Hydrothermal synthesis, characterization and acid catalytic activity of nano Ce-La oxide powder

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Ce-La oxide powder has been synthesized by hydrothermal method at 250°C using cerous nitrate, lanthanum nitrate and hydrazine hydrate as raw materials and characterized by X-ray diffraction, transmission electron microscopy and infrared spectra. The acid catalytic performance of the sample has been investigated in the reaction of acetic acid and n-butyl alcohol. The results show that La³⁺ is embedded into the cubic crystal lattice of CeO₂ and forms a homogeneous solid structure. The particle diameter of sample is less than 50 nm. Ce-La oxide solid solution possesses higher acid catalytic performance and its catalytic mechanism is of the proton acid catalysis type.

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The synthesis of ceria (CeO₂) and ceria-containing materials is of considerable interest for applications as diverse as catalysts, glass polishing, ultraviolet absorbers, luminous materials, solid oxide fuels and ceramics. CeO₂ can easily form solid solutions with other rare earth elements and with transition metals, which can improve the performance of CeO₂³. We have earlier reported the preparation of CeO₂-ZrO₂ solid solutions by coprecipitation and hydrothermal synthesis methods. These solid solutions show higher catalytic performance in three-way catalysis for car exhaust cleaning and in solid acid catalysis. In recent years, synthesis of nano materials have become of importance because of their unique properties. Hydrothermal method, as a wet chemistry method, offers many advantages compared to other methods, especially solid-state synthesis. One of the main advantages is that weak interactions (van der Waals, hydrophilic-hydrophobic interaction, etc) are not broken at lower temperature. The interactions involve self-assembling of molecular precursors and can play an important role during the formation of the oxide network. Herein, we report the hydrothermal synthesis of nano Ce-La oxide solid solution and its acid catalytic performance as well as the catalysis mechanism.

Experimental

Cerous nitrate (Ce(NO₃)₃.6H₂O), lanthanum nitrate (La(NO₃)₃.6H₂O) and hydrazine hydrate were of analytic purity and used as the starting materials. The nitrates of cerium (0.006 mol) and lanthanum (0.004 mol) (Ce/La mol ratio=0.6/0.4) were dissolved in 40 ml distilled water with vigorous stirring. Then, hydrazine hydrate was added dropwise to form a precipitate until the pH reached about 9.0. The mixture was put into a stainless steel autoclave with an inner volume of 60 cm³. After the autoclave was sealed tightly, it was placed in a thermostatted oven, heated at 250°C for 10 h. The precipitated particles were filtered, washed with distilled water and ethanol, and then dried in an oven at 80°C under an air atmosphere. The formula of the as-prepared sample is denoted as Ce₀.₆La₀.₄O₁.₈.

Characterization and catalytic activity

XRD was carried out on a Rigaku (Japan) D/Max-1200 X-ray diffractometer with Cu Kα (λ=1.54178Å). Scanning rate of 0.02°/s was applied to record the pattern in the 2θ range of 10-90°. The TEM image was recorded on a Hitachi H-800 transmission electron microscopy. The FT-IR spectra were obtained with a Nicolet spectrometer (model 205), using KBr pellet technique.

The activity test was performed in a three-neck flask with a water separator and thermometer containing n-C₄H₉OH (0.25mol), CH₃COOH (0.25mol) and a specific amount of catalyst (Ce₀.₆La₀.₄O₁.₈). After being heated under the reflux for some time, the reaction was stopped and the esterification rate was measured by the titration with CH₃COOH. After completion of reaction, the catalyst was filtered from the reaction liquid and used directly in the next esterification reaction.

Results and discussion

Figure 1 shows the XRD pattern of the sample. The reflection is similar to the CeO₂ cubic phase with
fluorite structure, indicating La$^{3+}$ ion has dissolved into the crystal lattice of CeO$_2$ forming a solid solution structure. The lattice parameter of Ce$_{0.6}$La$_{0.4}$O$_{1.8}$ is 0.5508 nm is larger than 0.5411 of CeO$_2$. The reason is that the ion radii of La$^{3+}$ (0.118 nm) is larger than that of Ce$^{4+}$ (0.097 nm), leading to expanding of the lattice cell. The particle size calculated by Scherrer formula is in the range 5 – 30 nm. From the TEM image (Fig. 2), it can be seen that the particle diameter can be estimated at 50 nm and 5 nm, which is consistent with XRD results. The FT-IR spectra of the sample shows a peak at ~ 3620 cm$^{-1}$, which may be attributed to –OH, indicating the existence of proton acid (Brönsted) sites in the structure of Ce$_{0.6}$La$_{0.4}$O$_{1.8}$.

**Catalytic activity**

The effect of reaction time on the catalytic activity was studied from 1.5 – 3.0 h. Results show that under conditions: CH$_3$COOH/n-C$_4$H$_9$OH mol ratio:1.0 and catalyst amount: 2 wt%, the conversion of CH$_3$COOH is highest when the time is 2.5 h.

Study on the effect of catalyst amount on the catalytic activity keeping CH$_3$COOH/n-C$_4$H$_9$OH mol ratio at 1.0 and reaction time as 2.5 h shows that conversion is highest when catalyst amount is 2 wt%.

At catalyst amount 2 wt% and reaction time 2.5 h, conversion of CH$_3$COOH is highest when CH$_3$COOH/n-C$_4$H$_9$OH mol ratio is 1:1.

The catalytic activity of the oxide was tested after being reused several times when CH$_3$COOH/n-C$_4$H$_9$OH mol ratio was kept at 1:1, catalyst amount at 2 wt% and reaction time at 2.5h. Conversion decreased slightly after the oxide was used three times. Ce$_{0.6}$La$_{0.4}$O$_{1.8}$ can be easily separated from reaction liquid, and thus, is a sort of green solid acid catalyst as replacement for traditional corrosive liquid acid such as H$_2$SO$_4$, HF, AlCl$_3$, etc.

**Acid catalysis mechanism**

The formation mechanism of acid sites depends on the structures of solid acids. For binary oxides, the formation of acid sites follows the Tanabe rule$^7$, which takes into consideration two aspects: Firstly, the coordination numbers for positive elements of every metal oxide after interblending And secondly, the coordination charge numbers of all oxygen atoms are determined by those of the The positive excess charge yields Lewis (L) acid sites and the negative excess charge yields Brönsted (B) acid sites. In the structure of Ce$_{0.6}$La$_{0.4}$O$_{1.8}$ solid solution...
(Fig. 3), every Ce$^{4+}$ is surround by eight O$^{2-}$ and every La$^{3+}$ is surround by seven O$^{2-}$. CeO$_2$ is the main component. According to Tanabe rule, coordination charge number of oxygen atom is –1/2, hence, the coordination charge of oxygen atom for La$_2$O$_3$ is also –1/2. The net value of change in every La-O bond should be (+3/7)-1/2, i.e., equal to -1/14. The total net value of charge in every La atom is 7 x (-1/14), i.e., equal to –1/2. Based on the above observations, proton acid catalysis mechanism is proposed for the studied reaction.

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References