

The mechanism of conversion of hydrocarbons on sulfated metal oxides.

Part II. Reaction of benzene on sulfated zirconia ¹[1]

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Abstract

The conversion of benzene on sulfated zirconia was studied in batch reactor, under mild conditions. The interaction of benzene with the catalyst is a complex process which is initiated by a one-electron oxidation, followed either by trapping of the generated cation–radicals to form sulfite esters on the surface, or by the reaction of the cation–radicals with the excess of benzene, followed by a cascade of coupling and cleavage reactions. The surface esters liberate phenol upon hydrolysis at the end of the reaction. Thus, benzene is retained on sulfated zirconia not because of protonation to benzenium ion, but because of formation of non-volatile products.

Together with our previous results on the reaction of adamantane on sulfated zirconia, the present work elucidates the mechanism of conversion of aliphatic hydrocarbons on sulfated metal oxides. The first interaction is a one-electron oxidation of the alkane, leading to an ion–radical pair, followed by recombination and rearrangement to generate sulfite esters on the surface, which are the active intermediates in the mechanism. The high activity of sulfated metal oxides in alkane conversion is due, therefore, to their one-electron oxidizing ability, leading to ion–radicals and then to surface esters. The latter either ionize generating carbocations, or eliminate forming olefins. Both these species can carry on carbocationic reactions with no requirement of superacidity, which these catalysts do not possess.

The oxidative mechanism predicts the existence of an induction period in the alkane conversions and a rapid deactivation of the catalyst, both in agreement with the experimental observations.

1. Introduction

Sulfated metal oxides (SMOs) have been described in literature as solid acids possessing superacidic strength [2]. The claim of their su-

peracidity has been based on two criteria. First, Hammett acidity measurements [3] as adapted for solids [4] gave for SMOs H_0 values below -12.2 (corresponding to 100% H_2SO_4) and in some cases below -16.04 [2,5]. Second, in hydrocarbon conversions such as alkane isomerization and cracking, these materials exhibited catalytic activities similar to aluminum halides and stronger than zeolites [5].

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We have shown from theoretical consideration that the Hammett acidity function (or any acidity function) cannot be applied to solid acids [1,6]. Solids thus belong to a class which we labeled *non-Hammett acids* [1,7]. The H_0 values found and reported for such materials are theoretically meaningless and do not reflect accurately their acid strength. Indeed, we have shown that the observed catalytic activity of SMOs for hydrocarbon conversions does not correlate with their reported H_0 values [1].

A different type of acidity measurement, temperature-programmed desorption (TPD) of volatile bases [8], was also applied to SMOs [9]. This method evaluates acidities of materials from the temperature of desorption of probe bases chemisorbed at low temperature on the surface. As the desorption temperature represents the temperature of decomposition of a surface salt, it is concluded that for the same base, the energy needed to revert the salt to the free acid and base will increase with the strength of the acid, whence the temperature of desorption will increase as well. The corollary of this statement is that for the reaction of the same acid with different probe bases, the desorption temperature will increase with the strength of the base.

The volatile bases normally used in TPD acidity measurements are ammonia and amines. In the TPD study of a sulfated zirconia promoted with Fe and Mn (FMSZ), however, the authors used benzene and substituted benzenes instead [9]. This choice of base was justified by a reference to previous use by our group of benzene as probe base for evaluation of superacid strength by NMR [10]. The higher temperature for desorption of benzene from FMSZ than from unpromoted sulfated zirconia (SZ) was interpreted as showing the greater acid strength of the former [9].

In the earlier investigation of benzene in superacids, 50% protonation of benzene was observed in 30:1 HF-TaF₅ [10], an acid shown later to be nearly 11 orders of magnitude stronger than trifluoromethanesulfonic acid (H_0

= -14.2) [11]. Benzene was fully protonated in 4:1 HBr-AlBr₃ and in 30:1 HF-SbF₅, but in the latter case only for a ratio of SbF₅ to benzene of 3 or more. At ratios of 2 or less, no protonation was observed. Instead, the hydrocarbon was converted by one electron oxidation to a polymer on account of the reduction of some Sb(V) to Sb(III) [10]a. If the TPD experiment was, indeed, recording the decomposition of a surface benzenium salt [9], then FMSZ would fully protonate benzene at a molar ratio of acid sites to hydrocarbon equal to 1, meaning that FMSZ was an acid stronger than HF-SbF₅. In addition, desorption of benzene at a temperature higher than 500°C would mean that the benzenium salt was stable up to that temperature. Such a stability was highly unlikely, because earlier attempts to record laser-Raman spectra of benzenium ion showed that the heat of the laser beam produced decomposition of the sample [12].

Our first doubts about the validity of the acidity measurements by TPD of benzene came from a comparison of benzene and pyridine desorptions from FMSZ. From the basicities of pyridine ($pK_a = 5.25$ [13]) and hexamethylbenzene (50% protonation in 91% H₂SO₄ [14], corresponding to a pK_a of ca. -10), and the basicity ratio of hexamethylbenzene to benzene (6×10^{10}) [15], we can evaluate that benzene is a base weaker than pyridine by 25–26 orders of magnitude. If the desorption temperatures were determined by the strength of the acid–base interaction, pyridine should desorb at a much higher temperature than benzene. We found, however, that under identical flow (He, 50 cc/min) and temperature increase rates (15°C/min) these two bases gave TPD desorption maxima at the same temperature, 560°C [7]. Moreover, the major components of the material eluted in the case of pyridine were CO₂ and SO₂. The same reaction products were observed in TPD experiments of benzene on FMSZ [16]. A systematic study of the catalysts SZ, FMSZ, and Pt/SZ demonstrated that both benzene and pyridine are oxidized to CO₂ on these materials

at high temperature, under flow conditions [17]. Therefore, TPD measurements of this kind [9,18] do not give results meaningful for the evaluation of acid strength.

In another study we have shown that an aliphatic hydrocarbon, adamantane (AdH), reacts with SZ at 65–150°C by one-electron oxidation giving oxygenated products. This demonstrates the oxidizing ability of this catalyst [1]. Considering, however, the numerous reports claiming SMOs as superacids [2,5], the question to be answered is whether SZ is, indeed, a solid superacid having oxidizing properties, or it is an unusual oxidizing agent with some acidic, but not superacidic properties. Indeed, the observation that benzene is desorbed as fully oxidized material at high temperature does not provide 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 retained at low temperature as benzenium ion, which was then oxidized at high temperature. Alternatively, retention of non-protonated benzene at temperatures well above its boiling point on the catalyst could be due to conversion of the former to some refractory materials which are oxidized to CO₂ at high temperatures. Identification of the precursors formed far below the temperature at which benzene is fully oxidized on SZ would be an indication of the mechanism. We addressed this question by a study of benzene on SZ at low temperature in a batch reactor, and report the results here.

2. Experimental

2.1. General

The reactants and solvents used were AR grade materials and were used as purchased. The catalyst surface area and sulfur content were measured as described before [19].

The GC–MS analyses were conducted on a HP 5890 Series II gas chromatograph/HP 5970

Series MSD, on a 50 m × 0.2 mm capillary column, coated with HP1 crosslinked silicone (0.33 μm), held at 150°C for 10 min, then heated to 280°C at a rate of 15°C/min and kept at 280°C for 40 min. The MS was acquired in the EI mode, at 70 eV.

2.2. Catalyst preparation

SZ was prepared in 10 g batches by the controlled impregnation technique, as described elsewhere [1,19], from Zr(OH)₄ (catalyst type SZCH), and from ZrO₂ (catalyst type SZCO). A solution of 1 N H₂SO₄ was used as sulfating agent. After sulfation, the samples were calcined at 600°C for 5 h (SZCH) and at 550°C for 4 h (SZCO). The catalyst samples were kept in closed vials in a desiccator until used. Each sample was characterized by sulfur analysis, BET surface area [19] and catalytic activity towards isomerization of methylcyclopentane (MCP) to cyclohexane [1,19]. The catalysts used in this work were similar in all respects to the materials described earlier [1].

2.3. Conversion of benzene

The catalyst (0.5–1.3 g) was introduced into a 12 cm × 5 mm I.D. glass tube and activated for 2 h, at 450°C in air. After activation, the tube was capped with a rubber septum and allowed to cool to room temperature. Benzene was injected with a syringe (molar ratio S:benzene = 1:6.5–1:20), the reaction vial was cooled in liquid nitrogen, and the tube was quickly sealed in flame. Upon reaching room temperature after sealing, the tube was shaken for mixing and immersed completely in an oil bath at room temperature. The temperature was raised to 100°C in ca. 45 min and held there for the desired length of time. At the end of reaction, the tube was cooled to room temperature and subsequently in liquid nitrogen, then it was cut open, after which the reaction mixture was extracted in a solvent, at boiling temperature. The solvents used were ether, benzene, and

anisole. In another extraction procedure, after the vial was cut open water was added to wet the solid and the mixture was kept for two hours at room temperature. The organic layer was decanted off, the remaining slurry filtered, and the catalyst extracted with benzene or ethyl ether upon boiling, several times. In both extraction procedures, the organic solution was then concentrated to a small volume. Phenol was observed in the extract from the latter procedure, but not from the former. The same concentration procedure was also applied to the solvents used for extraction, by evaporating an initial volume of solvent larger or equal to the initial volume of the organic extract until the final volume was equal to the final volume of the organic concentrate. No heavier compounds other than traces of toluene from the original benzene were detected by GC–MS analysis using the same instrumental conditions as specified above.

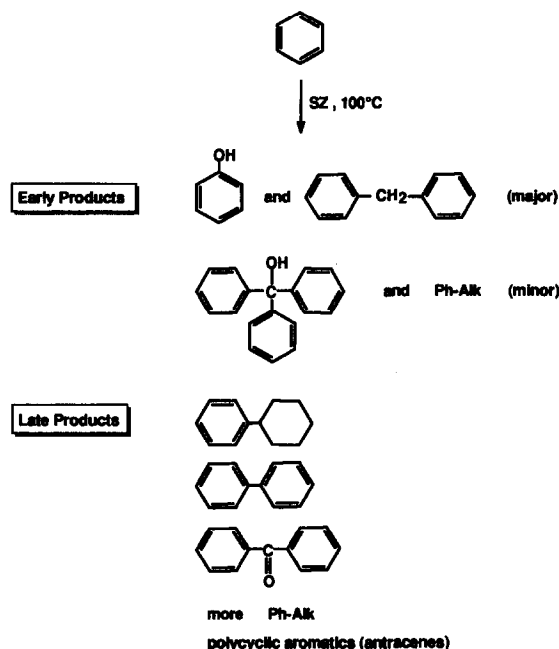
For the quantitative evaluation of benzene conversion on SZ by GC–MS analysis, adamantane (AdH) was chosen as integration standard. AdH was added to the reaction mixture after the vial was cut open, cooled to room temperature, and after the addition of water, but prior to the organic solvent. Due to the large number of products identified in this reaction, we established response factors for two compounds and considered them as being representative for the two most important classes of products obtained: toluene, representative for the products containing one aromatic ring, and diphenylmethane (DPM) representative for the products containing two (or more) aromatic rings.

The very short-time reaction of benzene on SZ was conducted by pouring ca. 1 g SZ, freshly activated and cooled to room temperature, into ca. 1 ml benzene, on a fine frit, followed by refluxing for 3 min. After filtering and cooling to room temperature, water was added to wet the catalyst and the mixture was allowed to stand for 2 h at room temperature. Fresh benzene was added and the slurry filtered again. The combined benzene extracts were sep-

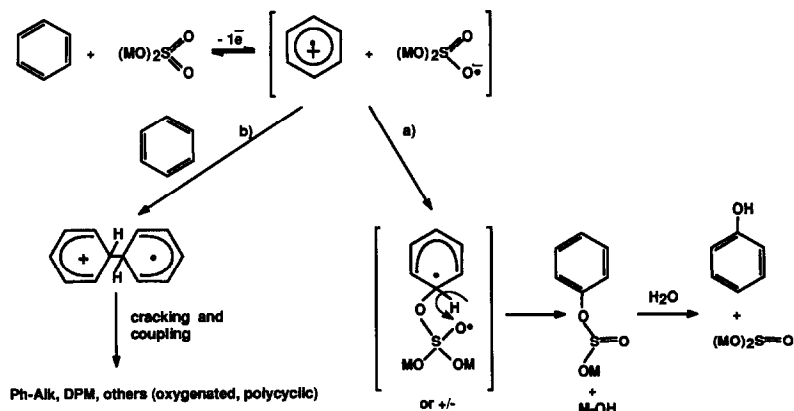
arated from water, concentrated as described above, and analyzed by GC–MS.

3. Results

The temperature (80–100°C) and the molar ratio of benzene to catalyst in our experiments (variable excess of benzene to acid sites, see Experimental) were chosen to reproduce the conditions existing during the adsorption step and the desorption of physisorbed benzene in the TPD experiments [7]. The products identified by GC–MS analysis are presented in Scheme 1. Two main classes have been identified: *oxidation* products, such as phenol (PhOH), triphenylcarbinol, and benzophenone, and *condensation and cleavage* products, represented by a large variety of compounds, such as DPM, alkylbenzenes (toluene, ethylbenzene, xylenes), biphenyl, phenylcyclohexane, and products of advanced condensation such as anthracene. DPM and PhOH were obtained in major amounts as early products of the conversion of benzene with SZ at 100°C. Triphenyl-



Scheme 1. Products of PhH on SZ at 100°C.



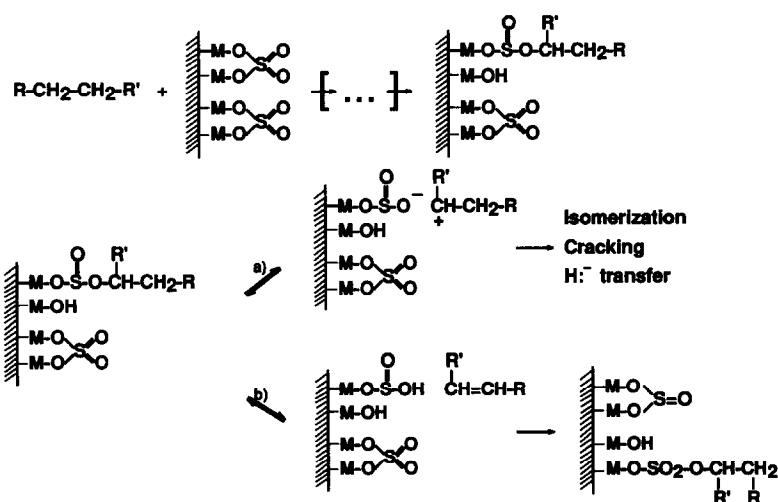
Scheme 2. Proposed mechanism of reactions of PhH on SZ.

carbinol and alkylbenzenes were also present, in minor amounts. After longer runs, we detected as late products phenylcyclohexane, benzophenone, biphenyl, more of alkylbenzenes, as well as anthracene and other heavy compounds.

Identification of the $C_{13}H_{12}$ product as DPM was uncertain at first, because the isomer methylbiphenyl (MBP) has a similar MS splitting pattern [20]. Although the MS splitting patterns of the two isomers DPM and MBP are extremely close, some minor differences in their mass spectra exist (m/z 91, 167, and 168) and help the identification. In addition, clean separation of standards of DPM and MBP (3- and 4-

isomers) was achieved by GLC, thus proving that the reaction product was DPM.

The product distribution in various runs is shown in Table 1. The quantities given there are calculated relative to the amount of DPM, taken arbitrarily as 1. It can be seen that at short reaction times (Table 1, entry 2) PhOH is the main reaction product. At very short reaction times and low temperatures (Table 1, entry 1), the product contained at least ten times as much PhOH as the other products, whereas the amount of DPM was too small to allow accurate integration. On the other hand, at long reaction times, heavy products predominated (Table 1, entry 6).



Scheme 3. Mechanism of reactions of alkanes on SZ.

GLC analysis using AdH as integration standard (see Experimental) indicated that 6.8 to 17.3 molecules of benzene per 100 acid sites were converted. This yield, however, does not include the highly dehydrogenated materials, too heavy to be eluted from the GC column, or insoluble in the extraction solvents. The catalyst after extraction was still dark and its further extraction in tetrahydrofuran gave a light-colored solid and a green–brown solution, which left a solid residue upon evaporation but did not give any peak except for the solvent in the GC.

The amount of PhOH observed increased when the sulfur loading increased from 1.24% (SZCH-0.95–2) to 1.31% (SZCH-2.00–2). A further increase in the percentage of sulfur to 1.54% (SZCH-3.00–2) had a smaller effect, if any.

It is noteworthy that PhOH was obtained only in the experiments in which the extraction procedure included treatment of the reaction mixture with water after the reaction. PhOH was, therefore, more strongly retained by the catalyst than the other products, particularly DPM. A possible explanation was that PhOH, more basic than the other products, was protonated on the catalyst and could not be taken up by the solvent. We checked this hypothesis by extracting the products with ethyl ether and with anisole. Each of these compounds is a stronger base than phenol and should displace the latter from its salts with the acid sites, particularly when added in large excess. The failure of extracting phenol with more basic but non-hydroxylic solvents *before treatment with water* shows that PhOH resulted from the reaction with water of a combination covalently bonded to the surface.

4. Discussion

PhOH and DPM were always identified in the reaction mixtures, even in the extreme case of boiling of benzene over the activated catalyst

for less than three minutes (Table 1, entry 1). This result together with the increase in the yield of PhOH with the increase of the sulfur content of the catalyst show that even at 80°C, the first interaction of benzene with SZ is not protonation, but oxidation. Therefore, out of the two hypotheses presented in the introductory section, regarding the state of the benzene molecule prior to desorption as fully oxidized product, the possibility that benzene be protonated at low temperature and retained as benzenium ion can be eliminated. Instead, non-protonated (physisorbed) benzene is oxidized to surface esters and products of condensation/oligomerization. This observation also explains the results of the TPD experiments: a fraction of the benzene originally adsorbed remains on the solid because it is converted to materials of lower volatility than benzene. As the temperature is increased further, the first-formed products are converted in turn to even heavier molecules. Thus, condensation is all the time one step ahead of desorption, until the destructive oxidation with formation of CO₂ sets in.

Based on the products obtained and their evolution during the run (Table 1), we propose the following mechanism of interaction of benzene with SZ (Scheme 2): SZ oxidizes benzene by one-electron abstraction, with the formation of the benzene cation radical and the anion radical from the catalyst as its counterpart. This ion–radical pair subsequently combine to give, after rearrangement, a combination of reduced sulfur (S IV) on the surface, the aryl sulfite ester (Scheme 2, path a). The surface esters liberate PhOH upon hydrolysis during the work-up of the reaction mixture. The hydrolytic formation of PhOH proves the existence of esters as precursors on the surface. Such species were postulated as intermediates in the reaction of AdH with SZ, where the alcohol was obtained by simple extraction [1] because an aliphatic ester ionizes easily, with the formation of the corresponding carbocation. The carbocation finds a hydroxyl group on the surface and reacts

to form adamantanol (AdOH). The similar formation of the high-energy phenyl cation from a phenyl ester is not possible.

An alternative mechanism, considered for AdOH formation from AdH on SZ, was direct hydride transfer to the catalyst, followed by capture of the carbocation by a surface hydroxyl group as nucleophile [1]. Such a mechanism in the present case would again require intervention of the phenyl cation as intermediate from benzene and can, therefore, be ruled out. Finally, direct electrophilic hydroxylation of the aromatic ring to give phenol can also be excluded, because such a reaction was shown to require the presence of hydroperoxides [21]. One-electron oxidation is, therefore, the only possible mechanism for phenol formation, via surface esters.

The benzene cation radical formed in the activation step can also react with another molecule of benzene (Scheme 2, path b), to give a $C_{12}H_{12}$ cation radical which, in turn, can initiate another chain of reactions with the formation of cleavage and recombination products. The mechanism is rather complex, since DPM or phenylcyclohexane which must result from processes of fragmentation and coupling are among the earliest stable, identifiable products. This pathway of the mechanism explains also the formation of biphenyl, alkylbenzenes, polycyclic aromatics, by cascade reactions, followed by oxidations which leads to oxygen-containing products such as triphenylcarbinol and benzophenone; oxidation of such large molecules is more likely to take place.

Formation of biphenyl could also be possible by dehydrocondensation (Scholl reaction), the mechanism of which is explained, for some molecules, by one-electron oxidation [22]. For our case this was, however, unlikely, because DPM should form by the Scholl reaction fluorene, which we did not observe.

Evidence for one-electron transfer reaction can be found in a study of the benzene–SZ interaction by ESR [23]. The assignment in that study of the ESR signal to biphenyl cation–radi-

cal [23] is intriguing, considering that biphenyl was observed in our experiments as a late and only minor product. The explanation of this discrepancy might be that biphenyl, even though present in quantities too small to be directly detected, is the only product which forms a cation–radical stable enough to be detected by ESR.

The present observations on the interaction of benzene with SZ and our previous results on the reaction of AdH on SZ [1] allowed us to develop the mechanism of interaction of aliphatic hydrocarbons with SMOs, shown in Scheme 3. In the initiation step, the organic substrate is oxidized by transfer of one electron to the catalyst with formation of the ion–radical pair, followed by recombination and rearrangement of the latter to form the surface ester (alkyl-sulfite) and the corresponding $-M-OH$ species, bonded to the surface. These activation steps (oxidative initiation, recombination and rearrangement) are represented in Scheme 3 by square brackets; they have been described in detail in Scheme 2, path a, and in our previous study of AdH on SZ (Scheme 1 of [1]). The surface ester once formed, can ionize (Scheme 3, path a) with the formation of a carbocation which then undergoes the typical reactions known in the acid catalysis of hydrocarbons (isomerization, cracking, hydride transfer). Ionization of alkyl sulfites $RO-SO-OR'$ is known to take place in solution [24]. Alternatively, the ester can undergo an elimination reaction (Scheme 3, path b), with the formation of an olefin, which can be easily protonated by the acidic function of the catalyst (superacidity is not needed) and thus initiate carbocationic reactions. The olefin itself can react as well with a remaining active site, also represented in Scheme 3, with the formation, by an addition reaction, of a sulfate ester (last step of path b, Scheme 3). The surface sulfate ester ionizes even more easily than the sulfite, producing carbocations able to continue the reaction chain. Meanwhile, inorganic sulfites (S IV) bonded to the surface are generated in the mechanism. These species are inac-

tive as oxidizing agents at low temperature and cannot initiate a new reaction chain.

An alternative pathway, cleavage of the initial cation–radicals with formation of free radicals, which dimerize, and carbocations which initiate the typical acid-catalyzed reactions (isomerization, cracking) is also possible. As we showed previously, this pathway is followed by cation–radicals of large alkanes even at low temperature [25].

The proposed oxidative mechanism can explain the higher catalytic activity of FMSZ compared to SZ in hydrocarbon reactions, due to its better oxidizing ability. The oxidizing potential of such a catalyst containing transition metals in their high oxidation state (Fe^{3+} , Mn^{x+}) must be higher than the oxidizing potential of SZ. This explanation is in line with other studies which mention that the enhancement in catalytic activity of SZ by addition of metal oxides like Fe, Mn, or Ni is not due to an increase in the acid strength or in the density of the acid sites, but possibly to an increase in the concentration of olefinic materials formed in the reaction [26,27].

Our mechanism, based on the identification of intermediates in the case of the interaction of adamantane [1] and benzene on SZ, shows that there will always be an initiation step, a time necessary for the formation of esters as active intermediates in the mechanism. The alkyl esters can either ionize or eliminate, creating carbocations or olefins. Following this step the reaction can continue easily, because the generated intermediate undergoes carbocationic reactions at a lower acidity than required for the initiation by hydride abstraction from, or protonolysis of the saturated hydrocarbon.

The reactivity pattern required by the formation of esters as active intermediates in the activation step is borne out by experiments reported in literature. Thus, studies of butane isomerization in flow reactor [5], [27] reported that under flow conditions the conversion is zero at time zero, after which it passes through a maximum and then it decreases with respect to time. This increase of conversion with time

under flow conditions reflects the induction period, necessary for surface esters formation along the length of the catalyst bed. Likewise, preliminary results from our laboratory showed that for the isomerization of MCP to CH on SZ in batch reactor [28] the conversion vs. time curves follow the proper kinetic behavior, but do not pass through the origin of axes. This time lag, which is shorter at higher temperatures, represents the induction time necessary for the formation of surface esters.

It is noteworthy that an induction period was observed in the isomerization of 2,3,4-trimethylpentane catalyzed by sulfuric acid. Sulfur dioxide was generated during that period [29]. Thus, oxidative initiation of carbocationic reactions intervenes in liquid phase as well when the acidity of the catalyst is insufficient for C–C or C–H protonolysis.

On the other hand, the rate of deactivation on SZ is fast and increases with temperature. It actually starts together with the activation step, at the early stage of reaction. Along the process, the deactivation is manifested by multiple available pathways: (a) the normally encountered deactivation due to coking, which increases with the increase of temperature, with the formation of heavy molecules by oligomerization of alkenes and coupling of free radicals, and (b) as an additional pathway, the deactivation due to the loss of oxidation ability, with formation of reduced sulfur species, unable to initiate another reaction chain by oxidation. This behavior explains why at the time when all the surface is covered with the active ester species, the deactivation becomes very fast.

5. Conclusions

The reaction of benzene on SZ at 100°C in batch reactor led to two main categories of compounds: oxidation and cleavage/recombination products. In the early stages of reaction, PhOH was the major product. Small amounts of DPM, alkylbenzenes and triphenylcarbinol were

also identified. In later stages, bi- and polycyclic aromatics became predominant.

The products obtained and the observation that PhOH was an early, major product are explained by the one-electron oxidation of the substrate as initiation step with formation of cation–radicals. The initiation is followed either by recombination of ion–radical species leading to surface esters, or by the reaction of benzene cation–radical with the excess of benzene present. Therefore, benzene is retained on the catalyst not by protonation, as benzenium ion, but by conversion to non-volatile products, as a result of condensation–oligomerization reactions.

The high one-electron oxidizing ability is the key to the enhanced catalytic activity of SZ in the conversion of saturated hydrocarbons. The one-electron oxidation followed by trapping of the cation–radicals on the surface leads to sulfite surface esters which can either ionize generating carbocations, or eliminate to form alkenes, both species able to carry on carbocationic reactions. In this way, carbocationic reactions are initiated at lower acidity than needed if the initiation took place by hydride loss from a substrate or by protonolysis, as in superacid chemistry. The initiation occurs on the account of the catalyst which is being reduced.

The activation of SZ by formation of esters between the organic substrate and the catalytic surface results in the existence of an induction period for the reaction. Another consequence characteristic for these catalysts is the fast deactivation, because of the availability of multiple pathways: coking by oligomerization of alkenes and coupling of free radicals, and loss of the oxidizing ability with the formation of reduced sulfur species as an additional path.

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