Oxidizing ability as the defining factor of reactivity of sulfated zirconia

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Reaction of benzene with sulfated zirconia (SZ) is an oxidation to a surface phenyl ester (sulfite or sulfate) which forms phenol by hydrolysis, and a complex mixture of alkylbenzenes and polycyclic aromatics; a mechanism involving a one-electron transfer from benzene to SZ is proposed; oxidation of a fraction of substrate to alkyl surface esters which then ionize to carbocations is the origin of the high catalytic activity of SZ for alkane isomerization.

Sulfated metal oxides (SMOs), particularly sulfated zirconia (SZ), have been described in literature as solid superacids,[1] and their high catalytic activity has been ascribed to superacidity.[1]

In one particular case, the superacidic strength of SZ promoted with Fe and Mn (FMSZ) was tested by temperature-programmed desorption (TPD) of benzene (PhH),[2] which indicated that PhH is fully protonated, similarly to pyridine (py) or ammonia, in similar TPD studies on other solid acids.

A first challenge to this representation came from the observation that py and PhH gave TPD desorption maxima from FMSZ at the same temperature (840 K).[3] From the basicities of pyridine (pK_a = 5.25)[4] and hexamethylbenzene (50% protonation in 91% H_2SO_4,[5] corresponding to a pK_a of *ca.* −10), and the basicity ratio of hexamethylbenzene to benzene (6×10^{10}),[6] we can evaluate a basicity ratio of py and PhH of 10^{26}. If the desorption temperatures were determined by the strength of the acid–base interaction, pyridine should desorb at a much higher temperature than benzene. Subsequently it was shown that the desorption peaks of PhH from FMSZ,[7] py from FMSZ,[8] and both py and PhH from several sulfated zirconia catalysts SZ, FMSZ and Pt/SZ[8] are due to CO_2, or CO_2 and SO_2.

The observation that benzene is desorbed as fully oxidized material at high temperature does not provide, however, information about the reaction of this molecule with the catalyst at lower temperature, prior to the desorption step. It was in principle possible, if SZ was superacidic, that benzene was protonated at low temperature and retained as benzenium ion, which was then oxidized upon increasing the temperature. In order to elucidate the mechanism, we have exam- ined the reaction of benzene on SZ at low temperatures (353–373 K), chosen to reproduce the conditions existing during the adsorption step and the desorption of physisorbed benzene in the TPD experiments.[3]

The SZ catalyst (1.57–1.70% S, 105–107 $m^2\ g^{-1}$, activated for 2 h at 450 °C in air, in a glass tube),[9] was covered with benzene, the reaction tube sealed with a flame, and heated at 100 °C. After the reaction, the phases were separated and the solid extracted with more benzene or diethyl ether at reflux. Alternatively, the reaction mixture was first soaked in water and subsequently extracted using the same solvents. During hydrolysis but prior to extraction, adamantane was added to the mixture as an integration standard. The extract after concentration was analysed by GCMS. For very short reaction time, the activated SZ was mixed with benzene on a fine frit, boiled for 3 min (blowing hot air), filtered off, soaked in water, then worked up and analysed as above.

Two main classes of products have been identified: *oxidation* products, such as phenol (PhOH), triphenylcarbinol, and benzophenone, and *cleavage* and *recombination* products, represented by a large variety of compounds, such as diphenylmethane (DPM), alkylbenzenes (toluene, ethylbenzene, xylenes), biphenyl, phenylcyclohexane, and products of advanced condensation such as anthracene. PhOH and DPM were obtained in major amounts as early products of the conversion of benzene with SZ at 100 °C. PhOH was obtained, however, only in the experiments including the water-treatment step. Triphenylcarbinol and alkylbenzenes were also present, in minor amounts. After longer runs, we detected as late products phenylcyclohexane, benzophenone, biphenyl, more alkylbenzenes, as well as anthracene and other heavy compounds. The relative amounts of products in two representative runs at 373 K, normalized to DPM, are shown in Table 1. The total conversion calculated as 100 × mmol benzene consumed (mmol sulfate^{-1}) is shown in the last line. Even after the 3 min reaction, we identified PhOH, DPM and alkylbenzenes, with PhOH as the major product.

The failure of PhOH to be extracted with a solvent of equal or greater basicity, such as diethyl ether, before water treatment, indicates that the former is not retained by an acid–base interaction. This observation identified PhOH as a hydrolysis product and indicates that the first reaction product was a phenyl ester (sulfite or sulfate).

Our results identify oxidation as the first reaction of benzene with SZ. In view of the failure of SZ to adsorb benzene from a gas flow at 373 K,[8] the acid–base interaction plays no role. In fact, even py was retained under similar conditions only in a molar ratio py : SO_4 of 1 : 60.[10]

Formation of hydroxylated products was also observed in the reaction of adamantane (AdH) on SZ.[11] Even though products requiring odd-electron precursors were observed, it was still possible that hydride transfer from AdH to the catalyst occurred.[11] Hydride transfer from benzene to form a phenyl cation can, however, be excluded. Likewise, electrophilic hydroxylation requires the presence of hydroperoxides.[12] Therefore, the likeliest oxidation mechanism for benzene consists of a one-electron transfer to the catalyst. This mechanism is also in agreement with the observation of an EPR signal upon adsorption of benzene on SZ at room temperature.[13]

The proposed reaction mechanism is shown in Scheme 1. Surface phenyl esters (sulfites) result from recombination of ion-radical pairs, followed by hydrogen shifts. Capture of the

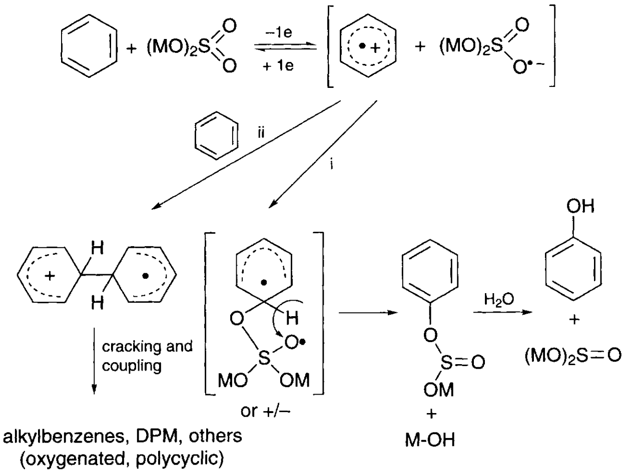
Table 1 Relative amounts of reaction products from PhH on SZ[a]

Product	Experiment 1 (0.5 h, 373 K)	Experiment 2 (24 h, 373 K)
Alkylbenzenes		1.70
PhC_6H_{11}		0.18
Ph–Ph		0.37
DPM	1	1
PhC_2H_4Ph		0.05
PhOH	2.98	0.28
Total conversion	6.80	17.3

[a] See text.

benzene radical cation by excess benzene can initiate another chain of reactions, responsible for the complex hydrocarbon product mixture.

We believe that the one-electron oxidation is the key to the high catalytic activity of SZ and of other SMOs for conversion of alkanes. Ionization of surface esters generates the carbocations which initiate isomerization and cracking at much lower acidity than required for hydride abstraction from, or protonolysis of the substrate by the catalyst.



Scheme 1 Proposed mechanism of reaction of PhH on SZ

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