MESOPOROUS SILICA GELS AND TiO_2/SiO_2 AND ZrO_2-SiO_2 MIXED OXIDES PREPARED VIA THE SOL-GEL METHOD

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Introduction

Mesoporous silica zirconia and silica titania aerogels with different Zr/Si and Si/Ti molar ratios were prepared using an experimental strategy via the sol-gel process. Pure SiO_2 oxide was prepared via the sol-gel process using tetraethylorthosilicate (TEOS) as precursor of silica and an autoclave (auto generated pressure). The TiO_2/SiO_2 and ZrO_2/SiO_2 supported oxides were prepared by incipient wetness impregnation of 2-propanol solutions of titanium isopropoxide and zirconium nitrate respectively. An experimental strategy was developed to obtain mesoporous SiO_2-ZrO_2 and SiO_2-TiO_2 mixed oxides via the sol-gel process The aim of this work was to investigate the synthesis of supported and mixed Ti-Si and Zr-Si materials and the effect of the silica content on the physical properties. The mesoporous supported oxides were dried and calcined at 500°C. The solids were characterized by nitrogen physisorption, pyridine chemisorption, ^{29}Si Nuclear Magnetic Resonance and X-ray diffraction. Characterization of the solids revealed that mesoporous materials with very narrow pore diameter distribution were obtained when using the autoclave procedure. Surface areas and pore size distributions were a function of ZrO_2 and TiO_2 content.

The properties of silica have been extensively studied by many authors, due to its wide range of applications [1,2]. Combinations of silica with a large number of other oxides have been reported [3]. Pure ZrO_2 and TiO_2 carriers have very small specific surface area, low thermal stability and high price, that makes them unsuitable for industrial applications. In order to overcome these drawbacks, increasing attentions has been paid to the development of mixed oxide supports by combining the higher surface areas and thermal stability of silica with the unique acidic properties of ZrO_2 and TiO_2. Mixed titania-silica and zirconia-silica materials are potentially useful in a number of technological applications, including catalyst. More particularly, previous work has been published on the silica-zirconia system as synthesized by the sol-gel method [1,4]. However, it is necessary to shed light on several issues concerning the synthesis and characterization of this system by using the sol-gel method. SiO_2- ZrO_2 mixed oxides have gained increasing attention in recent years because of their interesting characteristics and many applications, which include alkali-durable glasses, catalyst support and as an advanced ceramic material [8]. We will try to provide a consistent picture in order to clarify structure-property relationships in silica- zirconia materials based on the combined results of different characterization techniques such as x-ray powder diffraction, N_2 physisorption, ^{29}Si NMR spectroscopy and FTIR pyridine thermodesorption. The representative methods of preparation of porous materials in the SiO_2-ZrO_2 system are using a sol gel method, although the literature related to the synthesis of SiO_2-ZrO_2 is very scarce. The starting components are usually alcoholic solutions of alkoxides which undergo condensation reactions after initial hydrolysis. The homogeneous incorporation of Zr into a matrix is important to obtain materials that exhibit chemical, thermal and mechanical stabilities. The goal of the present work was to obtain mesoporous SiO_2-ZrO_2 and SiO_2-TiO_2 systems, based on a controlled hydrolysis-condensation process. The experimental strategy developed here allows one to obtain mesoporous materials when the gel is treated in an autoclave and heated to 150°C. Previous works in our group have pointed out the importance of a fine tuning of the synthesis conditions in order to produce solids with the desired characteristics. We decided to use them as supports to compare them with TiO_2 to see how TiO_2 in different environments would affect the interaction.

Materials and Methods

The materials were synthesized via sol-gel method, the precursors used for this sol-gel preparation were tetraethylorthosilicate as the SiO2 source, an inorganic Zr-containing salt as the ZrO2 source, and titanium isopropoxide as a source of TiO2, water as solvent and nitric acid as hydrolysis catalysts. After condensation, the resulting gel was split into three fractions. One fraction was dried at ambient temperature and pressure for 24 hours obtaining microporous materials, the second fraction, identified as primary synthesis was put into an autoclave and heated at 150°C for 24 hours, finally the third fraction was heated in an autoclave with water at 150°C (hydrothermal synthesis).

Results and Discussion

Our investigations indicated that the physical and chemical properties of silica-zirconia and silica-titania gels could be altered by changing the zirconia and titania content of these gels. X-ray diffraction patterns were obtained for the calcined samples at several ZrO_2 contents. Fig. 1 shows the amorphous diffraction patterns for samples with high SiO2 content (pure silica, Si-Zr (80-20) with autoclave, Si-Zr (60-40) with autoclave), whereas those corresponding to the samples dried in an autoclave at high ZrO2 content were crystalline. For the samples with high ZrO_2 content it is interesting to note that the tetragonal or cubic phases were observed.

Significance

Variations in the synthesis conditions produced solids of different characteristics. It was found that the ZrO_2 and TiO_2 content influence the texture, structure and morphology of the samples. The synthesis report here is a good alternative to obtain these mesostructured materials.

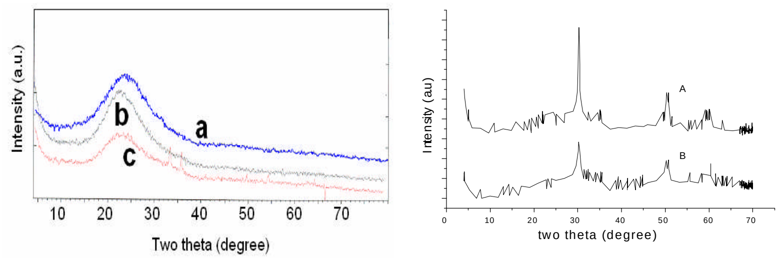

Fig.1.- XRD patterns of porous SiO2-ZrO2 with high SiO_2 content calcined at 550°C. Pure silica, (b) Si-Zr (80-20), (c) Si-Zr (60-40). XRD patterns of porous SiO_2-ZrO_2 with high ZrO_2 content calcined at 550°C.(A) Si-Zr (60% -40%) Si-Zr (20% -80%) .

References

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