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Journal of Molecular Catalysis A: Chemical 124 (1997) 67–78



The mechanism of conversion of hydrocarbons on sulfated metal oxides.

Part IV. Kinetics of the reaction of methylcyclopentane on sulfated zirconia ¹

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Received 6 November 1996; accepted 12 March 1997

Abstract

The liquid-phase isomerization of methylcyclopentane to cyclohexane on a sulfated zirconia catalyst (SZCH-3.5R, prepared by the controlled impregnation technique previously reported by the authors) was investigated in the stirred batch mode at four temperatures between 45 and 65°C. A kinetic analysis of the data was developed, which gave the rate constants for the isomerization (k) and catalyst deactivation (k_d), as well as the length of the induction period (t_0). The activation parameters for the isomerization reaction are $\Delta H^\ddagger = 16.3$ kcal/mol and $\Delta S^\ddagger = -30$ cal/mol · deg. The rate of deactivation, k_d , is about half of the isomerization rate (k) at 45°C; at 55°C and above, the deactivation is faster than the reaction. The length of the induction period decreases with the increase in temperature and with the increasing catalyst activity. All the results are as required by the bifunctional catalysis mechanism of the reactions of saturated hydrocarbons on sulfated metal oxides (initiation by oxidation followed by acid catalysis). For a reaction in a tube without stirring the induction period is longer. Also, the rate decreases with the increase in the amount of catalyst for the same substrate to catalyst ratio, indicating that the results are influenced by diffusion through the catalyst bed. Approximate values of the kinetic parameters can be obtained in that case by running the reaction for several quantities of catalyst with the same substrate to catalyst ratio and extrapolating to zero catalyst bed thickness. © 1997 Elsevier Science B.V.

Keywords: Sulfated metal oxides; Kinetics; Hydrocarbon conversion; Methylcyclopentane; Zirconia

1. Introduction

The mechanism of catalysis by sulfated metal oxides (SMO-s, invented by Holm and Bailey in 1962 [1]), has been a subject of interest for years. The most important feature of these mate-

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¹ Part III: A. Ghenciu and D. Fărcașiu, *Catal. Lett.*, 44 (1997)

29. Part II: A. Ghenciu and D. Fărcașiu, *J. Mol. Catal.* 109 (1996) 273.

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rials is a high activity for the reactions of saturated hydrocarbons. Kinetic data giving reliable activation parameters for these reactions are not available, however. The goal of the present study was to obtain such quantities. In addition, because the role of the hydride transfer step has been much discussed and debated, we chose to study a reaction for which this step is exothermic. As a background for the discussion, a short account of the development and status of our mechanistic understanding of the reactivity of SMO-s will be presented first. Like other groups (for reviews, see Refs. [2–4]), we have concentrated on sulfated zirconia, SZ, the most active catalyst in this class [5–10]. At first because of their catalytic activity [11], then from Hammett acidity measurements applied to solids [12–14], these materials were considered solid superacids [2–4,15–25]. For Fe- and Mn-doped SZ (SFMZ), TPD of pyridine (Py) and of benzene (PhH) were also offered as proof of superacidity [16,21]. There was, however, disagreement as to the nature of the acid sites responsible for activating saturated hydrocarbons: Lewis [26–28], or Brønsted [2,25,29,30].

We pointed out that solids are *non-Hammett acids* [5,9,31,32] and the H_0 values found [2–4] do not reflect the real acid strength of these materials. Indeed, the catalytic activity of SMO-s did not correlate with the reported H_0 values [9]. We also showed that the TPD experiments did not reflect acid–base interactions, because PhH and Py, differing in basic strength by a factor of 10^{25} , eluted from SFMZ at the same temperature [5]. Py in fact was largely oxidized, the elution peak consisting mostly of CO_2 and SO_2 . A study of PhH TPD from SFMZ conducted by another group showed total oxidation to CO_2 , but the authors still referred to the material as superacid catalyst [19]. Total oxidation of PhH and Py took place not only on SFMZ, but also on SZ and Pt/SZ, with oxygen supplied by the sulfate and also by the zirconia support [33].

We presented some years ago evidence to the thesis that there might be no such thing as a

solid superacid [34–36]. Along those lines, the idea of superacidic catalysis by SMO-s was criticized, noting that dopants such as Cu ions in AlCl_3 , or Fe and Mn ions in SZ can act as electron acceptors toward organic compounds [36]. Indeed, newer acidity evaluations indicated that SZ and SFMZ are weaker acids than H-ZSM5 [37,38]. Ammonia TPD indicated that SZ and SFMZ have similar acid strengths [39], but SO_2 was evolved in the ammonia TPD peak [40]. Water adsorption (0.5 to 3.8 moles per mole of sulfate) gave the same $\text{H}_3\text{O}^+/\text{H}_2\text{O}$ ratio as for H_2SO_4 , which was incompatible with superacidity of the starting SZ [41], but the sulfate groups might have been detached from the surface in the procedure. Isomerization of ^{13}C -labelled butane on SFMZ showed that dimerization to C_8 species and cleavage after skeletal rearrangement was involved [42,43], an indication of olefinic intermediates [37,38,42–44]. (Dimeric ion intermediates intervene, as shown by labeling experiments, in reactions of small alkanes on non-dehydrogenating catalysts, like AlCl_3 , to circumvent primary alkyl cations [45].) Intermediacy of alkenes in reactions of alkanes on SFMZ was also proposed in the subsequent study of Wan et al. [39]. It might be noted that another SMO, sulfated alumina, was first prepared as a less active, more selective catalyst than Al_2O_3 itself for O-methylation of phenol [46]. The same material was made later and claimed to be superacidic [47].

TPD of PhH and Py [33] showed that the mechanism of reactions is the same on SZ, SFMZ, and Pt/SZ. Model compound studies indicated that catalysis of saturated hydrocarbon conversion on SZ involves a one-electron transfer to the catalyst, after which the resulting organic cation-radical evolves at least in part by a free radical route before recombination with the catalyst and formation of a surface-bonded sulfite or sulfate ester. Ionization of the latter or elimination to an olefin followed by hydronation provides the route for carbocationic reaction without needing a superacidic catalytic site [6–10,48]. Fully formed carbocations need not

actually be formed, because isomerization can occur within cationoidic species [9,49] (weakly coordinated carbocations [50]). It has to be noted that in respect to the oxidizing component of their activity SMO-s are reactants or initiators rather than true catalysts.

As already noted [33], the existence of redox properties of SMO-s had been reported before [51–56], but the oxidizing and acid properties were considered separate functions of the catalyst. The influence of oxidation upon the acid catalyzed reactions was considered only in recommending that the catalytic reactions be conducted at temperatures lower than the onset of oxidation [55].

Initiation of a cationic reaction by a one-electron oxidation had analogies for alkane reactions (isomerization, cracking) in other media [57–61]. It explained the results and apparent contradictions of catalysis by SMO-s mentioned above, as well as detection of ESR signals from benzene on SZ [17] and the indication that catalyst deactivation is linked to the reduction of S(VI) [62]. Indeed, reduction of S(VI) to sulfide paralleling the decrease in activity of an SZ catalyst for 1-butene isomerization at 200°C was found by XPS [63] and H₂S was released in the reaction of butane on SZ at 250°C [64]. Formation of adamantanethiol and adamantyl sulfide from adamantane on SZ at an even lower temperature, 150°C, was also observed [6,8,9].

More recently, it was found that low-temperature reaction of butane on SFMZ does not conform to the superacid catalysis mechanism [65–67] and the amount of butane converted is stoichiometrically related to the dopant [67]. Also, calcination of SFMZ in air gave a better catalyst than calcination in He [68]. Finally, a comparison of SZ with AlCl₃ has shown that their patterns of catalytic activity in the isomerization of methylcyclopentane (MCP) are different [69]. All these findings agree with the bi-functional (oxidation plus acid catalysis), but not with acid-only catalysis (note that for alkanes the latter *would* require superacidic strength

of the catalyst). Further corroborating information is provided by MCP isomerization in this work.

2. Experimental

2.1. General

AR grade reactants were used as purchased. The sulfur content and surface area of catalysts were measured as reported earlier [70,71].

2.2. Catalyst preparation

The controlled impregnation technique was used to prepare the catalysts from zirconium hydroxide, indicated in text as SZCH-V, where V is the volume of 1 N H₂SO₄ (mL) per gram of Zr(OH)₄ used in the preparation. SZCH-VR indicates that the material was dried in a rotary evaporator, otherwise it was dried in a dish [71].

2.3. Kinetic measurements

Fixed bed experiments were run in a 14 mm long, 5 mm ID glass tube, as described before [9,70,71]. For experiments with stirring, the lower part of the tube was blown to a chamber of 30 mm total length and a diameter in the widest section (20 mm long) of 18 mm. A teflon-coated thin magnetic stirring bar was used. Addition of catalyst and reactant, and running the isomerization were accomplished as described before [9,69–71] and so was the GLC analysis of the reaction mixture [9].

2.4. Treatment of data

Plotting of data with the equations shown in the text was accomplished with the program SigmaPlot, developed by Jandel Scientific. The activation parameters and rate constants at dif-

ferent temperatures were calculated with the program C2Plus, from Refs. [72,73].

3. Results and discussion

The goal of the study was to obtain values of rate constants from which reliable activation parameters could be calculated. Rates of a number of reactions catalyzed by SMO-s have been reported in the literature: ring-opening of cyclopropane [3,4,74], dehydration of 2-butanol [4,74], methanol addition to isobutene [63], double bond migration (isomerization) of 1-butene [4,63,74], skeletal isomerization of butane [17,23,29,30,44,75–79], hexane [25,80], and cyclohexene [81], cracking of butane [65] and neopentane [66], and disproportionation of propane [82] and butane [23,77]. In most cases, however, the quantity reported was conversion of the reactant at an arbitrary time worked out to be expressed as a quantity with the dimension of a reaction rate. Considering the existence of both an induction period as shown above and a generally observed rapid deactivation encountered with this type of catalyst, such an approach cannot be considered satisfactory. An example of treatment which attempted to correct for deactivation was the extrapolation of instant rates of butane isomerization on FMSZ to time zero by Hsu et al. [75]. Looking from the other angle, an evaluation of the rate of deactivation of the SZ catalyst in the same reaction from the decrease of specific conversion with the time on stream was made by Yaluris et al. [78]. Another kinetic treatment was reported by Navío et al. for the isomerization of cyclohexene [81], but it neglected the deactivation of the catalyst and the temperatures employed were rather high (around 250°C) [81]; in addition, for the isomerization of an olefin, which is a relatively strong base, only the acidic function of the catalyst should be involved.

The possible role of hydride transfer from the starting material to the carbocation of the product as a rate-determining step was considered

for the reaction of hexane on Pt–SZ [80] as it was in general terms for other solid acids [83]. We chose MCP as substrate, to gather information for a case in which the hydride transfer step is exothermic.

Our first rate measurements on the isomerization of methylcyclopentane (MCP) to cyclohexane (CH) were made in the fixed bed mode, only shaking the tube for re-homogenization of the mixture after taking each sample. Most experiments of that group were conducted with the catalyst SZCH-0.95, the same catalyst used in our first mechanistic studies [5–10,48]. Its activity is similar with that of the catalyst prepared by the standard technique (percolation) [2–4], identified as SZPH-15 [71], and allows one to determine conveniently the progress of this particular reaction at 65°C [9,70].

The first observation was that the conversion of methylcyclopentane for a constant ratio of reactant to catalyst was a function of the total amount of sample, that is of the thickness of the catalyst bed, indicating the importance of diffusion through the catalyst bed. The progress of the isomerization (expressed as fraction of cyclohexane formed as a function of time) at five different quantities of catalyst in the tube (five values of the catalyst bed thickness) but the same reactant/catalyst ratio (4:1 by weight)) is represented in Fig. 1. The same type of conversion plots were obtained for experiments with a reactant/catalyst ratio of 2:1, but the conversion was higher. The second important finding was that the attempt at connecting the conversion vs. time line with the origin produces a marked inflexion, thus proving the existence of a reaction intermediate or an induction time, as required by the bifunctional catalysis mechanism. The intercept of the best line through the points with the abscissa gives an estimate of the length of this induction period. During that interval, oxidation via odd electron species to generate the reactive precursors of carbocations or cationoidic species occurs [6–10,48].

To eliminate the effect of diffusion through the bed, the fraction of CH formed after the

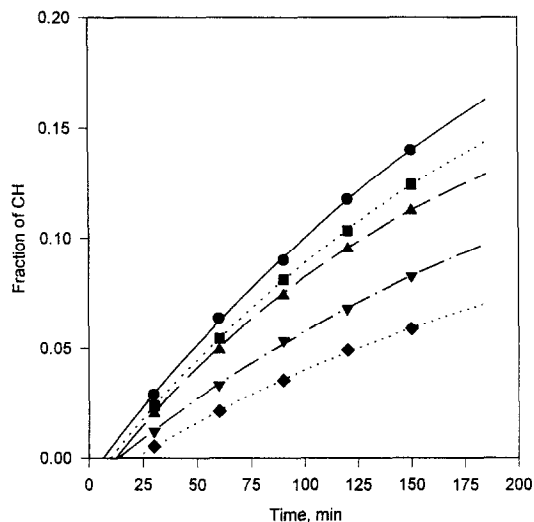


Fig. 1. Liquid phase isomerization of MCP in fixed bed. Catalyst, SZCH-0.95, substrate: catalyst ratio, 4/1. (●) 32.5 mg SZ, 125.2 mg MCP; (■) 63.9 mg SZ, 254.7 mg MCP; (▲) 79.9 mg SZ, 318.0 mg MCP; (▼) 126.5 mg SZ, 503.0 mg MCP; (◆) 188.8 mg SZ, 750.2 mg MCP.

same time of reaction in a series of experiments run with different quantities of catalyst, but the same ratio MCP/catalyst (4:1) is plotted as a function of the amount of catalyst in Fig. 2. (A similar plot was constructed for a 2:1 ratio MCP/catalyst.) The intercept with the ordinate axis, that is extrapolation to a catalyst thickness

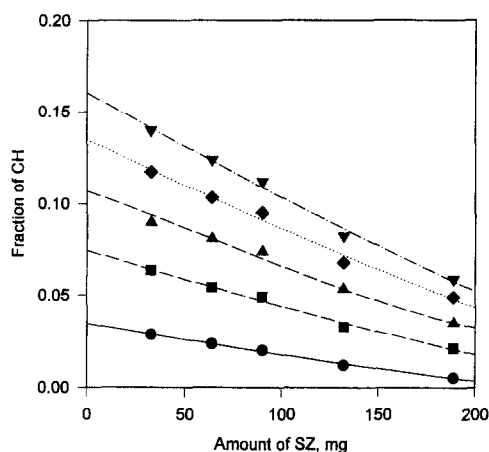


Fig. 2. Effect of the thickness of catalyst bed upon the degree of conversion (data from Fig. 2, substrate: catalyst ratio, 4:1). (●) conversion at 30 min; (■) conversion at 60 min; (▲) conversion at 90 min; (◆) conversion at 120 min; (▼) conversion at 150 min.

of zero, gives information about the conversions at each time not affected by diffusion through the bed. (The small particle size and existence of mesopores but not of micropores in the catalyst [84] were considered to minimize other mass transport effects.) These extrapolated values could then be used to assess rate constants, which were of the same order as the more accurate values obtained by the technique described below. The approach remains available when one has to run fixed-bed experiments. The diameter of the reactor has to be constant, of course.

To obtain more accurate values for the rate constants, we developed a different experimental technique. First, after conducting the study of optimization of catalyst preparation [71], we continued the kinetic study with the most active catalyst, SZCH-3.5R. (Note that our most recent mechanistic work [69] also used a catalyst of higher activity than the earlier studies [6–10]) A comparison of the two catalysts, SZCH-3.5R and SZCH-0.95, with each other and with the catalyst prepared by the standard procedure, SZPH-15 [70,71] is presented in Fig. 3. Second, the newer series of experiments were conducted after the demonstration by Ghenciu that, con-

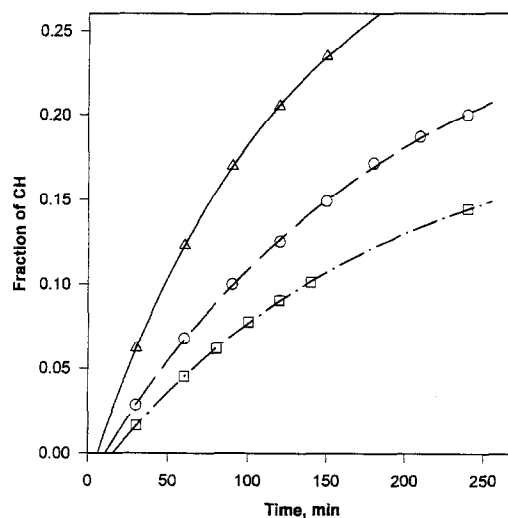


Fig. 3. Comparison of catalysts for isomerization of MCP (liquid phase, 65°C, no stirring). (▲) SZCH-3.5R; (○) SZCH-0.95; (□) SZPH-15.

Table 1
Conversion data for the isomerization of MCP (molar fraction of CH at given times)^a

Time (min)	45°C	55°C	60°C	65°C (I)	65°C (II)
5			0.0107		
7	0.0043	0.0096			
10				0.0340	0.0331
15			0.0302		
17	0.0115	0.0234			
20				0.0639	0.0624
25			0.0497		
27	0.0192	0.0364			
30				0.0882	0.0862
35			0.0675		
37	0.0263	0.0483			
40				0.1101	0.1071
45			0.0843		
47	0.0327	0.0604			
50				0.1289	0.1253
57	0.0401	0.0719			
67	0.0471	0.0824			
77	0.0535	0.0923			
87	0.0600	0.1025			

^a Catalyst: SZCH-3.5R, MCP/catalyst = 9:1; reaction with stirring, analyses by GLC.

trary to our earlier assessment [70], stirring increases the reaction rate [69]. It is possible that the reactor configuration and experimental procedure used in the early experiments resulted in contamination with atmospheric moisture.

In addition to taking care of the problem of diffusion through the bed, the dual improvement of stirring and use of a more active catalyst allowed us (a) to increase the substrate to catalyst ratio to 9:1 and (b) to run MCP isomerization experiments at temperatures even lower than 65°C. The results obtained at four temperatures are given in Table 1. To show the reproducibility of our procedure, two runs for the reaction at 65°C are presented in the table.

In all our runs we followed the isomerization of MCP only to small conversions. Nonetheless, we included the reversibility of the reaction in all our kinetic treatments, on the idea that the equilibrium constant is one of the very few parameters accurately known for the process studied and, therefore, the improvement in the quality of our treatment produced by its inclusion, no matter how small, should be welcome.

For a treatment of data by curve fitting it can be seen immediately that disregarding the reversibility would have little effect on the value found for the rate of reaction, but it would have a measurable effect on the value found for the rate of deactivation.

For the kinetic analysis we treated the reaction of MCP as a first order process, Eq. (1), in which x is the fractional conversion to CH and K is the equilibrium constant, $[\text{CH}]/[\text{MCP}]$. It should be noted that isomerization of cyclohexene on SZ was also reported to follow first order kinetics [81], even though the intermolecular reaction should be favored when the cationic/cationoidic species is generated in the presence of an excess of olefin. The pseudo-first order reaction constant in Eq. (1), k_r , incorporates the concentration of catalyst, C_{cat} . As this quantity cannot be defined, because we do not have a proper description of the nature of active sites involved in the rate-determining step (oxidizing? acid? combination of both? how strong?), we took care to use exactly the same ratio of catalyst to substrate in all experiments.

$$\frac{dx}{dt} = k_r(1-x) - \frac{k_r}{K}x \quad (1)$$

The constant k_r decreases during the reaction because of catalyst deactivation. In the first, approximate, treatment we considered that the deactivation between two consecutive samplings (typically 10 min interval) is negligible. Under these conditions, the integration of Eq. (1) between two sampling times, t_i and t_{i+1} leads to an average rate constant, $(k_r)_{i,i+1}$, given by Eq. (2), where the parameter M has the meaning defined in Eq. (3):

$$(k_r)_{i,i+1} = \frac{M}{(t_{i+1} - t_i)} \ln \left[\frac{(1 - Mx_i)}{(1 - Mx_{i+1})} \right] \quad (2)$$

$$M = 1 + 1/K \quad (3)$$

The values $(k_r)_{i,i+1}$, taken as the rate constants at the middle of the time interval between t_i and t_{i+1} for each of the four temperatures are plotted in Figs. 4–7. It can be seen that catalyst

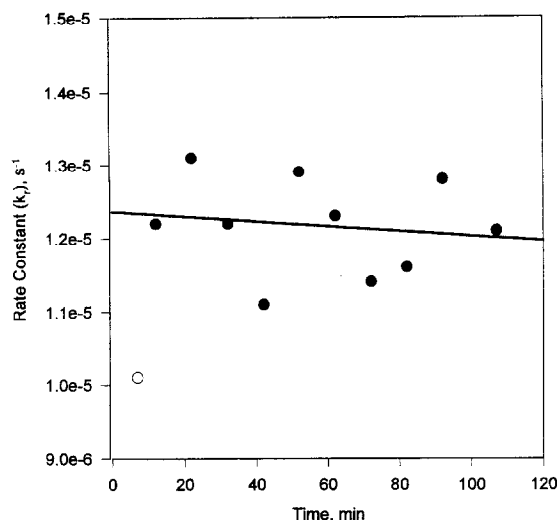


Fig. 4. Rate constants between consecutive points (average between two sampling times). Catalyst, SZCH-3.5R, reaction at 45°C. $k = 1.24 \times 10^{-5} \text{ s}^{-1}$; the first point (○) was left out of the correlation.

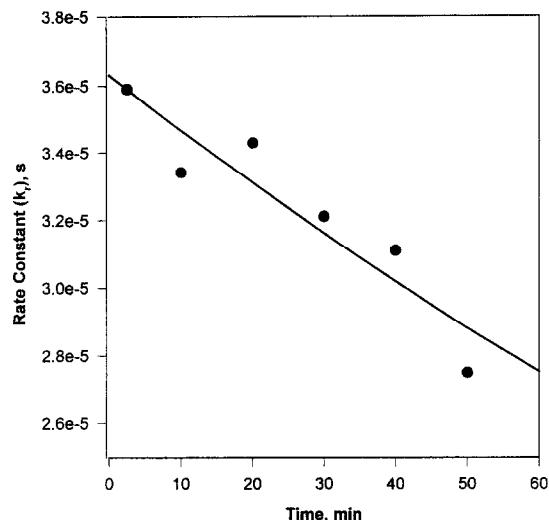


Fig. 6. Rate constants between consecutive points (average between two sampling times). Catalyst, SZCH-3.5R, reaction at 60°C. $k = 3.63 \times 10^{-5} \text{ s}^{-1}$.

deactivation goes from moderate at 45°C to severe at 65°C and that at the lowest temperature the point for $(k_r)_{1,2}$ had to be left out of the correlation, as it deviates from the line drawn through the other points by definitely more than the normal data spread. The increase in the value of rate constant from $(k_r)_{1,2}$ to $(k_r)_{2,3}$

shows that the reactive intermediates had not yet reached the steady concentration at that stage.

Extrapolation of the lines drawn through the points in Figs. 4–7 (exponential decay) to the ordinate gives values of the rate constants (k , given in the caption of each figure) for an

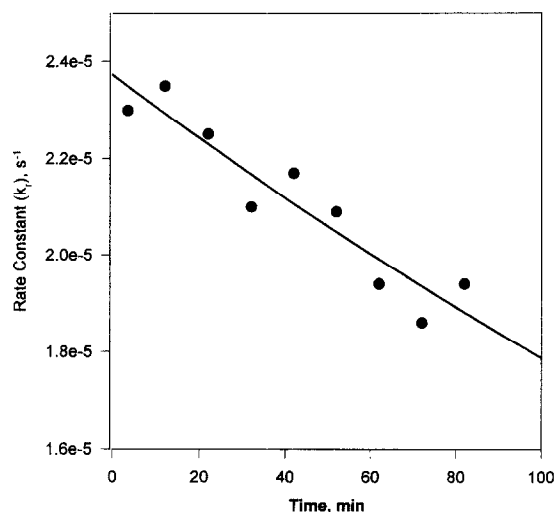


Fig. 5. Rate constants between consecutive points (average between two sampling times). Catalyst, SZCH-3.5R, reaction at 55°C. $k = 2.37 \times 10^{-5} \text{ s}^{-1}$.

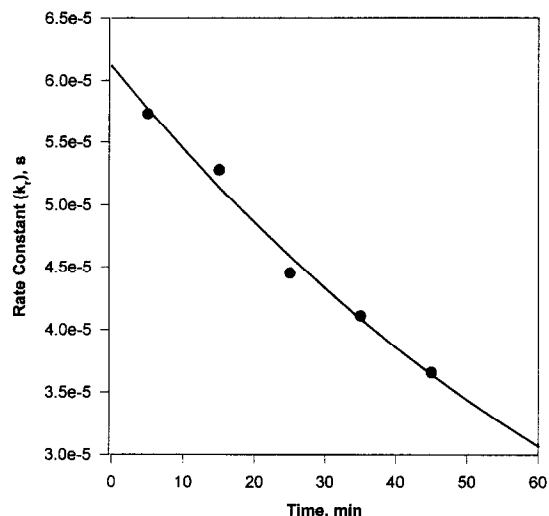


Fig. 7. Rate constants between consecutive points (average between two sampling times). Catalyst, SZCH-3.5R, reaction at 65°C. $k = 6.11 \times 10^{-5} \text{ s}^{-1}$.

idealized state in which the initiation/activation step would be complete, but there would be no deactivation as yet. A similar meaning is assumed by the rates at time zero in the work of Hsu et al. [75].

For a more rigorous treatment, deactivation is expressed by a first-order decrease in the kinetically effective catalyst concentration (number of sites), Eq. (4), in which k_d is the rate constant for catalyst deactivation or, more correctly, the logarithm of the fractional deactivation per time unit.

$$C_{\text{cat}} = (C_{\text{cat}})_0 \exp(-k_d t) \quad (4)$$

Upon substituting in Eq. (1), the initial concentration of catalyst is included in the pseudo-first order constant and then k_r is replaced by k , giving Eq. (5):

$$\frac{dx}{dt} = k(1 - Mx)\exp(-k_d t) \quad (5)$$

which is then integrated (Eq. (6)):

$$\int_0^x \frac{dx}{1 - Mx} = k \int_{t_0}^t \exp(-k_d t) dt \quad (6)$$

The integration limit t_0 in Eq. (6) represents the length of the induction period. This quantity was defined before in fixed-bed continuous experiments as the lag between $t = 0$ and the time (t_{max}) at which the observed conversion reached a maximum. As the reactant moves along the catalyst bed, the activation process (generation of the surface esters [6,8,9,48]) occurs in time along the bed. If there was no deactivation the time of maximum conversion would signal the moment when all the catalyst is fully active. It can be seen that this state is achieved earlier at the beginning than at the end of the catalyst bed. Deactivation starts as soon as the catalyst is activated and begins converting the feed; deactivation also progresses along the catalyst bed. Thus, the combination of the induction period and fast deactivation is responsible for the sharp maxima in the conversion-time plots, which are more pronounced at lower temperatures, observed in those experiments

[19,23,44,65,68,76,77,82]. The value of t_{max} should depend upon a number of factors, including, most likely the length of the catalyst bed. A study varying both the reactant flow and the length of the catalyst bed should be interesting. In our approach the induction period is defined as the time at which the conversion of the reactant to product begins, and is determined by the integration of the kinetic equation or extrapolation of conversion-time plot to zero conversion, rather than by direct measurement.

The integration of Eq. (6) gives Eq. (7):

$$\ln(1 - Mx) = M \frac{k}{k_d} (\exp(-k_d t) - \exp(-k_d t_0)) \quad (7)$$

and finally, after explication, Eq. (8):

$$x = \frac{1}{M} \left[1 - \exp \left(M \frac{k}{k_d} [\exp(-k_d t) - \exp(-k_d t_0)] \right) \right] \quad (8)$$

Fitting the experimental data in Table 1 with Eq. (8) gives the curves shown in Fig. 8 and the values for the rate constants of reaction (k) and

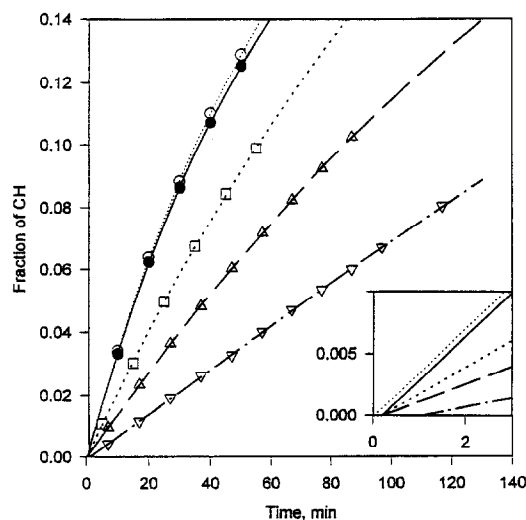


Fig. 8. Correlation of conversion (fraction of CH present at a given reaction time, from Table 1) with Eq. (8); insert, first 3 min of reaction. Temperatures: (∇) 45°C; (Δ) 55°C; (\square) 60°C; (\circ) 65°C (I); (\bullet) 65°C (II).

Table 2
Kinetic parameters for the reaction of MCP on SZ^a

	k (s ⁻¹) ^c	k_d (s ⁻¹)	t_0 (s)	K ^d
45°C	1.23×10^{-5}	3.22×10^{-6}	59.9	4.37
55°C	2.41×10^{-5}	5.24×10^{-5}	11.5	3.56
60°C	3.66×10^{-5}	7.65×10^{-5}	10.5	3.23
65°C (I) ^b	6.20×10^{-5}	1.92×10^{-4}	3.28	2.93
65°C (II) ^b	6.16×10^{-5}	2.07×10^{-4}	12.1	2.93

^a k , k_d , t_0 calculated with Eq. (8) and the data in Table 1. The values for t_0 were extracted from calculation at the same precision as the values for the rate constants and do not represent the measurable accuracy of the induction period in experiments.

^b Average values: $k = 6.18 \times 10^{-5}$, $k_d = 2.00 \times 10^{-4}$, $t_0 = 7.71$.

^c $\Delta H^\ddagger = 16.25 \pm 0.05$ kcal/mol, $\Delta S^\ddagger = -30.16 \pm 0.14$ cal/mol·deg (calculated as indicated in Section 2). Calculated values of k at other temperatures: 25°C, 1.94×10^{-6} ; 100°C, 6.04×10^{-4} ; 150°C, 9.13×10^{-3} .

^d Calculated from ΔH_f° and ΔG_f° values (at 25°C) given in Ref. [85].

deactivation (k_d), and for the length of the induction period (t_0) given in Table 2. Also given there are the values for the equilibrium constant at each temperature used in Eq. (3), calculated from literature data [85]. The rate constants k from Table 2 can be compared with the values arrived at in Figs. 4–7. The near-identity of the two sets of numbers is probably fortuitous, but it is unquestionable that the two approaches gave results that are at least very close, thus reinforcing each other.

As expected, the rate of deactivation increases with temperature and it is quite high. As a matter of fact, the deactivation is faster than the reaction at 55°C and above. As already discussed, the high rate of deactivation follows from the existence of multiple deactivation pathways: normal coking encountered in carbocationic reaction, polymerization by a free-radical pathway (in addition to cationic oligomerization) of the olefin intermediates, and loss of oxidizing ability, because the initiation step involves sulfate reduction (in this respect SZ is a reactant, not a catalyst) [48]. In addition, reduction of sulfate to sulfite (and at higher temperatures even to sulfide [6–9,63,64]) should also

reduce the acid strength of the catalyst. The higher temperature dependence of the rate of deactivation than of the rate of reaction is to be remembered if any attempt at using this catalyst for a practical purpose is to be made. An additional potential source of deactivation is the diffusion of moisture through the rubber septum, especially upon sampling.

The existence of an induction period, required by the bifunctional mechanism of catalysis by SMO-s, unquestionably appears from our experiments. It can be observed (Table 2 and Fig. 8, especially the insert) that the induction period shortens as the reaction temperature increases. A comparison of Fig. 1 with Fig. 8 and an examination of the curves in Fig. 3 show that the induction period is shorter for a more active catalyst. In experiments not shown here, it was shown that the induction period is also shorter for a higher catalyst to substrate ratio (an effect of reduction of the induction period by stirring needs also to be considered).

The activation parameters calculated [72,73] from the rate constants in Table 2 are $\Delta H^\ddagger = 16.3$ kcal/mol³ and $\Delta S^\ddagger = -30$ cal/mol·deg. The activation enthalpy is higher than the values reported for other isomerizations of saturated hydrocarbons on SMO-s. For example, the value $E_a = 10.7$ kcal/mol (between 100 and 140°C) in isomerization of butane on SZ [75] corresponds [86] to $\Delta H^\ddagger = 9.9$ kcal/mol; values $E_a = 10.5$ kcal/mol (between 30 and 55°C, $\Delta H^\ddagger = 9.9$ kcal/mol) [68], $E_a = 11.4$ kcal/mol (between 28 and 46°C, $\Delta H^\ddagger = 10.8$ kcal/mol) [75], and $E_a = 14 \pm 4$ kcal/mol (between 30 and 60°C) for the same reaction, the latter given together with a value $E_a = 19 \pm 1$ kcal/mol for the reverse reaction (isomerization of *i*-butane to *n*-butane between 30 and 60°C, the equilibrium constant being 2.08 at 45°C) [77] were reported for the conversions on SFMZ. It is possible that in some of the literature studies,

³ 1 cal = 4.184 J.

particularly those conducted at higher temperature, diffusion effects were important.

The large and negative activation entropy found by us suggests a high level of constraint at the transition state of the rate-determining step. Similar values were published [87] for carbocationic solvolyses of alicyclic substrates in hexafluoroisopropanol, a very strong hydrogen bond donor solvent [88]. Based on the observation that a reaction in which either the intramolecular isomerization of the carbocation, or the hydride transfer between the product cation and starting hydrocarbon is rate-determining should have an activation entropy close to zero [89], one might speculate that neither of these two steps is rate-determining in the isomerization of MCP on SZ. The former proposition is most likely, because the hydride transfer step in isomerization of MCP is exothermic. More examples should be investigated, however, before any secure conclusion on the role of the intramolecular isomerization step can be reached. Note that we cannot state at present whether the mechanism involves a chain reaction, that is we do not know how many molecules of hydrocarbon are converted for one oxidation elementary step. From an investigation of the effect of butene additions on the isomerization of *n*-butane on SZ and SFMZ it was concluded that in that case the process is a chain reaction with a chain length of 10–18 [90]. On the other hand, as mentioned above, another study found that the quantity of butane which can be converted on SZ doped with either Fe or Mn is 1:1 stoichiometrically related to the quantity of Fe and Mn in the catalyst [67].

4. Note added in the revision

A reviewer has indicated that the activation parameters should not be descriptive of the rate-determining step, because the steps preceding the latter in the catalytic cycle, which are at (pseudo)equilibrium, are folded into the measured activation enthalpy and entropy. We note

that insofar as the chemical steps are concerned, this representation contradicts the Curtin–Hammett principle [91]. It is, possible that some diffusion effects be still present, in which case the activation enthalpy determined represents a minimum value, thus making even less likely that the hydride transfer step be rate-determining. Important diffusion effects seem unlikely, however, because the rates determined at 5 temperatures between 45 and 65°C for a greater reactant:catalyst ratio (15:1) give about the same activation parameters as the runs at a 9:1 ratio discussed above. The scatter of points is greater, however, in the experiments with low amount of catalyst.

Acknowledgements

This work was supported by a grant (CTS-9528412) from the National Science Foundation.

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