Catalysis Letters 44 (1997) 29–35

A comparative study of the catalytic behavior of aluminum chloride and sulfated zirconia*,‡

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Received 12 September 1996; accepted 4 December 1996

At low conversion, isomerization of methylcyclopentane (MCP) to cyclohexane (CH) at 65°C is faster on sulfated zirconia (SZ) than on $AlCl_3$ containing traces of water, but the latter reaction reaches equilibrium much quicker because the former deactivates rapidly. Dimer formation ($C_{12}H_{22}$) occurs on SZ faster in the early stages and continues throughout the reaction, whereas $AlCl_3$ forms essentially no dimers at first, but in late stages of reactions, when a "sludge" is expected to be formed on $AlCl_3$, some dimers are observed, but always much less than on SZ. This difference was predicted, because on SZ the dimers are formed by two pathways, dimerization of free radicals formed in the oxidative initiation step and alkene alkylation by carbocations later on, whereas only the latter mechanism is available for $AlCl_3$. Pretreatment with SO_2, which is a good solvent for carbocations, increases substantially the activity of $AlCl_3$ (which retains up to 30% SO_2) most likely by generation of a liquid film which contains carbocations in solution. By contrast, SZ is completely deactivated by this treatment, possibly from a combination of traces of water and loss of oxidizing ability. Dimer formation on $AlCl_3$ increases appreciably after pretreatment with SO_2, as expected for the reaction in a liquid film where a higher concentration of carbocations facilitates bimolecular reaction. Dimer formation on SZ is much reduced, but not entirely suppressed by pretreatment with SO_2 and the distribution of isomers is different for the two catalysts after pretreatment, showing that some oxidizing ability is retained by SZ, even though the further conversion of hydrocarbon is inhibited. All these results provide further support for the bifunctional nature (initiation by one-electron oxidation followed by acid-catalyzed, carbocationic, reaction of intermediates like surface esters and alkenes formed in the first step) advanced earlier by the authors for the sulfated metal oxides.

Keywords: comparison of aluminum chloride and sulfated zirconia, catalysis mechanism on sulfated zirconia, one-electron transfer in acid catalysis, free-radicals in hydrocarbon conversions on sulfated zirconia, sulfated zirconia as bifunctional catalyst

1. Introduction

Catalysis by sulfated metal oxides (SMO), first described by Holm and Bailey in 1962 [1], has been a topic of interest for the past 17 years (reviews in ref. [2]). The general consensus has been that these materials are solid superacids, activating the saturated hydrocarbons by straight hydronolysis of C–H bonds [2,3]. Our experience with measurement of superacidic strength [4] made us doubt some of the literature conclusions [3b]. Also bothersome was the lack of agreement about the nature of sites generated in SMO and responsible for alkane activation; Lewis [5], or Brønsted [6]. We embarked, therefore, on a study of the mechanism of interaction of sulfated zirconia (SZ) and the highly active derivative doped with Fe and Mn ions (FMSZ) [3b]. We reported in 1993 that TPD of aromatics does not measure an acid–base interaction, because benzene and pyridine, having a basicity ratio of 10^{25} eluted from FMSZ at the same temperature [7]; for pyridine, the elution peak was mostly CO_2 and SO_2, indicating that the reaction is an oxidation. A study from another laboratory found that benzene is completely oxidized to CO_2 on TPD from FMSZ, but the authors still considered that the nature of activity of the material is superacid catalysis [3e]. A detailed investigation showed that oxidation of benzene and pyridine on TPD occurs not only on SFMZ, but on SZ and Pt-promoted SZ; the oxygen was supplied mostly by the sulfate, but to some extent also by the metal oxide lattice [8].

One of us has for years challenged the representation invoking solid superacidity [9], lately pointing out that the common trait of dopants such as Cu ions for $AlCl_3$, or Fe and Mn ions for SZ is their reactivity toward organic substrates as electron acceptors [9c]. Subsequently, we reported work showing that even unpromoted SZ oxidizes saturated hydrocarbons at temperatures as low as 65°C; species resulting from odd-electron intermediates were identified among the products [10]. Reaction with benzene at 80°C for very short times followed by hydrolysis led to phenol, indicating that the first product was a surface ester (sulfite or sulfate). Products of condensation and cleavage were observed in increasing amounts at longer reaction times [11]. We concluded, therefore, that SZ and other sulfated metal oxides are bifunctional catalysts, possessing an unusual one-electron oxidizing ability and strong but

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[*] Presented at the Thirty-fourth Annual Spring Symposium of the Pittsburgh-Cleveland Catalysis Society, 8–9 May 1996, Pittsburgh, PA, USA.

[‡] The mechanism of conversion of hydrocarbons on sulfated metal oxides, Part III. For Part II see ref. [12].

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not superacidic acid properties. The reactions of alkanes on these catalysts involve oxidation followed by trapping to a surface alkyl ester, which either by ionization or by elimination followed by hydronation can form the cationic or cationoidic species capable of undergoing isomerization at much lower acidity than required for the hydronolysis of C–H bonds [11,12]. This mechanism accounts for all the features of catalysis by SMO, such as very high activity, existence of an induction period, and rapid deactivation [11b,12]. Notably, one of the deactivation pathways is loss of oxidizing ability by sulfate reduction in the initiation step of the reaction [11b,12]. In this respect, SZ is not truly a catalyst, but a reagent.

There were previous data in the literature which can be explained by the bifunctional character, rather than by superacidic properties of SMO. Notably, interaction of benzene with SZ at room temperature generated an ESR signal [3c] and deactivation was considered to be tied to reduction of sulfate and to be reversed upon reoxidation [13]. Other papers providing independent corroboration of our results and mechanistic representation appeared after our first presentations, but before our articles were published: In one study, it was found that SZ and FMSZ do not possess very high Brønsted acidity but offer a low energy reaction pathway (perhaps generating olefins as intermediates) [14]. In another work, hydrogen sulfide was identified among products in the butane isomerization on SZ at 250°C [15].

New evidence confirming our view of the catalytic activity of SMO as a combination of oxidation and acid catalysis has appeared since we first presented it. Thus, a study of cracking of *n*-butane on SFMZ gave results which raised questions about the presumed superacidity and raised the possibility that the low-temperature reaction may involve catalyst functions other than the acidic function responsible for high-temperature cracking reactions [16]. Ammonia TPD on FMSZ has confirmed the conclusion based on NMR and FTIR [14] that this material is no stronger an acid than unpromoted SZ; formation of olefins and of C_8 species as intermediates from butane was proposed for the promoted catalyst [17]. (Intervention of C_8 intermediates from butane on FMSZ had been proven before ^{13}C labelling [18].) Finally, it was found that calcination of FMSZ in He results in a lower activity than calcination in air; a combination of a redox-active metal site and an acid site in close proximity was proposed to explain the high activity of FMSZ [19]. Nonetheless, probably because of its novelty, the mechanism which we proposed has been, with few exceptions [20], not much noticed in subsequent publications (for example, ref. [19] entirely overlooked our reports, e.g. [10a], given at meetings which its authors attended). It seemed that more data were necessary before the oxidation-initiated acid catalysis would be accepted.

To obtain such additional data, we undertook a comparison of SZ and aluminum chloride, a typical strong acid (most likely superacid [21]) catalyst. We examined the catalytic activity for isomerization of methylcyclopentane (MCP) to cyclohexane (CH), dimer formation, and effect of sulfur dioxide as an additive.

2. Experimental

2.1. General

MCP was AR grade, containing < 0.3% CH (GLC). $AlCl_3$, also AR grade, was not resublimed, because traces of water contained in the non-resublimed material assure its high Brønsted acidity [22]. A vacuum line was used for the addition of SO_2 to the samples through a tube with P_2O_2, by the technique described earlier [21a]. Catalyst surface area and sulfur content [23a], and composition of isomerization products (GLC, GC-MS) [10b] were determined as described before.

2.2. Catalyst

The SZ catalyst was prepared by the controlled impregnation technique with 3 ml of 1 N H_2SO_4 per gram of dry (150°C) $Zr(OH)_4$ [23a] and water evaporation in a dish [23b]. Drying (150°C, overnight) and calcination (610°C, 5 h) gave a material (symbol SZCH-3.00 [23b]) with 2.1% S and 110 m^2/g. The catalyst samples were kept in closed vials in a desiccator until used.

2.3. Conversion of MCP to CH

Experiments with SZ and $AlCl_3$ were run in parallel, using ca. 0.1 g catalyst and a weight ratio catalyst/substrate = 1/4, in 12 cm × 5 mm i.d. glass tubes, as described previously [10b,23]. SZ was activated in the reaction tube for 2 h at 450°C in air, then the tube was removed from the oven and capped with a rubber septum as soon as it could be handled, then allowed to cool to room temperature. In another series of experiments, a pre-weighed stirring bar was introduced in the tube before capping. The $AlCl_3$ was introduced in the pre-weighed reaction tube with stirring bar in a nitrogen-filled glove bag, then capped. After that, each reaction tube was re-weighed and MCP was added with a syringe. The septa were taped to withstand the vapor pressure during reaction. The tubes were shaken for mixing and immersed vertically in oil baths placed over magnetic stirring plates, thermostated at 65°C (SZ), and 65 or 55°C ($AlCl_3$).

For treatment with SO_2, a stopcock with a ground joint at the top was connected through a piece of vacuum rubber tubing to the glass tube containing the catalyst, inside the glove bag, and the assembly was attached to the vacuum line. SO_2 was introduced slowly into the vacuum line through the P_2O_5 tube, then collected into the tube with catalyst cooled in liquid nitrogen [21a], until after melting it just covered the catalyst. After stirring for ca. 1 min at −20°C (liquid N_2–acetone bath), all SO_2 was transferred carefully, to avoid bumping, into an empty tube attached to the line. The tube with catalyst was evacuated for a short time at < 0.5 Torr, re-weighed, and the isomerization experiment was run immediately. For each experiment of SO_2 pretreatment a parallel experiment was run simultaneously, following exactly the same procedure but closing the stopcock to the vacuum line before SO_2 was admitted. No difference was observed between the reaction of MCP on these batches of catalysts and on catalysts used directly after activation, thus showing that the extra manipulations had no effect upon the catalytic behavior.

The isomerizations were run both with and without stirring. The progress of reaction was monitored by taking samples (0.35 μl) and analyzing them by GLC; a few samples were analyzed by GC-MS.

3. Results and discussion

In our earlier work we chose isomerization of MCP to CH (eq. (1)) as a test reaction for characterization of SZ catalysts [10,23], because it can be conveniently studied in the liquid phase at 65°C. In addition, cracking to lower hydrocarbons is reduced, because two bonds would have to be broken. Indeed, only cyclohexane (CH) was found as low-molecule product ($\leqslant C_6$) from MCP on SZ [10,23]. The reaction of MCP on $AlCl_3$ is also clean [22]. Therefore we chose it as model reaction in this study, too:

$$\mathrm{MCP} \rightleftharpoons \mathrm{CH} \qquad (1)$$

In the comparison of the two types of catalysts, it was found that at short reaction times at 65°C, conversion of MCP on SZ was significantly greater than on $AlCl_3$, 9.15% in 55 min and 3.65% in 45 min, respectively. The conversion on SZ soon reached a plateau, however, indicating fast deactivation, whereas on $AlCl_3$ the reaction advanced smoothly to equilibrium (75% CH [10b]). For further comparison, particularly of the effect of SO_2, it was more convenient to run the reactions with $AlCl_3$ at 55°C.

In our previous work, formation of diadamantane (bis-adamantyl) isomers provided proof for the existence of adamantyl free radicals in the reaction of adamantane on SZ, because the normal way of formation of dimeric species in acid catalysis, alkylation of an alkene, is not available for adamantane [10]. It would be expected, however, that the same mechanism of dimer formation be available to other hydrocarbons, like MCP (eq. (2)), in addition to the carbocationic alkylation mechanism (eqs. (3a)–(3c), in which A^- is the anion derived from the catalyst). By contrast, only the latter mechanism is available for the dimer formation catalyzed by $AlCl_3$ [24]. We have, therefore, studied the dimer formation from MCP with these two catalysts.

$$2\mathrm{MCP}^{\bullet} \rightarrow C_{12}H_{22} \qquad (2)$$

$$\mathrm{MCP}^{+}.A^{-} \rightleftharpoons \mathrm{MCP}^{=} + \mathrm{AH} \qquad (3a)$$

$$\mathrm{MCP}^{+}.A^{-} + \mathrm{MCP}^{=} \rightleftharpoons C_{12}H_{21}^{+}.A^{-} \qquad (3b)$$

$$C_{12}H_{21}^{+}.A^{-} + \mathrm{MCP} \rightleftharpoons C_{12}H_{22} + \mathrm{MCP}^{+}.A^{-} \qquad (3c)$$

As seen in fig. 1, dimer formation is essentially nil in

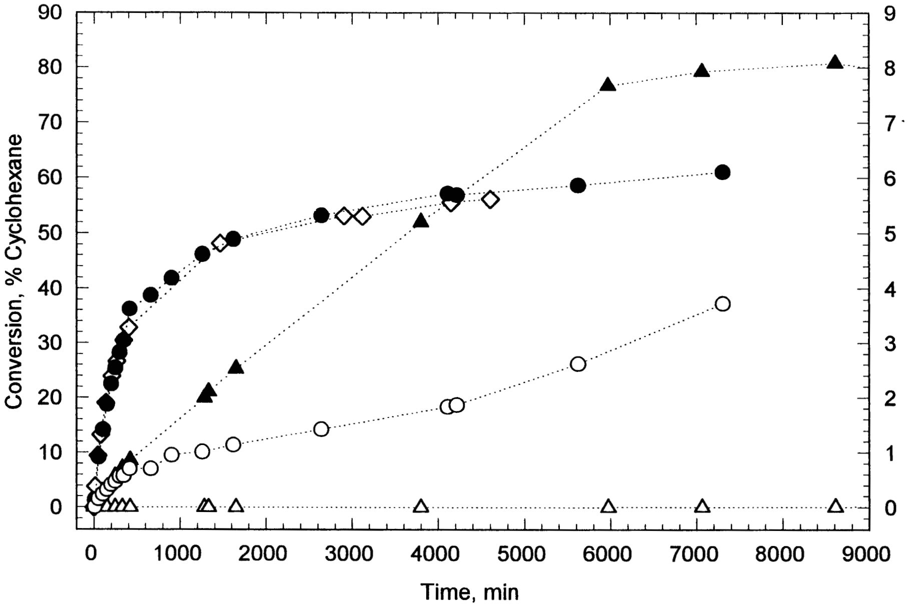

Fig. 1. Conversion and formation of dimers in the isomerization of MCP on SZCH-3.00 (2.1% S, 110 m^2/g) and on $AlCl_3$. (●) SZCH-3.00, MCP/cat = 4, 65°C (catalyst 0.1037 g, MCP 0.4148 g (0.554 ml)), no stirring; (○) dimers. (▲) $AlCl_3$, MCP/cat = 4 (catalyst 0.1171 g, MCP 0.625 ml), no stirring; (△) dimers. (◇) SZCH-3.00, MCP/cat = 4 (catalyst 0.0894 g, MCP 0.480 ml), 65°C, no stirring, run one month after activation.

the early stages of the $AlCl_3$-catalyzed reaction (straight acid catalysis). Dimers appear in late stages of the reaction, and continue to increase after the isomerization reaction approaches equilibrium, indicating that as the reaction progresses a "sludge" containing a larger concentration of carbocations is formed on the surface of the catalyst particles [25]. In that liquid phase, bimolecular reactions between carbocations and the small amounts of alkenes existing at equilibrium with the former in a strongly acidic or not very strongly superacidic medium are very much enhanced. The total amount of dimers is very low, however, even after the long reaction times. By contrast, dimers are formed at the fastest rate in the early stages of reaction on SZ and after reaching an early plateau their rate of formation increases again, somehow similar with what was observed at a much lower level for $AlCl_3$. At all stages, however, the amount of dimers is much larger on SZ than on $AlCl_3$. The structure of the dimers was not investigated more closely, but their GC-MS analyses are compatible with the dimethyldecalin structure indicated in the literature [24b]. Because isomerization of MCP dimers to dimethyldecalin does not involve a change in the degree of branching, its rate should be much faster than isomerization of MCP to CH [26], as it was, indeed, experimentally found [24b]. Some dimethyl-bis-cyclopentyl might also be present. A minor component of the fraction which we found to contain an ethyl group (ethyldecalin?) could have easily passed unnoticed in the older work [24b]. The results clearly confirm the mechanism [10–12] by which the dimers are formed by two different pathways on SZ, but only by one in the straight acid catalysis.

Molecules heavier than $C_{12}H_{22}$ were not identified by GC and GCMS analyses, but they are most likely present as solid residue ("coke") on the catalyst and constitute one of the multiple sources of deactivation described for SMO [11a,11b,12]. The amount of coke was too small for quantitative evaluation, but its presence was indicated by the yellow color of the catalyst after reaction.

Liquid sulfur dioxide is a solvent of low basicity and high polarity, used extensively as solvent for studies of persistent [27] carbocations in superacids [21c]. Due to its low boiling point, liquid SO_2 is also a good solvent for the deposition of indicators on solid acids for acidity measurements. We studied the effect of catalyst pretreatment with SO_2 upon catalytic activity and dimer formation in reaction of MCP on $AlCl_3$ and SZ.

Complete solubilization of $AlCl_3$ was observed upon stirring for 5–10 min with a large excess of liquid SO_2. For catalyst pretreatment in this work we added just enough liquid SO_2 to cover the solid in the tube and stirred the mixture for no longer than 2 min. The material left in the reaction tube after SO_2 was distilled off had a compact, glassy appearance and incorporated SO_2 which could not be removed by evacuation at room temperature, up to 30% of the original catalyst weight. Very little SO_2, undetectable by weighing, was retained, however, by SZ after an identical treatment. If the sample was "sacrificed" and opened at this stage, a strong odor of SO_2 was recorded. The isomerization tests were run immediately after pretreatment with SO_2, in all cases.

The results of MCP isomerization with the SO_2-treated catalysts are presented in fig. 2. It is seen that the cat-

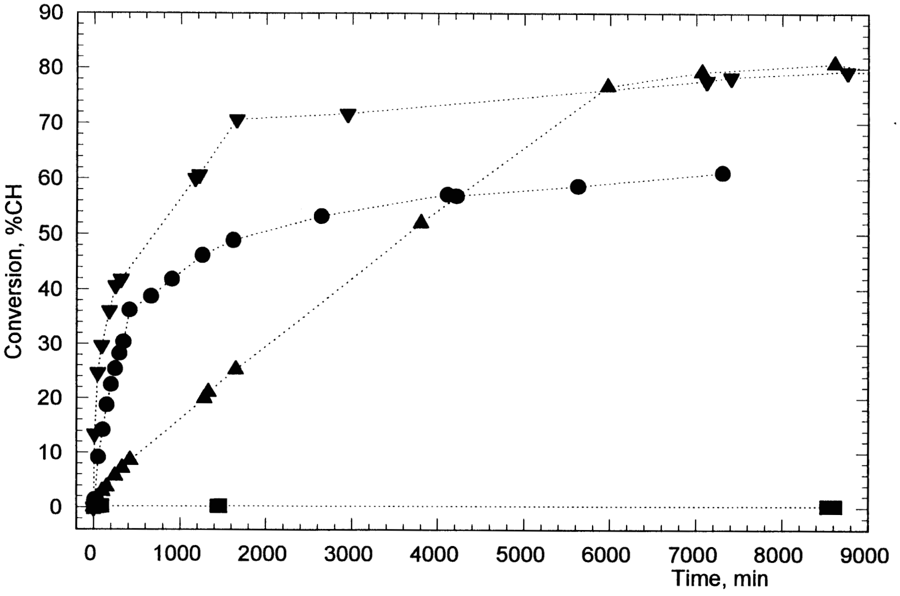

Fig. 2. Effect of catalyst pretreatment with SO_2 on the conversion of MCP to CH on SZCH-3.00 (2.1% S, 110 m^2/g) and on $AlCl_3$. (●) SZCH-3.00, MCP/cat = 4 (catalyst 0.1037 g, MCP 0.4148 g (0.554 ml)), 65°C, no stirring. (■) SZCH-3.00, MCP/cat = 4 (catalyst 0.0984 g, MCP 526 ml), 65°C, no stirring, SO_2 pretreatment. (▲) $AlCl_3$, MCP/cat = 4 (catalyst 0.1171 g, MCP 0.625 ml), 55°C, no stirring. (▼) $AlCl_3$, MCP/cat = 4 (catalyst 0.0755 g, MCP 0.403 ml), 55°C, no stirring, SO_2 pretreatment.

alytic activity of $AlCl_3$ increased dramatically after treatment with SO_2. MCP conversion at 55°C was faster than that on SZ at 65°C (reaction on SO_2-treated $AlCl_3$ at 65°C was too fast to be followed conveniently). It is likely that the sulfur dioxide retained on the surface is able to generate from the beginning of reaction a liquid layer in which carbocations are solubilized. The increase in reaction rates upon covering a solid acid with a very thin ("molecular") layer of a solvent for carbocations was exploited before in some catalytic processes [28].

By contrast, treatment with SO_2 deactivates SZ almost totally. The origin of this deactivation is difficult to assess, because only very small amounts of sulfur dioxide remain on the catalyst after evacuation. The possibility that traces of water in sulfur dioxide poison the catalyst is remote, because the gas was dried on P_2O_5 before entering the vacuum line, but if that was the reason, the SMO catalyst should have an exceedingly small number of extremely active sites. Furthermore, the nature of activity of those sites is different from that of aluminum chloride, which is activated by water far beyond the trace limit [22]. Another possible mechanism of deactivation is by loss of oxidizing ability of the SZ catalyst, but the effect observed is much too high for this possibility alone, because the treated catalyst still contains 2.1% S as sulfate and only a trace of SO_2. Thus, it is most likely a combination of causes which produce deactivation. Also noticeable is the fact that most of the conversion to CH (less than 1%) on the pretreated SZ occurs in the first 10–15 min. In any event, the effect of SO_2 upon SZ is totally different from that upon aluminum chloride.

Pretreatment with sulfur dioxide also influences the formation of dimers, as seen in fig. 3. For $AlCl_3$, the quantity of dimers increases significantly and they appear earlier in the process. This is exactly as expected if the role of the sulfur dioxide retained on the catalyst is to generate a liquid film on the surface, in which a kinetically significant concentration of persistent carbocations at equilibrium exist. For SZ, however, dimer formation is inhibited by pretreatment with SO_2, such that less dimers are formed than in the reaction of SO_2-pretreated $AlCl_3$.

The distribution of $C_{12}H_{22}$ isomers is also different on the two pretreated catalysts, because of the reduced ability of deactivated SZ to isomerize the dimers formed by free-radical coupling. We should note that in the reaction of adamantane on SZ catalyst deactivation affected less the oxidizing ability than the further conversion of the hydrocarbon [10].

Two additional observations must be recorded. First, contrary to the earlier report [23], *stirring increases significantly the rate of conversion on SZ*. Thus, for a 4 : 1 substrate to catalyst weight ratio at 65°C, the conversion after 90 min was 15% without stirring and 22% with stirring. Second, we observed that a catalyst sample calcined at 610°C and activated at 450°C retained full catalytic activity after being stored in the rubber septum-capped glass tube, in a desiccator for one month; we did not test a longer storing time. The results obtained with the fresh and stored catalysts are shown in fig. 1. Catalysts subjected only to the first step (610°C) were stored in a desiccator for more than a year and showed no activity loss if activated to 450°C immediately before use.

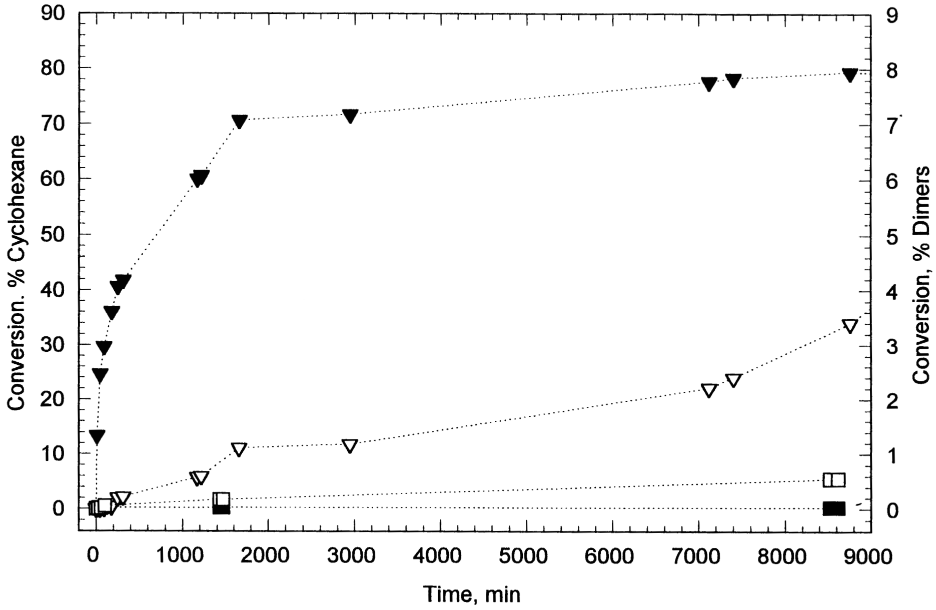

Fig. 3. Effect of catalyst pretreatment with SO_2 on the formation of dimers in the reaction of MCP to CH on SZCH-3.00 (2.1% S, 110 m^2/g) and on $AlCl_3$. (■) SZCH-3.00, MCP/cat = 4 (catalyst 0.0984 g, MCP 0.526 ml), 65°C, no stirring, SO_2 pretreatment; (□) dimers. (▼) $AlCl_3$, MCP/cat = 4 (catalyst 0.0755 g, MCP 0.403 ml), 55°C, no stirring, SO_2 pretreatment; catalyst retained ~ 30% weight after SO_2 evacuation; (▽) dimers.

4. Conclusion

The completely different effect of sulfur dioxide on catalytic activity and the qualitative and quantitative differences in the pattern of dimer formation in reaction of MCP show that the mechanism of activation of saturated hydrocarbons is different for SZ and for $AlCl_3$ (promoted by traces of water). The results also confirm the existence of two pathways for formation of dimers in the case of the SZ catalyst. The bifunctional nature (one-electron oxidation combined with acid catalysis) of catalysis by sulfated metal oxides advanced in our previous reports [10–12] predicted the formation of dimers by a free-radical pathway, especially in the initial stages (initiation period) of the reaction (eq. (4)). Obviously, a typical strong acid (in particular a superacid) catalyst should not behave that way (eq. (5) [22b]):

$$\begin{aligned}&(ZrO)_2SO_2 + RH \rightleftharpoons [(ZrO)_2SO_2^{\bullet -} + RH^{\bullet +}]\\ &\rightleftharpoons [HO{-}Zr(ZrO)SO_2^{\bullet} + R^{\bullet}] \begin{cases} \nearrow R{-}R \\ \searrow HO{-}Zr(ZrO)SO_2{-}R \\ \qquad \rightarrow \text{ionization and isomerization}\end{cases} \qquad (4)\end{aligned}$$

$$\begin{aligned}&H_2O.AlCl_3 + RH \rightleftharpoons H_2 + HO{-}AlCl_3^{-} + R^{+}\\ &\qquad \rightarrow \text{isomerization} \qquad (5)\end{aligned}$$

The current experiments are in full agreement with these predictions.

Acknowledgement

This work has been supported by a Grant (CTS-9528412) from NSF.

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