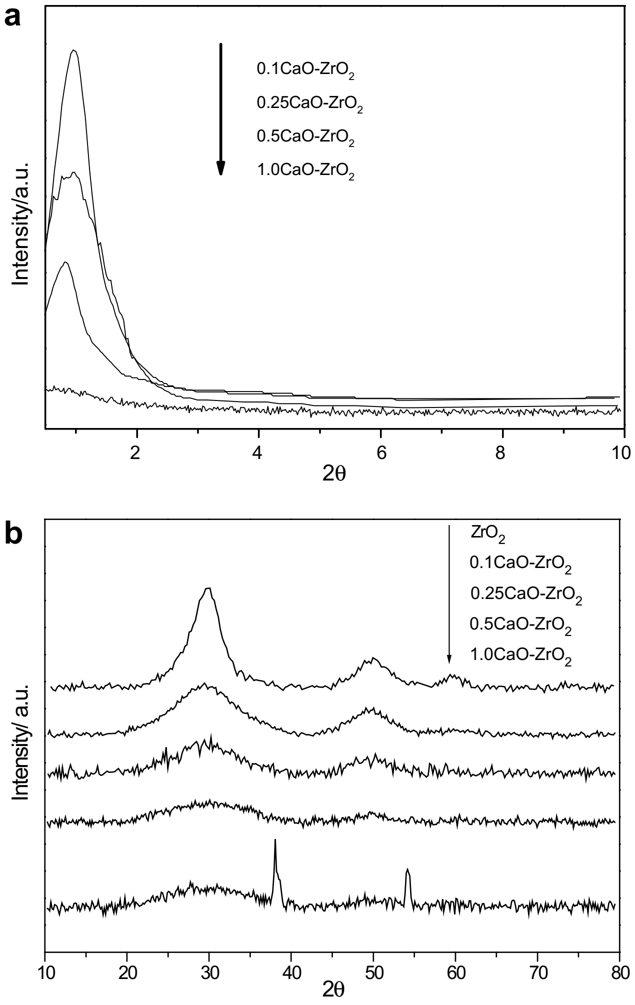

Fig. 1. XRD patterns of $CaO–ZrO_2$ nano-oxides.