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Preparation and Characterization of Nanoporous Ceria Containing Heteroatoms, With and Without a Matrix

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Abstract. We have been interested in the synthesis and study of porous ceria, because of its importance in several catalytic applications, and notably in automobile exhaust catalysts. The mesoporosity of these solids is susceptible to changes in synthesis conditions such as pH and concentration of the cerium and other cations precursors used. The use of organic matrices to control pore production during synthesis, was also investigated. In this contribution we present results from the synthesis of mixed Mn(III/IV) cerium (IV) oxide precipitated from aqueous solution. The interest presented by these samples was that they had higher BET surface area as well as pore volume than the pristine ceria. The samples were studied using nitrogen adsorption, X-ray diffraction, diffuse reflectance FTIR (DRIFTS) and TGA.

Keywords: adsorption, ceria, template, manganese (III), FTIR spectroscopy

1. Introduction

There has been much recent interest in the preparation of inorganic solids with controlled porosity in the microporous and mesoporous range, or with other desirable surface properties, incúding the use of porous materials in air or water pollution control. Ceria (CeO_2), in particular, has attracted much interest because of its use as an additive in the so-called triodic automobile exhaust catalyst (Nunan et al., 1992), but also because of its use as a catalyst in its own right, or as a catalyst support. Ceria, or more recently ceria-zirconia (Hartridge et al., 2002; Kapoor et al., 2001) acts as an excellent oxygen store (see, for example, Terribile et al., 1997) in the catalyst, which is thus rendered a very effective catalyst for combustion. Ceria also enhances nitric oxide dissociation when added to various supported metal catalysts, which is another important function of the automotive exhaust catalyst. Ceria or metal supported on ceria have been found to catalyse such diverse reactions as methanol oxidation to CO and H_2 (Shen and Matsumura, 2000) CO oxidation to CO_2 (Overbury et al., 1999), and reduction of NO and N_2O to N_2 (Putna et al., 1998). In addition, several reports have appeared on the catalytic activity of mixed metal-cerium oxides.

At the University of Cyprus there is a long-standing interest in the synthesis and study of porous ceria (Pashalidis et al., 2000; Kyriacou et al., 2002; Theocharis et al., 2002). Work so far has concentrated studying ways of enhancing and stabilising higher porosity, as well as studying the chemistry of the surface. Two strategies have been used, the insertion of controlled amounts of dopants on the one hand (Curtufeld et al., 2003), and the use of organic matrices on the other (Lyons et al., 2002). Both these strategies have been used successfully in these laboratories. In some cases, the resulting solid had a lower BET surface area and lower pore volume than pristine ceria, whereas in other cases, especially where an organic template such as humic acid was used, an enhanvcement of both properties was observed. The mesoporosity of these solids is not intra-crystalline in the sense that the porosity of zeolites is, but depends upon aggregation of primary particles, and as such is susceptible to synthesis conditions such as pH and concentration

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of the cerium and other cations precursors used. In the present paper we present the results of an investigation into the use of a surfactant, namely CTAB. Also, the use of manganese ions as dopants is discussed. Manganese was employed because it possesses a number of stable oxidation states.

2. Experimental

The chemical reagents used for the preparation of stock solutions were reagent grade and were used without further purification. The chemicals were in the form of the nitrate salts and were obtained commercially from Aldrich or Fluka. Pure ceria samples were prepared by precipitation of ceria from aqueous solutions containing 0.01 M Ce^{4+} by adding 1 M NH_3 solution. The precipitate was dried at 523 K. The surface acid sites concentration was measured using Hammett titrations, with phenolphthalein as indicator, and a 0.1 M NaOH solution as base.

Mixed oxide samples were prepared by the co-precipitation from aquatic solutions of the cations ($[Ce(IV)] = 0.01$ M) by adding equal volume of 1 M NH_3 solution under controlled conditions. Manganese (II) nitrate was used as the heteroatom source at the appropriate concentration. Where an organic matrix was employed, a similar procedure was used. However, in the case where the matrix was a surfactant such as CTAB, then a hydrothermal technique was used: a 0.1 M surfactant solution was used and the reaction was carried out at 373 K for at least 24 h in an autoclave. It was found that the solid with highest BET surface area was obtained when the pH was adjusted to 11.5, and the reaction time to 96 h. The surface properties were investigated by nitrogen adsorption isotherm analysis and FTIR spectroscopy. The nitrogen adsorption isotherms were measured at 77 K using an ASAP 2000 analyser (Micromeritics) after outgassing the samples under vacuum (0.15 Pa) at 423 K. FTIR spectroscopy was carried out with a Shimadzu spectrophotometer (FTIR-8501) using both KBr and the DRIFTS method. The total pore volume referred to below, corresponds to the pore volume measured from the nitrogen isotherm, at $p/p^{\circ} = 0.995$. Thermogravimetric recordings were obtained using a Shimadzu TGA apparatus in flowing air. The catalytic efficacy of ceria samples was measured vis à vis to oxidation of NO to N_2. A continuous flow method was used, and measurements were carried out at various catalyst temperatures. The gaseous mixture used was 0.25% NO, 1% H_2, 5% O_2 and the rest helium. Mass flow controllers were used to control concentrations. The effluent gas synthesis was determined by quadrupole mass spectrometry. A Balzer mass spectrometer was employed. X-ray diffraction was carried out on a Shimadzu powder diffractometer using Cu Kα radiation in the 2Θ range 5–70°.

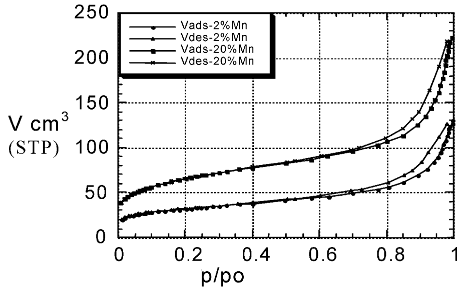

Figure 1. Nitrogen adsorption isotherms for ceria samples containig 2% Mn and 20% Mn.

3. Results and Discussion

Figure 1 shows the adsorption isotherms for samples containing 2 and 20 mole percent manganese ions as dopants. Table 1 summarizes the adsorption data for all manganese-containg samples, together with those for pristine ceria for comparison. The pore volume for the manganese-containing samples is consistently higher than for the pristine sample, whereas the BET surface area for all manganese concentrations above 2 percent is significantly higher. Figure 2 shows the FTIR spectra for the samples containing 2 and 20 mole percent. From a comparison with the spectrum for pristine ceria, it is clear that number of peaks near 3400 cm^{-1} which are usually to OH stretching is higher for manganese containing samples than for the pure ceria. A sharp peak

Table 1. Adsorption data for ceria samples dooped with manganese ions.

Sample	S_{BET} (m^2/g)	Pore volume (cm^3/g)
Pure CeO_2	80	0.08
2% Mn	113	0.19
2% Mn calcined for 2 h at 673 K	52	0.11
20% Mn	232	0.31
20%Mn calcined for 2 h at 673 K	99	0.23
30% Mn	219	0.29

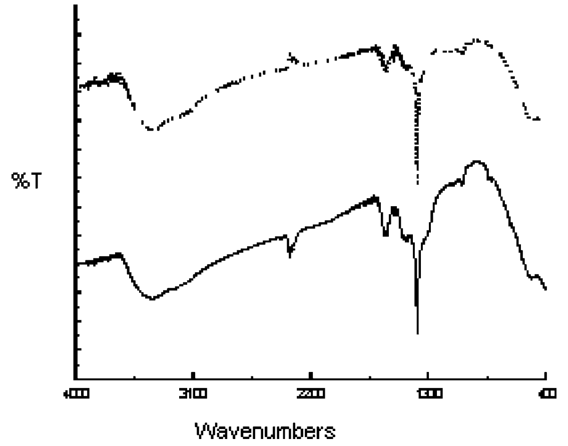

Figure 2. FTIR spectra for ceria samples with 2 and 20% Mn. The latter is depicted with a dashed line.

at 1250 cm^{-1} which has been previously assigned to Ce-(OH) groups is also present in these spectra, but with a modified shape. From Fig. 1, it can be seen that both isotherms are of type II in the IUPAC classification with an H3 type hysteresis loop suggesting the presence of ill-defined pseudomesopores.

The observations from the FTIR spectra indicate that the heteroatoms are associated with surface OH groups. X-ray diffractogrammes for the samples containing 2 and 20 percent manganese ions and of pure ceria have shown that the only phase present was the fluorite-like cerium (IV) oxide one. Comparison of the diffractogrammes of the samples has shown different intensity ratios as well as peak widths for the three samples, indicating differences in particle size, extent of crystallinity, as well as differences in composition. It appears, therefore, that a solid solution of manganese oxide/ceria is generated. This is indicated also, bu the enhanced acidity of the manganese-bearing samples, as indicated by acid-base Hammett titrations. Specifically, pristine ceria has a surface acid sites concentration of 3.5 mol (100 g^{-1}) compared with 3.84 for 2 percent Mn, 4.10 for 20 percent Mn, and 4.83 for 30% Mn. It should of course be pointed out that acidity in the current context means sites which are acidic enough to react with NaOH. The percent mole concentration of Mn in the solids measured by ICP atomic spectroscopy indicated that this was of the same magnitude as the concentration of Mn(II) in the mother solution, which is the one reported here.

So far as the 30 percent manganese containing ceria sample is concerned, X-ray diffraction has indicated the presence of a highly crystalline second phase, which has been identified as Mn_2O_3. Measurements with a magnetic balance have indicated that manganese was present in these samples as Mn(III)/Mn(IV). It should be noted that the manganese presursor used was manganese (II) nitrate.

A number of authors have suggested different strategies for the synthesis of mesoporous oxides in the presence of surfactants in concentrations higher than the critical one for micellisation. Many such experiments, however, led to structures which were prone to collapse upon calcination to remove the template. It should be noted that heating to a minimum temperature of at least 673 K is required.

In this presentation, we discuss the use of a cationic surfactant, namely CTAB in a Ce(IV) solution with a pH > 8, which is above the isoelectric point for cerium oxide (6.75). Under these circumstances an organic-inorganic complex is formed leading to a mesoporous solid upon calcination. CTAB can be easily detected by FTIR spectroscopy, due to characteristic bands at 2850 and 1600 cm^{-1} which are present in the sample before calcination, and absent after calcination. Calcination was carried out at 673 K and 723 K. The surface properties for these solids are presented in Table 2, whereas the nitrogen adsorption isotherms are presented in Fig. 3. It can be clearly seen that use of an organic template results in a significant increase in the apparent surface area compared with ceria prepared without a template. Furthermore, whereas in the latter case a type II isotherm with a hysteresis loop was obtained indicating the presence of ill-defined pseudomesopores, in the former case the isotherm was of type IV indicating the presence of real mesopores.

In Table 2, the various samples are described in terms of the concentration of the precursors in the reaction mixture. Thus, O.1 Ce/0.1CTAB indicates that a 0.1 M cerium ammonium nitrate solution was used with a 0.1 M CTAB one. It can be seen from the Table that

Table 2. Adsorption data for ceria samples prepared in the presence of CTAB.

Sample	S_{BET} (m^2/g)	Pore volume (cm^3/g)
0.1Ce/0.1CTAB	128	0.24
0.05Ce/0.1CTAB	119	0.16
0.01Ce/0.1CTAB	131	0.22
0.1Ce/0.1CTAB 2%Eu	126	0.18
0.1Ce/2%Eu/NH_3	47	0.04

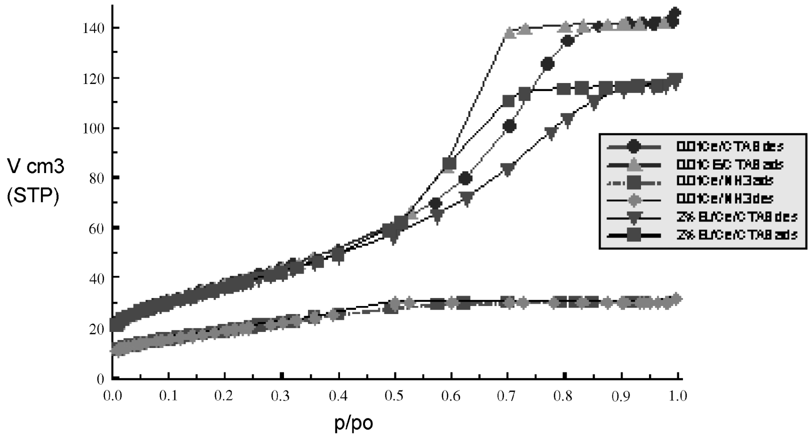

Figure 3. Comparison of nitrogen adsorption isotherms of ceria prepared with and without an organic matrix.

contrary to what has been previously observed for the case where no surfactant was used and the preparation method was homogeneous precipitation, here there is no dependence on cerium concentration of the BET surface area. This indicates that the mechanism of precipitation of cerium oxide in the presence of the surfactant is significantly different to that in its absence. It suggests that there is interaction between the micelles and the cerium ions in solution, and as polymerization of the Ce—O—Ce bonds takes place, of the ceria framework. Furthermore, where the reaction was carried out at a basic pH lower than 11.5 (but still above the isoelectric point of cerium oxide), the extent to which this interaction takes place is decreased given the lesser number of surface OH groups through which this is achieved, leading to a lowering of the BET surface area. For example, a sample prepared with a 0.01 M Ce(IV) solution at a pH of 10 had a BET surface area of only 60 m^2 g^{-1}.

The presence of mesopores in the samples prepared in the presence of CTAB as well as the absence of microporosity was shown by the use of t-plots. The shape of the hysteresis loop was of the H2 type according to the IUPAC classification indicating pores of the so-called ink bottle shape. If an anionic surfactant such as SDS was used, upon calcination at 673 K for removal of the template, a solid with a low surface area of 10 m^2 g^{-1} was obtained. This can be explained by the fact that the interaction between the surfactant and the ceria particles as well as the Ce^{4+} ions in solution was very weak, as both specied are negatively charged. Thus, no templating effect was expected to be observed.

Samples containing Eu^{3+} ions as template were prepared with and without a template. The BET surface area of the sample prepared with CTAB (Table 2, Fig. 3) and containing 2 mole percent europeum ions was comparable to the pristine samples, whereas the sample prepared without CTAB had significantly lower BET surface area and pore volume. This is contrary to the situation that obtains for the Mn-containing samples. All samples with the exception of the 30 mole percent Mn were shown by XRD to consist of a single phase. It appears therefore that the presence of these heteroatoms leads to a more open structure, without significant long-range disruption of the ceria fluorite structure.

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