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Activation of Ethane in the Presence of Solid Acids: Sulfated Zirconia, Iron- and Manganese-Promoted Sulfated Zirconia, and Zeolites

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Ethane was activated in the presence of solid acids [sulfated zirconia (SZ), iron- and manganese-promoted sulfated zirconia (FMSZ), HZSM-5, and USY zeolite] at 1 atm, 200–450°C, and ethane partial pressures in the range 0.01–0.2 atm. The data were measured with a flow reactor at low conversions ($<$0.005) such that reaction of ethane took place in the near absence of alkenes. Catalysis was demonstrated for ethane conversion in the presence of FMSZ at 450°C and 0.2 atm ethane partial pressure, but the reactions were not shown to be catalytic for the other solid acids and other conditions. FMSZ was active for converting ethane into methane, ethene, and butane at an ethane partial pressure of 0.2 atm and at temperatures of 200–300°C; the other solid acids had no detectable activities under these conditions. At higher temperatures, each of the solid acids was active for conversion of ethane into ethene; butane and methane were also formed in the presence of FMSZ, HZSM-5, and USY zeolite, whereas methane was the only other hydrocarbon observed in the presence of SZ. The initial (5 min on stream) selectivities to ethene at approximately 0.1% conversion, ethane partial pressure of 0.2 atm, and 450°C were approximately 98, 94, 97, and 99%, for SZ, FMSZ, HZSM-5, and USY zeolite, respectively. Under the same reaction conditions, the initial rates of ethane conversion were 0.15×10^{-8}, 3.5×10^{-8}, 3.9×10^{-8}, and 0.56×10^{-8} mol/(s · g) for SZ, FMSZ, HZSM-5, and USY zeolite, respectively. The reactivities are consistent with chemistry analogous to that occurring in superacidic solutions and with the suggestion that FMSZ is a stronger acid than the others investigated here.

INTRODUCTION

Sulfated zirconia (SZ) and iron- and manganese-promoted sulfated zirconia (FMSZ) have been suggested to be superacids because of their extraordinarily high activities for low-temperature *n*-butane isomerization (1, 2). Although the addition of iron and manganese to sulfated zirconia increases its catalytic activity for *n*-butane isomerization by two to three orders of magnitude at 28°C, the roles of these promoters are still debated (3–5). Because chemisorption, infrared, and NMR data gave no indication of extraordinarily strong acidity (6–10), it was suggested (6–10) that the acid strengths of the zirconia-supported catalysts were not higher than those of zeolites, e.g., HZSM-5.

Consistent with the lack of evidence of extremely strong acid sites, Adeeva *et al.* (3) hypothesized that butene, which is presumably formed by dehydrogenation of *n*-butane, is an intermediate in *n*-butane isomerization, which was inferred not to require a superacid. Consistent with the suggestion of Adeeva *et al.*, Wan *et al.* (4) proposed a bifunctional mechanism involving a metal redox site in FMSZ (iron at the surface), where butane is dehydrogenated to give butene, and a nearby acid site, where butene is protonated to form the carbenium ion $C_4H_9^+$, which undergoes isomerization. Farcasiu *et al.* (5) attributed the high activity of zirconia-supported catalysts in alkane isomerization to an "exceptional one-electron oxidizing ability" leading to the formation of cation radicals, which are then presumably converted into sulfite and sulfate esters, which are ionized to yield carbocations that undergo isomerization.

Recent reports of conversions of propane and of ethane into higher-molecular-weight hydrocarbons at 200°C in the presence of FMSZ, however, are consistent with the earlier hypothesis that FMSZ behaves like a superacid (11, 12). Propane was postulated to be protonated to form $C_3H_9^+$, which was inferred to collapse to give either a methane and ethyl cation, $C_2H_5^+$, or an H_2 and propyl cation, $C_3H_7^+$ (11). The carbenium ions ($C_2H_5^+$, $C_3H_7^+$) then presumably react with propane to form C_{3+} aliphatic hydrocarbons, consistent with what Olah *et al.* (13) demonstrated for reaction in the superacid FSO_3H/SbF_5.

Ethane was observed to react similarly to give propane. Ethane was converted into butane in the presence of FMSZ at 200°C (12); the rate of ethane conversion was one to two orders of magnitude lower than that of propane conversion. The ethane conversion data were also suggested to indicate very strong acidity of FMSZ.

The objective of the present investigation was to use ethane as a probe molecule to examine the catalytic and/or reactive nature of FMSZ, extending the work that has recently been communicated (12). Here we compare the performance of FMSZ with the performance of SZ, HZSM-5 zeolite, and USY zeolite for low conversions of

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ethane. A specific objective was to use FMSZ to explore the reaction chemistry of ethane at temperatures far lower than those at which conventional solid acids have usually been tested. Because of the relatively unreactive nature of ethane, only few data are available for its reactions in the presence of acids at temperatures $<500°C$. At temperatures $>500°C$, ethane reacts to give ethene, C_{2+} aliphatics, and aromatics in the presence of solid acids, e.g., HZSM-5 (14, 15), or bifunctional catalysts, e.g., Ga/HZSM-5 (14), Mn/HZSM-5 (16), or Pt/HZSM-5 (17, 18). The activity of HZSM-5 increased by orders of magnitude when the dehydrogenation functions were incorporated into the acidic catalyst (14, 16).

EXPERIMENTAL

Materials

SZ was prepared by calcination of sulfated zirconium hydroxide (Magnesium Elektron, Inc.) at 650°C in a muffle furnace with static air. FMSZ, containing approximately 1 wt% iron, 0.5 wt% manganese, and 1.8 wt% sulfur, was prepared by stepwise incipient wetness impregnation of sulfated zirconium hydroxide with aqueous iron nitrate and manganese nitrate solution (19). The impregnated material was also calcined at 650°C in the muffle furnace.

The BET surface areas of SZ and of FMSZ, measured by N_2 adsorption, were 100 and 90 m^2/g, respectively; other physical properties are reported elsewhere (20). USY zeolite, with a Si/Al atomic ratio of 8.9 and a surface area of about 800 m^2/g, was provided by the Davison Division of W. R. Grace and Co. Ammonium form ZSM-5, with a Si/Al atomic ratio of 25 and a surface area of about 420 m^2/g, was supplied by Conteka; it was converted into HZSM-5 by treatment in air flowing at 500°C for 1.5 h.

Reaction Experiments

The reaction system and pretreatment conditions for SZ, FMSZ, and USY zeolite are described elsewhere (19). The zirconia-supported materials and the zeolites were activated by heating to 450°C in flowing N_2 and in flowing air, respectively. The feed stream of ethane, containing 20 mol% ethane (Liquid Carbonic) in N_2 diluent, was sometimes diluted further with N_2 to give various ethane partial pressures. The impurities in the 20 mol% ethane stream were 30 ppm methane and 20 ppm propane. The reaction conditions were as follows: temperature, 200–450°C; pressure, 1 atm; inverse space velocity, $(1–80) \times 10^4$ $(g \cdot s)/(mol$ of ethane fed); ethane partial pressure, 0.01–0.2 atm; and run length, 4–20 h. Gas-phase hydrocarbons and H_2 were analyzed with an on-line gas chromatograph (Hewlett–Packard 5890A) equipped with an Al_2O_3/KCl PLOT column and flame-ionization and thermal conductivity detectors.

RESULTS

Definitions

Ethane conversion, normalized selectivity, and conversion to products are defined as follows (20): normalized conversion of ethane to each gas-phase hydrocarbon product (containing n carbon atoms) is defined as ($n \times$ number of moles of product)/(2 × number of moles of ethane fed); normalized selectivity for formation of an individual product is defined as (normalized conversion to gas-phase product)/(ethane conversion to gas-phase products). Ethane conversion is defined as the sum of the individual gas-phase product conversions. If conversion of ethane is differential, the rates of ethane conversion or product formation are (ethane conversion)/(inverse space velocity) or (normalized conversion to product)/(inverse space velocity). The units of each rate of product formation are (mol of ethane equivalent)/$(s \cdot g)$.

Performance of FMSZ in Ethane Conversion

As reported earlier (12), the number of ethane molecules reacted per sulfate group in the presence of FMSZ at 450°C, 0.2 atm ethane partial pressure, and 1.8×10^5 $(g \cdot s)/(mol$ of ethane fed) inverse space velocity was >1 after 18 h of reactant flow. If it is correct to assume that the number of active sites is less than or equal to the number of sulfate groups, then catalysis was demonstrated under these reaction conditions. At the lower temperatures, the rates of ethane conversion were lower, and the data may represent stoichiometric rather than catalytic reactions.

The lowest temperature at which FMSZ was observed to be active in converting ethane (into butane and ethene) was 200°C. The conversion of ethane decreased with time on stream at each temperature investigated in the range 200–350°C, whereas at higher temperatures the ethane conversion first decreased, then increased, and then decreased again (Fig. 1). The products observed in the temperature range 200–450°C were H_2, methane, ethene, and butane, with trace amounts of propane and aromatics.

The normalized conversions to each of the products at 250, 350, and 450°C are illustrated in Figs. 2, 3, and 4, respectively. Conversion to ethene decreased with time on stream at temperatures $\leq 350°C$ (as did ethane conversion), but at each of the higher temperatures investigated, it decreased and then increased with time on stream, followed by another decrease. Conversion to butane declined monotonically as a function of time on stream at each temperature; the selectivity to butane decreased with increasing temperature at a given time on stream. At an inverse space velocity of 3.66×10^5 $(s \cdot g)/mol$, initial selectivity to butane decreased from 30% at an ethane conversion of 0.0001 and 200°C to 10% at an ethane conversion of 0.001 and 400°C. Methane was observed at temperatures $\geq 250°C$, and plots

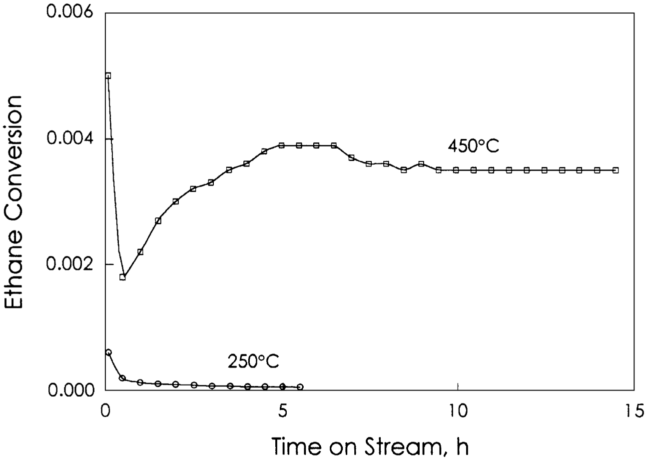

FIG. 1. Conversion of ethane at 250 and 450°C in the presence of FMSZ. Feed ethane partial pressure, 0.2 atm; inverse space velocity, 3.7×10^5 (s · g)/mol of ethane.

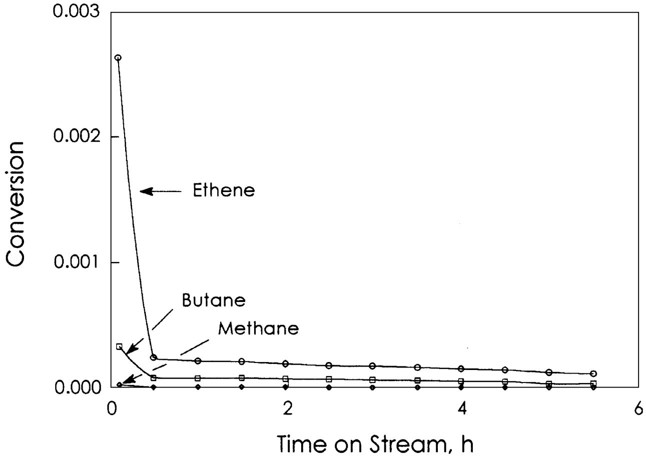

FIG. 3. Conversion to ethene, butane, and methane in the presence of FMSZ at 350°C. Feed ethane partial pressure, 0.2 atm; inverse space velocity, 3.7×10^5 (s · g)/mol of ethane.

of conversion to methane vs time on stream are similar to those characterizing conversion to ethene (Figs. 3 and 4). The remaining product, H_2, was observed only at temperatures >400°C and after 1 h on stream. The molar ratio of H_2 to ethene in the product passed through a maximum, with values ranging from 0 to 1.8 (Fig. 5).

Initial rates of the reactions at 450°C and 0.2 atm ethane partial pressure were determined by extrapolating the decreasing conversions to zero time on stream and plotting these conversions as a function of inverse space velocity (Fig. 6) to determine the slopes (rates). The rates of ethene and of methane formation were approximately 3.5×10^{-8} and 0.08×10^{-8} mol/(s · g).

Rates of methane and of ethene formation at 450°C are plotted in Fig. 7 as a function of ethane partial pressure. The data are approximately consistent with a power-law rate expression, with the reaction orders in ethane being 1.3 and 0.7 for formation of methane and of ethene, respectively. The rate constant for conversion of ethane into methane was found to be 0.54×10^{-8} mol/(s · g · atm$^{1.3}$) and that for ethane conversion into ethene was found to be 9.9×10^{-8} mol/(s · g · atm$^{0.7}$).

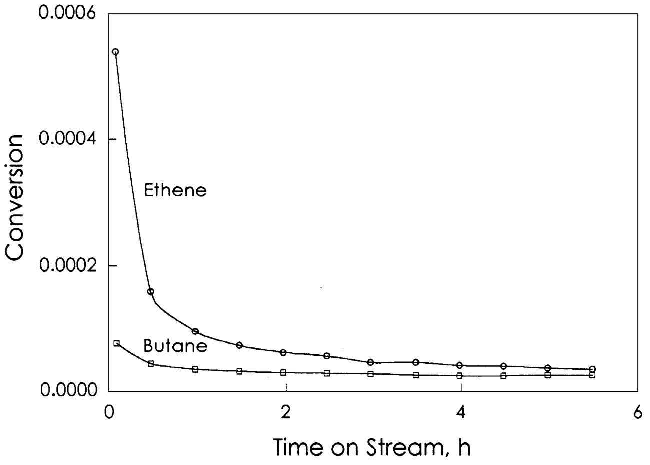

FIG. 2. Conversion to ethene and butane in the presence of FMSZ at 250°C. Feed ethane partial pressure, 0.2 atm; inverse space velocity, 3.7×10^5 (s · g)/mol of ethane.

The color of the FMSZ was unchanged (rust colored) after reactions carried out at temperatures <400°C; however, the FMSZ turned black after operation at temperatures >400°C.

Performance of SZ in Ethane Conversion

Because the activity of SZ for ethane conversion is an order of magnitude less than that of FMSZ, the data presented here for SZ and the comparison with the results stated above for FMSZ suggest that the reactions observed with SZ might be noncatalytic. The reaction of ethane in the presence of SZ at temperatures >300°C gave H_2 and ethene as the only observed products, except that the methane product was sometimes observed at 5 min on stream. Reaction of ethane in the presence of SZ was assumed to be differential (as the conversions were lower than those observed with FMSZ). At 450°C and 0.2 atm ethane partial pressure, the rate of H_2 formation was below the detection limit [1×10^{-9} mol/(s · g)] during the first 7 h on stream, and it increased and then decreased with increasing time on stream; in contrast, the rate of ethene formation first decreased and then increased (Fig. 8). Trace amounts of butane were observed at 5 min on stream at 450°C.

Performance of USY Zeolite in Ethane Conversion

The conversions of ethane in the presence of USY zeolite were low (as they were in the presence of SZ), and the reactions have not been shown to be catalytic. Ethane in the presence of USY zeolite was converted into H_2 and

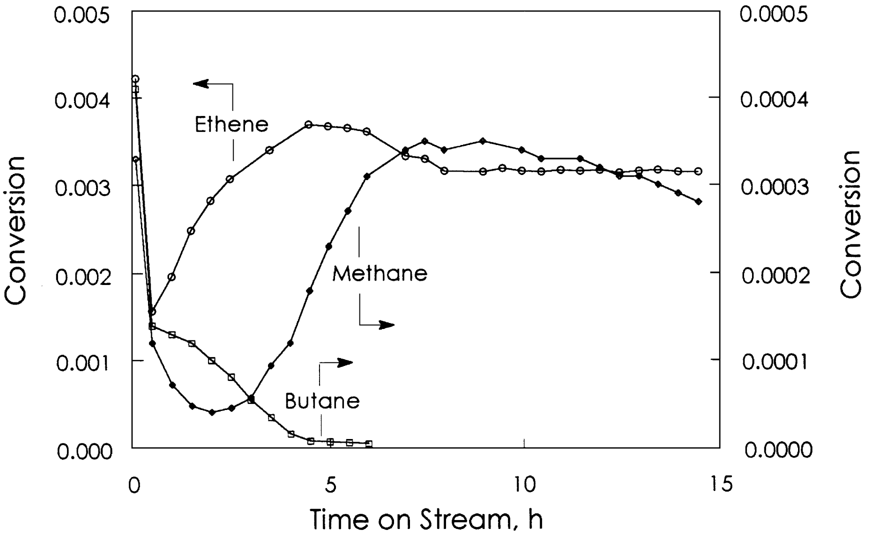

FIG. 4. Conversion to ethene, butane, and methane in the presence of FMSZ at 450°C. Feed ethane partial pressure, 0.2 atm; inverse space velocity, 3.7×10^5 (s · g)/mol of ethane.

ethene at temperatures >300°C, and methane was sometimes observed at 5 min on stream. Conversions of ethane (typically, 0.001) were assumed to be differential for estimation of reaction rates. In contrast to the results observed for SZ or FMSZ, the rate of H_2 and of ethene formation in the presence of USY simply decreased with increasing time on stream at 450°C and 0.2 atm ethane partial pressure (Fig. 9). The amount of H_2 observed during ethane conversion fell below the detection limit after 1 h on stream.

Performance of HZSM-5 Zeolite in Ethane Conversion

The reactivity of ethane in the presence of HZSM-5 zeolite at 450°C was comparable to that of ethane in the presence of FMSZ, but the reactions were not run long enough to demonstrate whether they were catalytic. Ethane was converted into ethene and into butane (but only at temperatures >400°C) in the presence of HZSM-5. No H_2 was detected under any conditions. The rates of ethene, methane, and butane formation at 450°C decreased with increasing time on stream (Fig. 10).

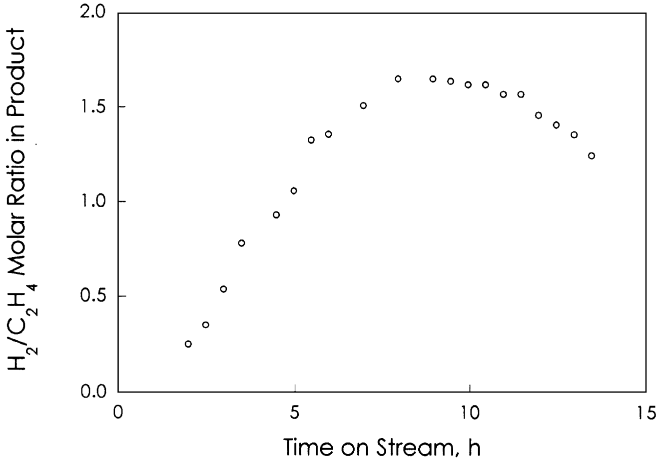

FIG. 5. Molar ratio of H_2 to ethene in the product during ethane conversion in the presence of FMSZ at 450°C. Feed ethane partial pressure, 0.1 atm; inverse space velocity, 4.6×10^4 (s · g)/mol of ethane.

Comparison of the Solid Acids

The initial (5 min on stream) selectivities observed for FMSZ, SZ, HZSM-5, and USY zeolite at various ethane conversions at 450°C and 0.2 atm ethane partial pressure are summarized in Table 1. At a conversion of roughly 0.001, FMSZ is characterized by the lowest ethene selectivity (94%), whereas USY zeolite is characterized by the highest (99%). Butane, formed with a selectivity of 4.1% in the presence of FMSZ and 1.8% in the presence of HZSM-5, was not observed with SZ and USY zeolite. However, at a conversion of 0.003, a small amount of butane was also observed in the presence of USY zeolite. At 400°C and an ethane conversion of 0.001, the selectivity to butane in the presence of FMSZ was 10%, whereas the selectivity to butane in the presence of HZSM-5 was negligible. In the presence of FMSZ, selectivity to ethene decreased with increasing ethane conversion, whereas selectivity to butane increased with ethane conversion.

At 450°C and 0.2 atm ethane partial pressure, the initial rates of ethane conversion in the presence of SZ, FMSZ, HZSM-5, and USY zeolite were estimated to be 0.15×10^{-8}, 3.5×10^{-8}, 3.9×10^{-8}, and 0.56×10^{-8} (mol of ethane equivalent)/(s · g), respectively. If the number of active sites is assumed (arbitrarily) to be equal to the number of SO_4^{2-} groups in the zirconia-supported materials and if this number is assumed to be equal to the number of Al atoms in the zeolites, then the rates of ethane conversion in molecules/(site · s) are 0.36×10^{-5}, 8.3×10^{-5}, 6.0×10^{-5},

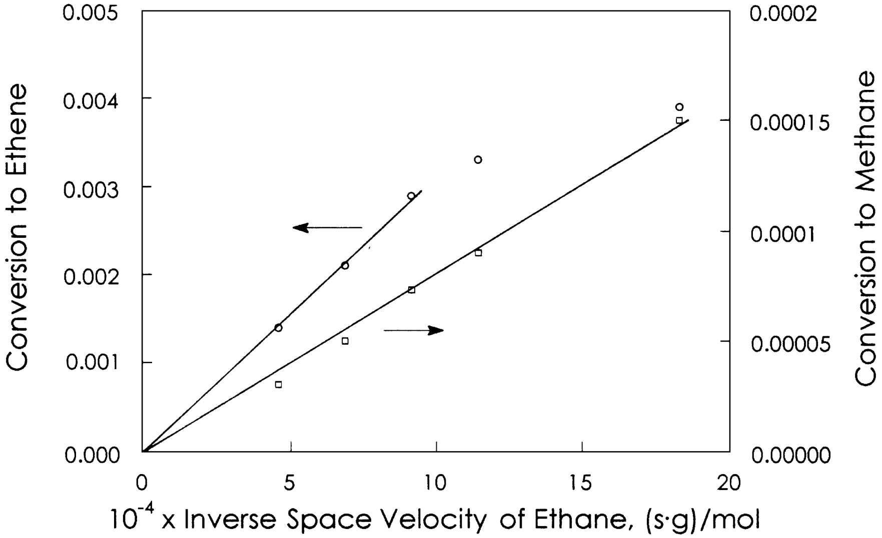

FIG. 6. Differential conversion to ethene and methane in the presence of FMSZ at 450°C. Feed ethane partial pressure, 0.2 atm; inverse space velocity, (4–20) × 10^4 (s · g)/mol of ethane.

and 0.33 × 10^{-5}, respectively, for SZ, FMSZ, HZSM-5, and USY zeolite.

The data shown in the Arrhenius plots (Fig. 11), representing rates of ethene formation at 0.2 atm ethane partial pressure in the presence of FMSZ, SZ, and USY zeolite, lead to estimates of the apparent activation energies (E) and preexponential factors (A'), as follows: 10, 31, and 43 kcal/mol, respectively, and 2.6 × 10^{-5}, 2.1, and 6.6 × 10^4 mol of ethane equivalent/(s · g), respectively. A' and E are defined by the equation

$$r = A'e^{(-E/RT)}, \qquad [1]$$

where r is the reaction rate.

The temperature dependence of the rate of methane formation in the presence of FMSZ and the rate of ethene formation in the presence of HZSM-5, determined from data at 400 and 450°C only, corresponds to apparent activation energies of 71 and 25 kcal/mol, respectively, and preexponential factors of 1.3 × 10^{13} and 1.6 mol of ethane equivalent/(s · g), respectively. Because of the low methane formation rates observed with the other three solid acids, the data were not sufficient to determine the Arrhenius parameters.

A plot of A' on a logarithmic scale at an ethane partial pressure of 0.2 atm as a function of E for the rates of ethene and of methane formation in the presence of each solid acid indicates a linear relationship (with a regression coefficient of 0.998, Fig. 12), suggesting a compensation effect (21).

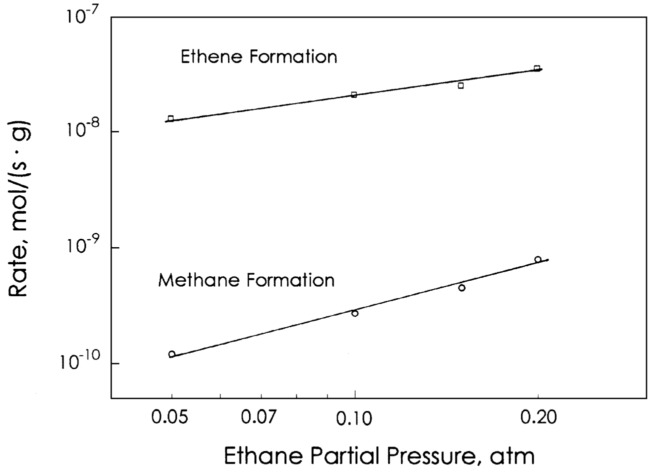

FIG. 7. Rates of ethene and of methane formation as a function of ethane partial pressure in the presence of FMSZ at 450°C.

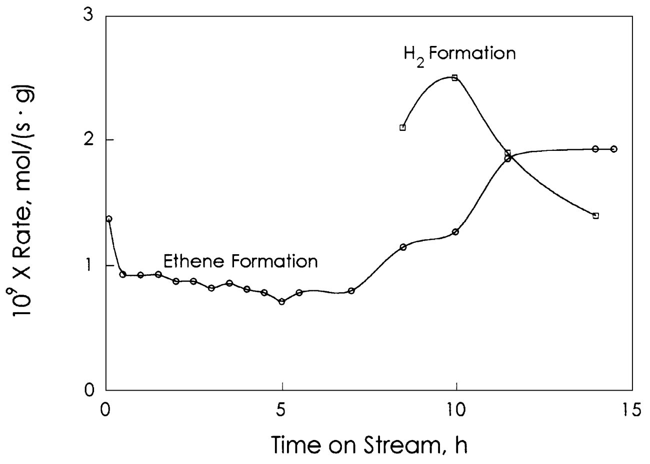

FIG. 8. Rates of ethene and of H_2 formation at 450°C in the presence of SZ. Feed ethane partial pressure, 0.2 atm; inverse space velocity, 1.8 × 10^5 (s · g)/mol of ethane.

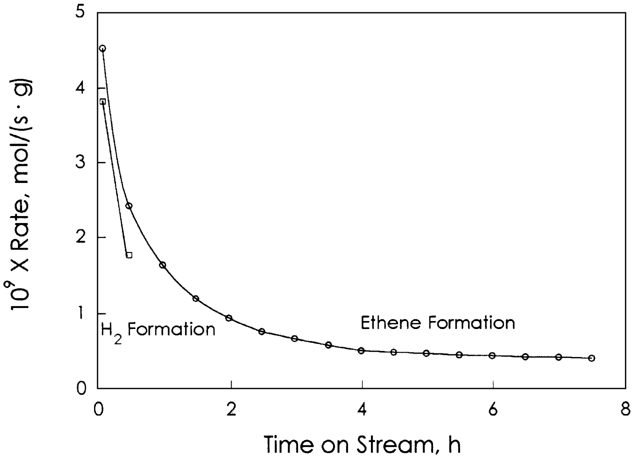

FIG. 9. Rates of ethene and of H_2 formation at 450°C in the presence of USY zeolite. Feed ethane partial pressure, 0.2 atm; inverse space velocity, 1.8×10^5 (s · g)/mol of ethane.

TABLE 1

Comparison of Initial Selectivity[a] for Ethane Conversion in the Presence of FMSZ, SZ, and USY Zeolite at 0.2 atm Ethane Partial Pressure and 450°C

Solid acid	$10^{-5} \times$ inverse space velocity [(s · g)/mol]	Ethane conversion (%)	Normalized selectivity (%) Methane	Ethene	Butane
FMSZ	1.83	0.38	3.4	89.7	6.9
FMSZ	1.14	0.29	2.6	91.1	6.3
FMSZ	0.46	0.13	1.7	94.2	4.1
SZ	7.32	0.12	3.8	96.2	0
SZ	1.83	0.03	3.2	96.8	0
HZSM-5	0.28	0.11	0.9	97.3	1.8
USY	7.32	0.30	1.7	96.8	1.5
USY	1.83	0.08	0.7	99.3	0

[a] Data taken at 5 min on stream.

DISCUSSION

Thermodynamics of Ethane Reactions and the Limits of Differential Conversions

If ethane conversion is approximated as two reactions, dehydrogenation and ethane coupling to give *n*-butane and H_2,

$$C_2H_6 \rightarrow C_2H_4 + H_2 \qquad [2]$$

$$2C_2H_6 \rightarrow n\text{-}C_4H_{10} + H_2, \qquad [3]$$

then the equilibrium conversions determined from thermochemical data (22) are as shown in Fig. 13. These results show, for example, that the maximum allowable conversion of ethane to ethene at 450°C is <0.011.

In view of the thermodynamics results, we recognize that the plot of ethane conversion vs inverse space velocity at 450°C (Fig. 6) is nearly linear up to a conversion of approximately one-fourth of the equilibrium conversion (0.003); thus, the data demonstrate differential conversions. As the conversion increased further and approached the equilibrium value, the rate declined (Fig. 6).

High-Temperature (300–450°C) Conversion of Ethane

In the temperature range 300–450°C, ethane was converted in the presence of each of the following solid acids: FMSZ, SZ, HZSM-5, and USY zeolite. The conversion

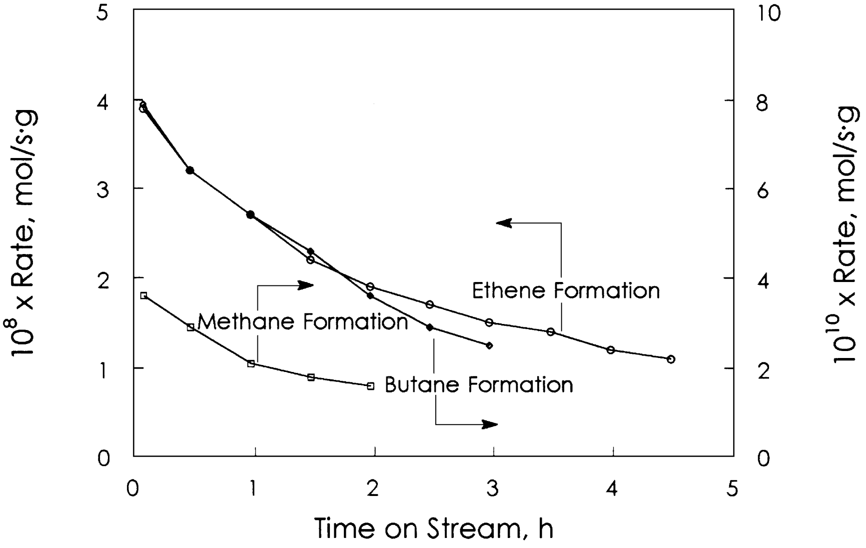

FIG. 10. Rates of ethene, of butane, and of H_2 formation at 450°C in the presence of HZSM-5 zeolite. Feed ethane partial pressure, 0.2 atm; inverse space velocity, 0.28×10^5 (s · g)/mol of ethane.

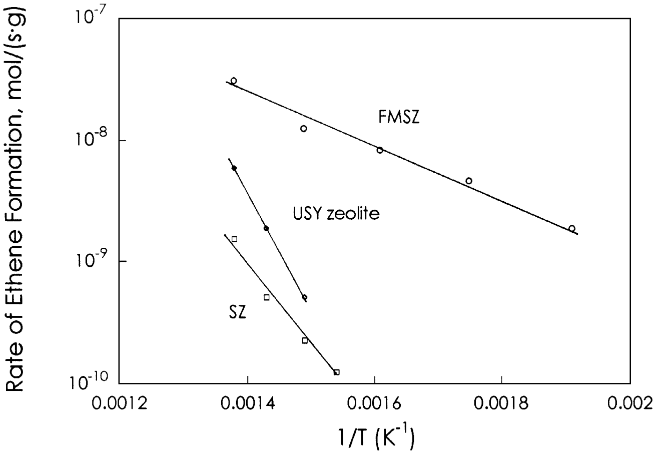

FIG. 11. Arrhenius plot for rate of ethene formation from ethane in the presence of FMSZ, SZ, and USY zeolite. Feed ethane partial pressure, 0.2 atm.

per unit mass of solid at 0.2 atm ethane partial pressure and 450°C decreased in the following order: HZSM-5 $\geq$ FMSZ > USY > SZ. If the rates of ethane conversion are normalized per SO_4^{2-} group (for FMSZ and SZ) or per Al atom (for the zeolites), the activity order becomes FMSZ > HZSM-5 > SZ $\geq$ USY. We emphasize, however, that this latter order does not necessarily correspond to the activity per reactive site, as these sites remain to be identified in the zirconia-based materials.

The rate of the ethane conversion at 500°C and 0.2 atm ethane partial pressure in the presence of HZSM-5 [1.2×10^{-7} mol/(s · g)], estimated on the basis of extrapolation of the Arrhenius plot of Fig. 11, agrees well with the rate observed by Hagen *et al.* [2×10^{-7} mol/(s · g)] (15); the HZSM-5 of Hagen *et al.* had a Si/Al ratio of 15, whereas that of the HZSM-5 reported here was 25.

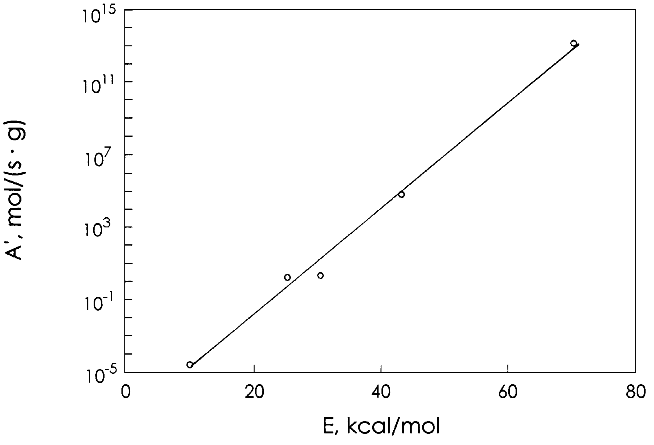

FIG. 12. Compensation effect for conversion of ethane to ethene in the presence of FMSZ (*E*, 10 kcal/mol), SZ (*E*, 31 kcal/mol), HZSM-5 (*E*, 25 kcal/mol), and USY (*E*, 43 kcal/mol) zeolite and conversion to methane (*E*, 71 kcal/mol) in the presence of FMSZ.

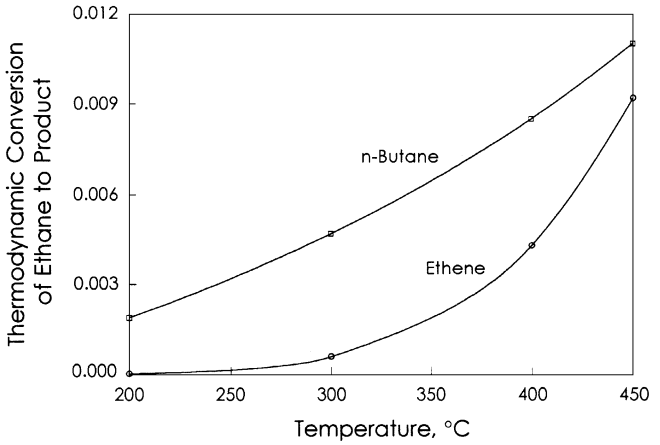

FIG. 13. Thermodynamic limitations of ethane conversion into ethene and *n*-butane (22). The points were calculated from thermochemical data.

The dehydrogenation selectivity (measured at 450°C and an ethane conversion of about 0.001) decreased in the following order: USY > HZSM-5 > SZ > FMSZ (Table 1). Thus, these data provide no evidence to suggest that the promotion of SZ by iron and manganese has any effect on dehydrogenation activity, although iron and manganese have been suggested (3–5) to increase the activity for dehydrogenation of *n*-butane. However, the data of Table 1 show clearly that these promoters increase the overall activity for ethane conversion, as they do for propane conversion (20) and *n*-butane isomerization (2).

Catalytic dehydrogenation of alkanes by metals or metal oxides typically occurs at high temperatures (>500°C), at which these reactions are thermodynamically favorable (23). The mechanisms by which alkanes are dehydrogenated on metal surfaces, typically involving dissociative adsorption of the alkane, are different from the mechanism of dehydrogenation catalyzed by solid acids such as HZSM-5, which involves protonation of the alkane to form a (penta-coordinated) carbonium ion transition state followed by decomposition to give H_2 and carbenium ions (24). In the first hour on stream, almost stoichiometric amounts of H_2 and ethene were observed in the presence of USY zeolite. Thus the products are explained as the result of ethane dehydrogenation occurring via a carbonium ion transition state (20).

At longer times on stream, the amount of H_2 formed was slightly less than that corresponding to stoichiometric dehydrogenation of ethane (Fig. 9), suggesting that there were subsequent reactions of H_2; the data obtained after about an hour on stream indicate amounts of H_2 in the product that were too little to detect.

The selectivity for methane formation from ethane in the presence of USY zeolite was two orders of magnitude less than that for ethene or H_2 formation. Methane could have been formed either by cracking (20) or hydrogenolysis

(14) pathways. Hagen *et al.* (15) suggested that a secondary hydrogenolysis reaction of ethane could take place after H_2 was formed from primary dehydrogenation reactions with HZSM-5 at temperatures >500°C, although the sites for hydrogenolysis were not identified.

Butane was sometimes observed with USY zeolite at 450°C and at ethane conversions >0.003. If the reaction mechanism for the formation of butane were analogous to that in classical carbenium ion chemistry, the primary ethene product (formed by dehydrogenation of ethane) would be expected to react with $C_2H_5^+$ to form $C_4H_9^+$, which would then abstract a hydride to form butane. $C_4H_9^+$ might be expected to be deprotonated to give butene if hydride transfer were slow relative to deprotonation. We emphasize, however, that butene products were not observed.

The product distribution for ethane conversion in the presence of HZSM-5 was similar to that observed for USY zeolite, except that H_2 was never observed with HZSM-5. The lack of H_2 in the product is again consistent with the hypothesis that ethane reacted with H_2 to give methane as secondary product (14). The H_2 formed could also have reacted with coke precursors on the surface, consistent with the lower rate of deactivation observed for HZSM-5 than for the other materials. The selectivity for formation of butane in the presence of HZSM-5 was higher than that in the presence of USY zeolite, but lower than that observed for FMSZ at a given conversion and temperature (Table 1).

In the presence of FMSZ, the products observed were those corresponding to dehydrogenation, cracking (or possibly hydrogenolysis), and oligomerization (possibly from the reaction of ethene with $C_2H_5^+$). The selectivity for butane formation decreased with increasing temperature. In contrast to the behavior observed with HZSM-5 or USY zeolite, the activity of FMSZ at temperatures >400°C first decreased and then increased with time on stream followed by another declining period, suggesting autocatalysis (12). Autocatalysis has been suggested to be an indication of the buildup of chain carriers resulting from decomposition of the carbonium ion $C_2H_7^+$, to give CH_3^+ (with methane) or $C_2H_5^+$ (with H_2), which then presumably act as Lewis acid centers in further reactions with ethane. The suggested occurrence of these secondary reactions (autocatalysis) in the presence of FMSZ, but not the zeolites, thus has been used as a basis for suggesting a very strong acidity of the FMSZ, enough to allow the formation of the primary carbenium ions CH_3^+ and $C_2H_5^+$ as further chain carriers (12).

The molar ratio of H_2 to ethene observed at 0.1 atm ethane partial pressure and 450°C increased during ethane conversion in the presence of FMSZ from 0 after 1 h on stream to 1.8 after 10 h on stream, and then decreased gradually, indicating that formation of H_2 and ethene involved complicated pathways and was not a simple stoichiometric dehydrogenation proceeding via a carbonium ion transition state. H_2 might have been involved in secondary hydrogen transfer or secondary hydrogenolysis reactions.

The observed reaction orders in ethane for formation of ethene (0.7) and of methane (1.3) also suggest that cracking and dehydrogenation reactions via carbonium ion transition states were not the only pathways occurring during ethane conversion with FMSZ. The data are not sufficient to determine the chemistry, but they are consistent with the suggestion that the presumed carbonium ion transition states collapsed into H_2 and $C_2H_5^+$ or methane and CH_3^+, with $C_2H_5^+$ then either undergoing secondary reaction with ethane (or ethene) to form heavier hydrocarbons and coke or losing a proton to form ethene, and with CH_3^+ undergoing hydride transfer with ethane to give methane. If the rates of methane and ethene formation were accounted for by carbonium ion reactions only, the reaction orders in ethane for each of these two reactions would be expected to be 1. Presumably, because there were additional pathways that favored the formation of methane and disfavored the formation of ethene at higher ethane partial pressures, the observed reaction order in ethane for methane formation rate became >1, whereas the reaction order in ethane for ethene formation rate became <1.

We emphasize that the suggested occurrence of carbonium ion reactions is based only on the product distribution and kinetics data and that this basis is not sufficient to establish firmly the occurrence of such reactions. The observations made at the higher temperatures do not exclude the possibility of reactions proceeding by classical carbenium ion chemistry (which does not involve protonation of ethane); oligomerization involving reactions of carbenium ions with alkenes would account for the C−C bond-forming reactions.

The apparent activation energies for dehydrogenation and for cracking reactions in the presence of FMSZ differ by a factor of 7, in contrast to recent theoretical calculations representing ethane conversion in the presence of HZSM-5, which led to the prediction that the two reactions should have about the same activation energy (25). According to the theory (25), the reactions are concerted and proceed through adsorbed carbonium ion transition states; the reactions are simply first order, but the reaction orders determined in this work are different from unity and are consistent with the occurrence of significant secondary reactions at conversions as low as a fraction of a percent. The apparent activation energy for ethane conversion to ethene in the presence of HZSM-5, determined in the temperature range 400–450°C (25 kcal/mol), is much lower than the theoretical prediction (64 kcal/mol) (25). The observed apparent activation energy observed with USY zeolite (43 kcal/mol) is closer to the theoretical value, and, correspondingly, the dehydrogenation reaction of ethane is postulated to be more nearly a simple reaction with this zeolite than with HZSM-5. We suggest that both further experimental work and further theoretical work are needed to reconcile the differences and that USY zeolite may be the better choice of solid acid for a comparison of experimental results with theoretical predictions.

SZ also converted ethane into H_2 and ethene, with a minor occurrence of cracking (or hydrogenolysis); the rates of H_2 and of ethene formation as a function of time on stream in the presence of SZ were nearly the same as those observed in the presence of FMSZ. Behavior suggestive of autocatalysis was observed for SZ, although the rate of ethene formation was about four times lower than that observed with USY zeolite. No butane was formed in the presence of SZ under any of the experimental conditions, possibly because the conversion of ethane might have been too low (<0.002).

Low-Temperature (200–300°C) Conversion of Ethane

Ethane was converted in the presence of FMSZ at temperatures <300°C, but it was not converted in the presence of the other solid acids. This comparison suggests that the other materials may be less strongly acidic than FMSZ. The observed gas-phase products were methane, ethene, and butane, which are the same as those observed at temperatures >300°C (H_2 was observed at the higher temperatures but not at the lower temperatures). If the acid strength of FMSZ were comparable to that of HZSM-5 or that of USY zeolite, then the zeolites would also be expected to be active in converting ethane into these products in the temperature range 200–300°C. However, the zeolites were not found to be active for ethane conversion at temperatures <300°C; therefore, although it is not established that the essential difference between FMSZ and the other catalysts has to do with the acid strength, the data suggest that there are significant differences between it and the other solid acids.

Because the products observed during ethane conversion in the presence of FMSZ at the lower temperatures are consistent with those observed in superacidic solutions, we hypothesize that the chemistry occurring with FMSZ at temperatures <300°C may be analogous to that observed in superacidic solutions (13). However, comparisons of the reactions of ethane in the presence of the solid and liquid acids can be no more than qualitative because of the different reaction conditions and the lack of quantitative data for the solution reactions; the temperature of the solution reaction was −78°C, whereas that of the reaction with FMSZ was 200°C. The initial molar ratio of cracking to dehydrogenation products in ethane conversion in superacidic solutions was roughly 10 (as shown by the ratio of methane to H_2) (13). In contrast, this ratio was only 0.1 when ethane reacted in the presence of FMSZ (as estimated on the basis of the ratio of methane to ethene).

If the ethane conversion chemistry observed in the presence of FMSZ were analogous to that in superacidic solutions, the transition states for dehydrogenation and cracking reactions would presumably be adsorbed carbonium ions, which can be formed by protonation of C−H and C−C bonds in ethane. This initiation step is also hypothesized to occur in the reaction of ethane with other solid acids at temperatures >300°C. In superacidic solutions, ethane is protonated to form a free carbonium ion, $C_2H_7^+$, which collapses to give either H_2 and $C_2H_5^+$ or methane and CH_3^+; $C_2H_5^+$ would be deprotonated to give ethene. Oligocondensation to give *n*-butane is expected to proceed as ethane combines with adsorbed $C_2H_5^+$ to form $C_4H_{11}^+$, which is then deprotonated to give butane. This oligocondensation step differs from the oligomerization step proposed to take place at temperatures >300°C, whereby the former involves reaction of $C_2H_5^+$ with ethane, and the latter involves reaction of $C_2H_5^+$ with ethene.

If the reaction in the presence of FMSZ proceeded by mechanisms analogous to those prevailing in liquid superacids, H_2 would be expected as a product in addition to methane, ethene, and butane. However, H_2 was not observed in the gas-phase products at temperatures <300°C, possibly because of secondary reactions.

It is important to point out that we do not rule out the possibility that classical carbenium ion chemistry also occurred in this temperature range and contributed to the products observed in the gas phase. Whenever alkenes are formed, they are readily protonated and lead to classical carbenium ion reactions.

CONCLUSIONS

Each of the four solid acids, SZ, FMSZ, HZSM-5, and USY zeolite, was found to be active for conversion of ethane at temperatures >450°C, but the product distributions varied from one material to another. Catalysis was demonstrated for ethane conversion in the presence of FMSZ only at 450°C and 0.2 atm ethane partial pressure, but not for the other acids. SZ converted ethane into ethene, H_2, and small amounts of methane in the temperature range 300–450°C. Under the same conditions, USY zeolite converted ethane into ethene and H_2, with traces of butane and methane, whereas HZSM-5 converted ethane into ethene, butane, and methane. FMSZ was the only material that converted ethane at temperature as low as 200°C; the products were ethene, butane, and methane, and at temperatures >300°C, H_2. The observation of approximately equal rates of formation of ethene and of H_2 at conversions <0.003 in the presence of USY zeolite suggests that the dehydrogenation of ethane proceeded via a carbonium ion transition state. Formation of butane from ethane at temperatures >400°C in the presence of FMSZ, HZSM-5, or USY zeolite is consistent with the hypothesis that oligomerization of ethene takes place as a secondary reaction. However, if the chemistry of formation of butane at lower temperatures in the presence of FMSZ were analogous to the chemistry in superacidic solutions, butane might also have been formed by oligocondensation of ethane. Evidence of autocatalysis was observed, but only with the sulfated zirconia-supported materials, suggesting that reactions of ethane in the presence of SZ and FMSZ could be different from reactions of ethane in the presence of the zeolites. The reactivities are consistent with chemistry analogous to that occurring in superacidic solutions and with the suggestion that FMSZ is a stronger acid than the others investigated here.

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