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Synthesis of SO_4^{2-}/ZrO_2/MCM-41 as a new superacid catalyst†

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A new SO_4^{2-}/ZrO_2/MCM-41 superacid catalyst has been successfully synthesized and is *ca.* 2.5–3 times more active than the conventional SO_4^{2-}/ZrO_2 superacid catalyst for MTBE synthesis and *n*-pentane isomerization.

It is well known that zirconia, when modified with anions such as sulfate, forms a highly acidic or superacidic catalyst. In recent years, sulfated zirconia superacids have attracted increasing attention because these catalysts are found to be well suited for catalyzing reactions of industrial importance, such as hydrocarbon isomerization, etherification reactions, *etc.*[1–8] However the non-uniform pore size and relatively small surface area of SO_4^{2-}/ZrO_2 may limit its potential application for catalyzing bulky molecules. The use of M41s and other mesoporous materials,[9–12] which have very uniform mesopores and very high surface area, as catalyst supports for SO_4^{2-}/ZrO_2 should greatly expand the catalytic properties and capabilities of SO_4^{2-}/ZrO_2 for some applications. This is because such mesoporous materials, which have relatively small diffusion hindrance, can aid the diffusion of bulky organic molecules in and out of their mesopores quite easily.[9] Although many superacid catalysts have been developed using silica, alumina and microporous zeolites as supports,[2–8] there are still many limitations in their applications because of diffusion problems. Although a direct preparation of mesoporous sulfated zirconia has been recently reported,[13] the resulting materials had relatively small surface areas compared to that of conventional SO_4^{2-}/ZrO_2 and they were not tested for a particular reaction. Up to now, no silica-based M41s superacid materials nor gas-phase synthesis of MTBE from methanol and *tert*-butyl alcohol on acidic mesoporous catalysts have been reported. In this work, the active superacid SO_4^{2-}/ZrO_2 component has been successfully supported on the surface of MCM-41 to form a new SO_4^{2-}/ZrO_2/MCM-41 superacid catalyst, which is found to be 2.5–3 times more active than the conventional SO_4^{2-}/ZrO_2 superacid catalyst for MTBE synthesis and *n*-pentane isomerization.

$Zr(OH)_4$ was supported onto the surface of MCM-41 through chemical liquid deposition and hydrolysis of $Zr(OPr^n)_4$. Pre-dried siliceous MCM-41 powder having a BET surface area of 1311 $m^2\ g^{-1}$ and a pore diameter of 31.1 Å was dispersed into a mixed solution of $Zr(OPr^n)_4$ and *n*-hexane under vigorous stirring. After evaporating off the solvent, the solid was transferred into a glass container containing an NaCl-saturated aqueous solution at the bottom of the container in order to achieve complete hydrolysis at room temp. overnight. Pure $Zr(OH)_4$ was also prepared through hydrolysis of anhydrous $ZrCl_4$ in ammonia solution with a pH of 9–10.[3] After drying both samples at 100 °C overnight, the two resulting solids were immersed into 0.5 M H_2SO_4 solution at room temp. for 30 min. The sulfated $Zr(OH)_4$/MCM-41 and $Zr(OH)_4$ were then filtered off, dried at 100 °C overnight and calcined at 600 °C in air for 3 h to form SO_4^{2-}/ZrO_2/MCM-41 and SO_4^{2-}/ZrO_2. The content of ZrO_2 in the SO_4^{2-}/ZrO_2/MCM-41 catalyst was analyzed by ICP to be *ca.* 41 wt%. It should be noted that, when $ZrCl_4$ was used as a precursor in the preparation of $Zr(OH)_4$/MCM-41, the mesoporous structure of MCM-41 collapsed in the basic medium required for the hydrolysis of $ZrCl_4$.

XRD was used to characterize the regular mesoporous structure of MCM-41 and the resulting crystalline phase of bulk and supported ZrO_2. Fig. 1 shows that, for SO_4^{2-}/ZrO_2 calcined at 600 °C, three intense diffraction peaks at *ca.* 30, 50 and 60° and several small peaks at *ca.* 35 and 62° can be observed. These diffraction peaks show the presence of the tetragonal ZrO_2 crystalline phase, rather than the monoclinic ZrO_2 phase, and the absence of other impurities. This result shows that the introduction of SO_4^{2-} anions can remarkably stabilize the metastable tetragonal ZrO_2 phase, which is known to be an ideal crystalline phase for high catalytic activity.[2,4,6] The XRD pattern of SO_4^{2-}/ZrO_2/MCM-41 shows three clear and intense peaks below 10°, showing that the regular hexagonal mesostructure of the MCM-41 support is still maintained even after it has gone through the processes of chemical liquid deposition of ZrO_2, impregnation of sulfuric acid and high-temperature calcination. Furthermore, only a very small XRD peak at *ca.* 30° is observed on SO_4^{2-}/ZrO_2/MCM-41, showing that most of the ZrO_2 has been highly dispersed on the MCM-41. However, when this XRD picture is enlarged 5 ×, three diffraction peaks at *ca.* 30, 50 and 60° can be observed. This shows that, under very high loading of zirconia, a very small amount of ZrO_2 clusters (present as tetragonal ZrO_2 phase) might be formed within or outside the MCM-41 structure. BET analyses show that SO_4^{2-}/ZrO_2/MCM-41 (686 $m^2\ g^{-1}$) has a much larger surface area than SO_4^{2-}/ZrO_2 (101 $m^2\ g^{-1}$). The pore size of SO_4^{2-}/ZrO_2/MCM-41 (29.1 Å) is less than that of MCM-41 (31.1 Å), showing that the supported ZrO_2 has been dispersed onto the surface of mesopores of MCM-41.

The *in situ* FTIR spectrum of SO_4^{2-}/ZrO_2 measured after evacuation at 400 °C for 2 h shows an absorption band at 1378 cm^{-1}, corresponding to the asymmetric stretching frequency of covalent S=O; this band is often regarded as the characteristic

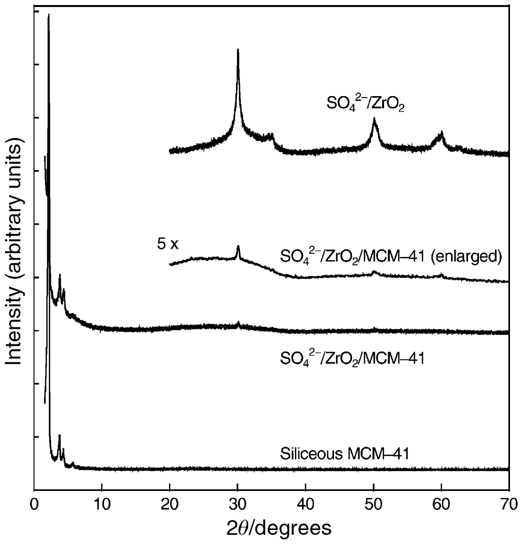

Fig. 1 XRD patterns of SO_4^{2-}/ZrO_2 and SO_4^{2-}/ZrO_2/MCM-41 superacid catalysts calcined in air at 873 K for 3 h and of siliceous MCM-41.

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† Electronic supplementary information (ESI) available: characterization data for catalysts. See http://www.rsc.org/suppdata/cc/b0/b006051h/

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band of SO_4^{2-} on promoted superacids.[2–4,6] This band shifts to 1363 cm^{-1} for SO_4^{2-}/ZrO_2/MCM-41; the shifting is attributed to the influence of the interaction between ZrO_2 and framework SiO_2. TGA spectra show that both samples display common double-stage weight-loss features: the first below 200 °C (due to the evaporation of physically adsorbed water and other molecules), and the second between 580 and 900 °C (attributed to the removal of SO_4^{2-} species interacting with ZrO_2). The similarities of the decomposition temperature between these two samples indicate that the distribution of SO_4^{2-} species on both SO_4^{2-}/ZrO_2 and SO_4^{2-}/ZrO_2/MCM-41 is quite similar. Based on the amount of weight loss, SO_4^{2-}/ZrO_2 and SO_4^{2-}/ZrO_2/MCM-41 calcined at 600 °C contain 5.8 and 7.6 wt% of sulfate ions, respectively. Since the ZrO_2 content in SO_4^{2-}/ZrO_2/MCM-41 is nearly half of that in SO_4^{2-}/ZrO_2, this result shows that the highly dispersed ZrO_2 on MCM-41 can expose more ZrO_2 and adsorb more SO_4^{2-} anions than bulk crystalline ZrO_2.

The acid strengths of SO_4^{2-}/ZrO_2 and SO_4^{2-}/ZrO_2/MCM-41 samples calcined at 600 °C for 3 h were measured by the change of the color of a Hammet indicator added to the dried powder sample dissolved in the solvent. Both samples are found to have an H_0 value around -13.8 (measured in 2,4-dinitrotoluene), a typical value for superacids,[2–6] showing that they are *ca.* $10^4 \times$ more acidic than 100% H_2SO_4. After calcination at 650 °C for 3 h, the acid strengths for both samples were increased to H_0 *ca.* -16.0 (measured in 1,3,5-trinitrobenzene).

Pyridine adsorption *in-situ* IR spectra were measured for both samples to measure the presence of Bronsted and Lewis acid sites. This was done by first pretreating a self-supporting wafer (15 mg) of the sample at 400 °C for 3 h under a vacuum of 10^{-6} mbar before adsorbing an excess of pure pyridine at room temperature, followed by evacuation at 200 °C for 30 min.[8] FTIR spectra on these two superacid catalysts show that they contain strong Bronsted acidity (at 1540 cm^{-1}) and Lewis acidity (at 1450 cm^{-1}). The intensities of Bronsted acid (having an integrated area of 1.20) and Lewis acid (having an integrated area of 1.43) sites of SO_4^{2-}/ZrO_2/MCM-41 are much stronger than the Bronsted acid (0.70) and Lewis acid (1.00) sites of SO_4^{2-}/ZrO_2. Both TGA and FTIR results show that SO_4^{2-}/ZrO_2/MCM-41 has more exposed Bronsted and Lewis acid sites than SO_4^{2-}/ZrO_2.

For the isomerization of *n*-pentane, which is a model reaction for characterizing the catalytic properties of these superacid catalysts, 0.5 g of powder catalyst was placed in a glass batch reactor and activated in vacuum at 250 °C for 3 h before 1 ml of pure *n*-pentane was introduced into the reactor and the reaction carried out at 60 °C under vigorous stirring. For the gas-phase synthesis of MTBE from MeOH and Bu^tOH in a fixed-bed reactor, the catalyst (0.20 g) was dehydrated in a flow of helium before a mixture of MeOH and Bu^tOH (with a molar ratio of 10 : 1 and a WHSV of 10 h^{-1}) was pumped into the reactor heated at 140 °C. Table 1 shows that both superacid catalysts have rather high activities for both reactions, with SO_4^{2-}/ZrO_2/MCM-41 always showing higher catalytic activity than SO_4^{2-}/ZrO_2. For the isomerization of *n*-pentane, the TON of SO_4^{2-}/ZrO_2/MCM-41 is almost 3 × that of SO_4^{2-}/ZrO_2, while the selectivity of product to isopentane is 98–99% for both catalysts. Increasing the batch reaction time gradually increases the TON of both catalysts to approach the equilibrium value. For the synthesis of MTBE, the TON of SO_4^{2-}/ZrO_2/MCM-41 is nearly 2.5 × that of SO_4^{2-}/ZrO_2, while a complete selectivity to MTBE is obtained on both catalysts. With an increase of reaction time, the TON of both catalysts remain almost unchanged. The reaction results show that the higher catalytic activity of SO_4^{2-}/ZrO_2/MCM-41, as compared to SO_4^{2-}/ZrO_2, is attributed to the increase of the number of active acid sites due to the highly exposed and easily accessible active sites of SO_4^{2-}/ZrO_2 on the surface of MCM-41. All of these results further elucidate the advantages of using a high BET surface area and uniform mesoporous material as a support for superacid catalysts for MTBE synthesis and other acid-catalyzed organic reactions in the future.

Table 1 Catalytic activities of SO_4^{2-}/ZrO_2 and SO_4^{2-}/ZrO_2/MCM-41 superacid catalysts

		SO_4^{2-}/ZrO_2		SO_4^{2-}/ZrO_2/MCM-41	
Reactant	*t*/min	TON[a]	Selec.(%)	TON[a]	Selec.(%)
n-Pentane	60	0.27	98[b]	0.81	100[b]
	200	0.41	98	1.19	99
	360	0.50	98	1.36	99
	600	0.54	98	1.42	99
MeOH + Bu^tOH	60	4.11	100[c]	10.10	100[c]
	180	4.13	100	10.13	100
	360	4.11	100	10.12	100
	600	4.12	100	10.10	100

[a] TON: mol of products/mol of Zr in the catalyst. [b] Selectivity of isopentane. [c] Selectivity to MTBE.

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