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pH Effect on the Preparation by Sol-Gel Method of ZrO_2/SiO_2 Catalysts

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pH effect on the preparation of ZrO_2/SiO_2 catalysts by sol-gel method was studied. Basic and acidic media were used during the gelation of tetraethoxysilane (TEOS) and zirconium acetate. In acid medium the catalysts showed high acidity and high specific surface area up to 805 m^2/g, whereas in the basic preparations the opposite effect was observed.

Zirconium oxide is one of the most promissing catalyst for a large number of reactions. The important acid-base properties shown by this oxide have great applications in classical acid-base reactions i.e. dehydration of alcohols and hydrocarbons dealkylation. The acidity and, consequently, the activity of ZrO_2 are dramatically improved by the addition of sulfate ion, resulting new and powerfull catalysts.[1)] Zirconium oxide is also used as catalyst support, and Mo/ZrO_2 hydrotreating catalysts are homogeneously prepared.[2)] Skeletal isomerization on Pt/ZrO_2[3)] and CO hydrogenation on Pd/ZrO_2 were performed.[4)] However, the main problems to use zirconium oxide as catalyst or support are the low surface area as well as the low stability to thermal treatments.[5)] In this direction the use of yttrium or magnesium oxides seems to be a good alternative to stabilize the zirconium oxide.[5)] However, it is well known in heterogenous catalysis that the stabilization of the active phase is accomplished by its deposition on an inert support. In this way important progress is obtained impregnating silica gel with ZrOCl.[6)] In the present communication the sol-gel method (simultaneous gelation of zirconium acetate and tetraethoxysilane) is used as an altenative to obtain high surface area ZrO_2/SiO_2 catalysts.

Two types of catalysts were prepared: ZrO_2/SiO_2-OH (basic) and ZrO_2/SiO_2-H (acid). The general procedure was the following: In a flask containing 36.8 ml of tetraethoxysilane (TEOS) and 10 ml of HCl (36% vol) or

Table 1. Effect of Zirconium acetate on the specific surface area, pore size, and acidity for the various ZrO_2/SiO_2 catalysts

Sample	ZrO_2 wt%	BET area $m^2\ g^{-1}$	Mean pore diameter	Acidity (meq) $NH_3\ g^{-1}$	10^4 Acidity / BET area
ZrO_2/SiO_2-H-1	1.3	620	55	0.079	1.2
ZrO_2/SiO_2-H-3	4.0	741	56	0.155	2.1
ZrO_2/SiO_2-H-5	6.7	805	45	0.162	2.0
SiO_2 -H	--	550	60	0.000	--
ZrO_2/SiO_2-OH-1	1.3	34	179	0.023	6.7
ZrO_2/SiO_2-OH-3	4.0	47	154	0.039	8.2
ZrO_2/SiO_2-OH-5	6.7	23	155	0.056	24.3
SiO_2-OH	--	110	120	0.000	--

NH_4OH (35% NH_3) were added drop by drop 36 ml of an aqueous solution containing; a) 0.293, b) 0.879, and c) 1.465 g of $Zr(OH)_2(COOCH_3)_2$ in order to obtain 1.3, 4.0, and 6.7 wt% of ZrO_2 on SiO_2. The solution was stirred and refluxed at 80 °C during 5 h. After gelation the solids were dried at 110 °C and then calcined at 500 °C during 12 h. For reference two samples of SiO_2 in which the TEOS was gelated in acid or basic medium were prepared.

Specific surface areas were determined in an automatic Micromeritics ASAP 2000. Pore size distribution was calculated from BJH method and the BET equation was used to calculate the specific surface area.

In Table 1, the BET areas as well as the mean pore size distribution are reported. The main differences found between both preparations are the following: in ZrO_2/SiO_2-OH catalysts small BET areas comprised between 23 to 47 m^2/g and a large mean pore size diameter of around 150 Å were found. In contrast in ZrO_2/SiO_2-H preparations the BET areas are surprisingly higher (up to 805 m^2/g), and exhibit a very narrow pore size distribution, the mean pore diameter is around 50 Å.

The different textures obtained in both catalysts are certainly due to the preparation step. The simultaneous gelation of TEOS and zirconium acetate produce important effects on the gel and hence on the textural properties. The gelation of TEOS prepared as references, show, in acid or basic medium specific areas of 110 and 550 m^2/g respectively, Table 1.

Electron micrographs were obtained in a STEM JEOL 100CX electron microscope and they are shown in Fig. 1. The micrographs using scanning transmission mode show the aggregation state crystallites in a single grain.

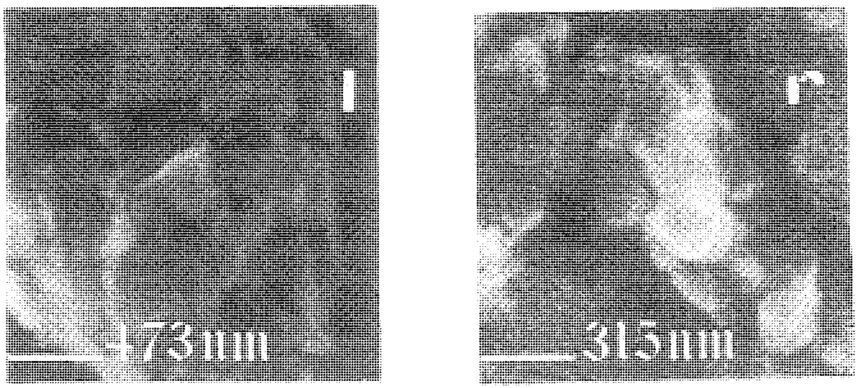

Fig. 1. STEM electron micrographs of the ZrO_2/SiO_2 at 3% wt catalysts: left) acid medium, right) basic medium.

The crystallites size are extremely small, i.e. about less than 10^3 angstroms diameter in basic preparation. However, acid samples has smaller crystals diameter i.e. from 200 to about 600 Å.

The preparation of ZrO_2/SiO_2 by the sol-gel method has also important effects in the acidity of the solids. The total acidity was calculated by the adsorption at 200 °C of NH_3 using a calibrated loop coupled to a six way valve. The saturation of the NH_3 adsorption was recorded in a conductivity electrometer. The results in Table 1 show a high acidity in acid catalysts preparation and a very low one for the basic preparations. Moreover, an important effect of the ZrO_2 content on the total acidity is clear, Table 1.

Thermal NH_3 desorption for the acid samples is reported in Fig. 2. In this thermographs, a desorption peak about 300 °C is present. It increases as a function of the zirconia content.

Silica glasses with high specific surface area are obtained by gelation of TEOS in HCl acid.[7)] The hydrolysis of TEOS in acid medium is performed via the formation of pentacoordinated species.[8)] If HCl acid is used the formation of a Si-Cl bond is postulated in the pentacoordinated complex $Si(OEt)_4Cl$.[9)] Hence, surface area blows up. Nevertheless, in basic medium nucleophiles are formed and they shorten the netwoork during postgelation.

In the present study, the addition of zirconium acetate to the gelation medium has two effects on acid medium: a) the specific area is increased, and b) an important acidity is observed. In basic medium the opposite phenomenon is observed, Table 1.

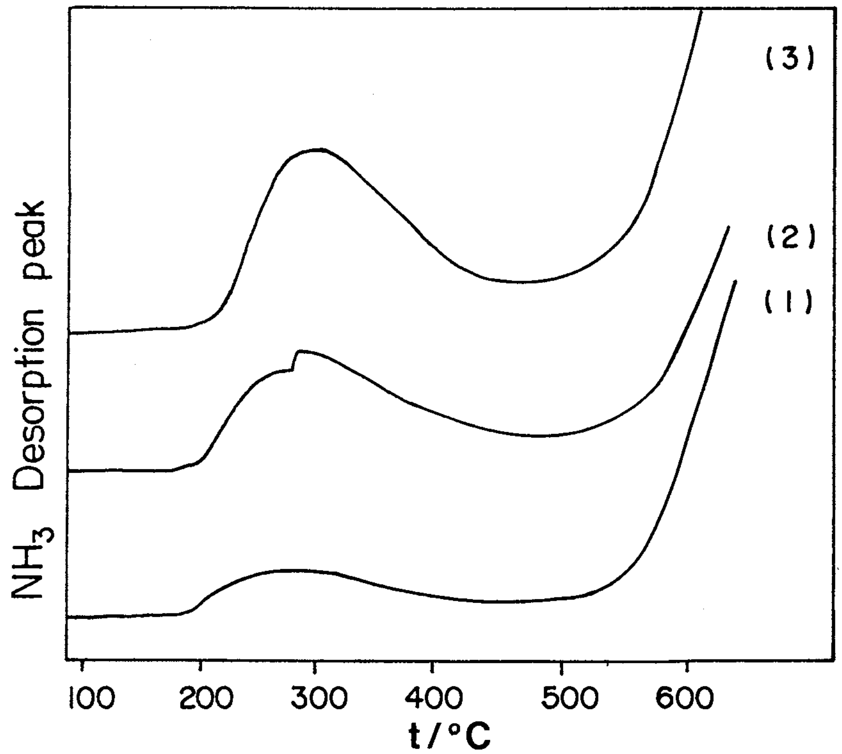

Fig. 2. Ammonia thermodesorption for the ZrO_2/SiO_2 -H catalysts at various ZrO_2 contents: 1) 1.3, 2) 4.0, and 3) 6.7% wt.

The above results show that the preparation of ZrO_2/SiO_2 by the co-gelation of TEOS and zirconium acetate (sol-gel method) is a good alternative for the obtention of solids with controlled acidity and for the obtention of catalysts with specific surface areas comprised between 27 and 805 m^2/g. The large effects obtained, on acidity as well as on specific areas, allow us to predict multiple applications of these solids in a large number of chemical reactions.

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