H–D exchange between CD_4 and solid acids: $AlCl_3$/sulfonic acid resin, promoted and unpromoted sulfated zirconia, and zeolite HZSM-5

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The H–D exchange reaction between CD_4 and each of a family of solid acids (the zeolite HZSM-5, sulfated zirconia, iron- and manganese-promoted sulfated zirconia, and $AlCl_3$/sulfonic acid resin) was investigated with a batch recirculation flow reactor; the data determine initial rates of the exchange reaction giving CD_3H at temperatures ranging from 440 K for $AlCl_3$/sulfonic acid resin to 688 and 703 K for the zeolite and promoted sulfated zirconia, respectively. Extrapolated results show that the reaction is three orders of magnitude faster with the $AlCl_3$/sulfonated resin (an analogue of the very strongly acidic combination of $AlCl_3$ and H_2SO_4) than with HZSM-5 or promoted sulfated zirconia and two orders of magnitude faster with the latter than with sulfated zirconia.

KEY WORDS: H–D exchange; methane; solid acids; zeolite HZSM-5; sulfated zirconia; aluminum chloride/sulfonic acid resin; iron- and manganese-promoted sulfated zirconia

1. Introduction

The H–D exchange between methane and solid acid catalysts is one of the simplest test reactions for characterization of the reactivities of these catalysts; the mechanism of this reaction involving the zeolite HZSM-5 and CD_4 is well understood, with experimental and theoretical values being in good agreement with each other [1–4]. We report rates of this test reaction providing a comparison of the reactivities of solid acids having a wide range of acid strengths and catalytic activities for alkane conversion, namely, (a) sulfated zirconia (SZ), (b) iron- and manganese-promoted sulfated zirconia (FMSZ), (c) $AlCl_3$ supported on sulfonic acid resin (an analogue of the very strongly acidic combination of $AlCl_3$ and H_2SO_4), and (d) HZSM-5.

2. Experimental

2.1. Preparation of solid acids

The solid acids investigated in the H–D exchange reaction with CD_4 were prepared as follows:

HZSM-5 (Davison Division of W.R. Grace and Co.) with a Si/Al atomic ratio of 14 and a surface area of 339 m^2/g, as reported by the supplier, was calcined *in situ* at 550 °C in 20% O_2 in dry N_2 for 1.5 h.

SZ containing 1.8 wt% S was prepared from sulfated zirconium hydroxide (Magnesium Elektron) which was calcined in stagnant air at 650 °C for 3 h and activated *in situ* in flowing dry N_2 at 450 °C for 1.5 h [5].

FMSZ was made by incipient wetness co-impregnation of sulfated zirconium hydroxide (Magnesium Elektron) with an aqueous solution of iron and manganese nitrates (Aldrich, 98+% $Fe(NO_3)_3\cdot 9H_2O$ and 98% $Mn(NO_3)_3\cdot 6H_2O$). Dropwise addition of 12 ml of a 0.693 M iron nitrate and 0.236 M manganese nitrate solution to 38.95 g of dried (120 °C, 24 h) sulfated zirconium hydroxide took place over approximately 3 h with continuous mixing with a mortar and pestle. An additional 1.6 ml of deionized water in 0.5 ml aliquots was used to rinse the iron–manganese solution quantitatively into the sulfated zirconium hydroxide. The final amount of liquid was determined by the point of incipient wetness, indicated when a few taps with a pestle formed a sheen on the surface of the paste. The resultant solid was dried at 120 °C for 24 h and calcined in stagnant air by heating at 5 °C/min to 650 °C and holding at 650 °C for 3 h. The FMSZ, containing about 1.5 wt% Fe, 0.5 wt% Mn, and 1.8 wt% S, was activated *in situ* in flowing dry N_2 at 450 °C for 1.5 h.

$AlCl_3$/sulfonic acid resin was prepared from the macroporous sulfonic acid ion-exchange resin Amberlyst 15 (Rohm and Haas, 0.1–2.0 mm beads), which was first dried by evacuation at 106 °C for 5 days [6]. A 1 inch diameter Pyrex synthesis reactor was loaded under N_2 in a dry box with 10.1 g of the dried Amberlyst 15 followed by a 1.5 inch long plug of glass wool and then 16.5 g of $AlCl_3$ (Anhydrous, Fisher Certified, 99.7+%). The tube was heated to 108 °C around the region containing $AlCl_3$ and to 114 °C around the region containing Amberlyst 15. A flow of dry N_2 at 10 ml/min passed through the reactor, entering through the end containing the $AlCl_3$ and carrying it as vapor over and into the beads of Amberlyst 15 for 14 days [6]. The Al content of the resultant solid was found by atomic absorption spectroscopy to be 3.8 wt%. Loading of the synthesis reactor, storage of the resin-supported $AlCl_3$, and transfer to the H–D exchange

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reactor were all carried out in a N_2-filled drybox. The drybox atmosphere was circulated through traps to remove O_2 and H_2O. Typical O_2 and H_2O concentrations were <1 ppm.

2.2. Measurement of rates of H–D exchange to give CD_3H from CD_4

In each H–D exchange reaction experiment, the reactor was loaded with about 2.7×10^{-5} mol of CD_4 (30 Torr) (Cambridge Isotope Laboratory, deuterium isotopic purity 99%), mixed with N_2 (540 Torr) (Puritan Bennett, 99.997%, dried by passage through a bed of zeolite 4A particles and deoxygenated by flow through a bed of supported Cu particles) and brought into contact with about 0.5 g of particles of each of the solid acids in a stainless-steel recirculating batch reactor having a total volume of 19 ml. The gases were mixed in a manifold at room temperature and then released into the reactor and circulated with a stainless-steel bellows pump through a 0.25 inch diameter tube containing the solid acid. The reactant mixture was continuously leaked into a mass spectrometer through a 1/16 inch diameter, 4 inch long evacuated stainless-steel tube, the end of which was constricted and positioned in the reactant gas stream. The leak rate corresponded to a pressure loss in the reactor of <5 Torr/h.

A UTI model 100C quadrupole mass spectrometer incorporated in a catalyst testing and evaluation system (Advanced Scientific Designs, Inc., RXM-100) was used in the SIM mode to monitor the $m/e = 28$, 20, 19, 18, 17, and 16 signals. The mass spectrometer signals were normalized to the $m/e = 28$ signal. The $m/e = 20$ signal was assigned to CD_4 and the $m/e = 19$ signal to CD_3H. To limit changes in the degree of ionization of the product gases resulting from changes in pressure in the mass spectrometer or large changes in composition of the gases in the mass spectrometer, the pressure in the mass spectrometer was increased from the background of 10^{-9} Torr up to 2×10^{-5} Torr with a leak of helium.

The mass spectrometer was calibrated by measuring the signals of $m/e = 28$ and 20, when the reactor was loaded with mixtures of CD_4 and N_2 at a total pressure of 570 Torr and CD_4 partial pressures from 0.08 to 30 Torr. A plot of the $m/e = 20$ signal vs. the CD_4 concentration was linear (least-squares $R^2 = 0.998$). The linear calibration for CD_4 was used for the measurement of CD_3H. The difference in ionization cross sections of CD_4 and CD_3H is expected to have caused a small (<3%) systematic overestimation in the concentration of CD_3H, but this is regarded as insignificant [7].

The FMSZ, SZ, and HZSM-5 samples were treated *in situ* as stated above, and the reactor was cooled to the reaction temperature and then evacuated prior to introduction of the CD_4/N_2 mixture. The $AlCl_3$/sulfonic acid resin was sealed in the reactor under N_2 in the dry box, and the reactor was placed into a preheated, temperature-controlled furnace and evacuated prior to introduction of the CD_4/N_2 mixture. The evacuation time was kept to a minimum, typically <5 min. The reaction temperature was measured with a stainless-steel-clad thermocouple in the bed of solid acid particles, and the oven temperature was controlled with a signal from a thermocouple external to the reactor. After introduction of the reaction mixture into the reactor, a period of 5−10 min as required for the reactor temperature to stabilize.

The $m/e = 18$, 17, and 16 signals representing the products obtained with the SZ, FMSZ, and HZSM-5 samples were not used for quantification of further reaction because they represented combinations of water and CD_2H_2, CDH_3, and CH_4. Some of the water adsorbed during storage on the SZ and FMSZ samples (which were activated by heating in dry N_2) was removed during activation; however, some water remained and was necessary for high reactivity [8,9].

In the reaction experiments, data were collected for 5–30 min after the temperature had stabilized, for conversions up to 10%, except for the experiment with FMSZ at 430 °C, in which a higher conversion was measured.

3. Results

3.1. Conversions in the H–D exchange reaction

Typical plots of concentration of CD_3H resulting from the exchange reaction vs. time were approximately linear, as exemplified by the data for HZSM-5 (figure 1); the rate of the exchange reaction was determined as the slope of the best least-squares linear fit of the concentration vs. time data. The one exception to this pattern was the data obtained for FMSZ at 430 °C, which gave a plot with significant curvature (figure 2). The high-conversion data show that the CD_3H concentration reached a maximum when the rate of formation of CD_3H from CD_4 was roughly equal to the rate of conversion of CD_3H to form CD_2H_2. To estimate the initial rate from these data, the derivative of the least-squares optimized fit of the CD_4 concentration vs. time data was evaluated at the initial CD_4 concentration; the fit ($R^2 = 0.995$) is obscured by the data points.

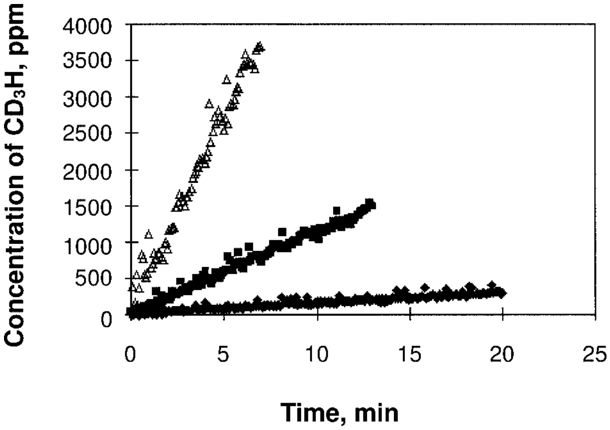

Figure 1. Conversion of CD_4 and HZSM-5 to give CD_3H. Conditions: reactant partial pressure 30 Torr of CD_4 in 540 Torr of N_2, 0.5 g of HZSM-5. Reaction temperature: (◆) 304, (■) 362, and (△) 415 °C.

The rate data are summarized in the Arrhenius plot of figure 3. Repeat measurements of the H–D exchange rate were made for HZSM-5 at 308 and 360 °C and for FMSZ at 355 °C; the data indicate standard deviations in these rates of 13, 20, and 0.5%, respectively.

In each experiment, a 10% conversion of the CD_4 would have exchanged about 3×10^{-6} mol of D atoms onto the surface. The numbers of acid sites able to participate in the H–D reaction on SZ and FMSZ are not known well. An estimate of the number of strong acid sites based on ammonia adsorption data is 7×10^{-5} mol/g or roughly one per sulfur atom in SZ and FMSZ [10]. The number of acid sites is assumed to be the same as the number of aluminum atoms in HZSM-5, about 4×10^{-4} mol/g. The $AlCl_3$/sulfonic acid resin contains of the order of 10^{-3} mol of Brønsted acid sites/g [6]. On the basis of these estimates, we infer that at the highest CD_4 conversion of 50% (which was reached only during the measurement at 430 °C with FMSZ), roughly 25% of the strong surface Brønsted acid sites would have been deuterated; in all of the other measurements of reaction with zirconia-containing samples, less than about 10% of these sites would have been deuterated. In all the measurements of reaction with HZSM-5 and the $AlCl_3$/sulfonic acid resin, less than 2% of the acidic sites would have been deuterated.

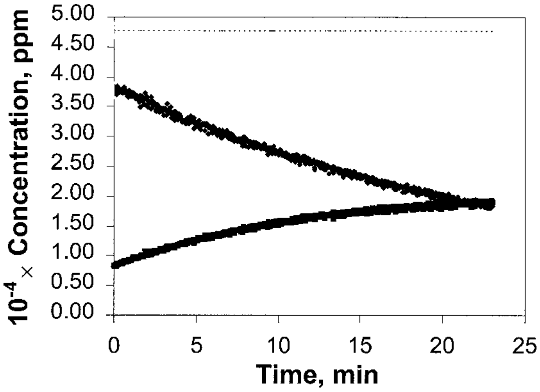

Figure 2. Conversion of CD_4 into CD_3H in the presence of FMSZ. Conditions: 30 Torr of CD_4, 540 Torr of N_2, 0.5 g of FMSZ, 430 °C. (♦) (upper curve) CD_4, (■) (lower curve) CD_3H; the dotted line represents the initial concentration of CD_4.

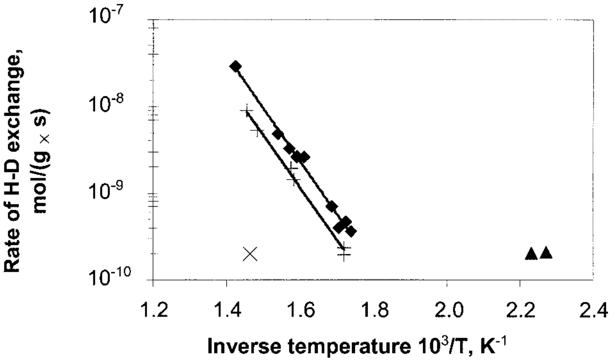

Figure 3. Reactivities of solid acids for H–D exchange with CD_4. Conditions: 30 Torr of CD_4, 540 Torr of N_2, 0.5 g of solid acid. (×) SZ, (+) HSZM-5, (♦) FMSZ, and (▲) $AlCl_3$/sulfonic acid resin.

3.2. Rate data

The rates that could be measured were bounded at the lower end by a detection limit of the apparatus of about 2×10^{-10} mol/(g min) and the upper end by the stability limitations of the solid acids. The rate data representing FMSZ and HZSM-5 gave good straight-line Arrhenius plots, allowing the calculation of apparent activation energies for the exchange reaction (figure 3). R^2 values of 0.989 and 0.996 were found for FMSZ and HZSM-5, respectively. The apparent activation energies and preexponential factors are summarized in table 1.

Data characterizing the $AlCl_3$/sulfonic acid resin were obtained only at relatively low temperatures, with the upper temperature determined by the stability limit of the resin, which begins to desulfonate at 150 °C [11]. The lower reactivities of the other solid acids limited the measurability of rates to much higher temperatures (about 300 °C) than those applicable to the resin; the reactivity of SZ was so low that measurements could be made only at a single temperature (figure 3).

The rate measured for FMSZ at 410 °C was 1.5×10^{-8} mol/(g s), nearly the same as that characterizing HZSM-5 and two orders of magnitude greater than that characterizing SZ. The value for $AlCl_3$/sulfonic acid resin at 160 °C is 2×10^{-10} mol/(g s) at a temperature 120 °C lower than the lower limit of measurable reactivity of either FMSZ or HZSM-5. We extrapolated the data for FMSZ and HZSM-5 to 160 °C by using the Arrhenius plots of figure 3, finding the $AlCl_3$/sulfonic acid resin to be three orders

Table 1

Apparent activation energies and pre-exponential factors for H–D exchange of CD_4 with solid acids.

Solid acid	Apparent activation energy (kJ/mol)	Pre-exponential factor (mol/(g s))	CD_4 pressure (Torr)	Temperature range (K)	Ref.
HZSM-5, Si : Al = 14	115 ± 15	4.4	30	581–688	This work
FMSZ	116 ± 14	12	30	593–703	This work
ZSM-5, Si : Al = 13	103[a]	–	13	620–750	Kramer et al. [1]

[a] Calculated from data presented in the cited publication.

of magnitude more reactive than either FMSZ or HZSM-5 and SZ two orders of magnitude less reactive than FMSZ or HZSM-5.

4. Discussion

4.1. Comparison with literature results for HZSM-5

The H–D exchange rates observed for CD_4 and HZSM-5 can be compared with the experimental observations and theoretical predictions of Kramer et al. [1,2], who measured the decline in the infrared absorption associated with the O–H groups in HZSM-5 (with a Si : Al atomic ratio of 13) in the presence of CD_4 at about 410 °C and 13 Torr. The comparable rate measured in this work is about four times greater than that reported by Kramer et al. [1,2] at the same temperature but at a different CD_4 partial pressure. For a better comparison of the rates of exchange with the two different zeolite samples, we estimated the rates of exchange per Al site and corrected for CD_4 partial pressure by assuming a first-order reaction in CD_4 [2]. Adjustment of the rates reported by Kramer et al. results in values of 0.6×10^{-5} mol/(mol-Al s) and 0.8×10^{-5} mol/(mol-Al s) for their rate measured for HZSM-5 and for their theoretical rate calculated for HZSM-5, respectively [1]. The comparable exchange rate for our HZSM-5 sample at 410 °C is 0.8×10^{-5} mol/(mol-Al s). The agreement is good.

4.2. H–D exchange as a test reaction

Rezgui et al. [12] found methane to be unreactive in the presence of SZ at 450 °C, but in the presence of FMSZ it reacted to give ethane, ethylene, and acetylene, with the maximum reaction rate after an induction period at 450 °C and a pressure of 152 Torr being 1.4×10^{-9} mol/(g s), about two orders of magnitude less than that of the H–D exchange reaction (estimated from the Arrhenius dependence and assuming a first-order dependence on methane partial pressure). Thus, the H–D exchange reaction proceeds nearly in the absence of side reactions in the presence of these solid acids and provides a good basis for comparison of their reactivities.

Furthermore, the data show that the H–D exchange reaction proceeded without an induction period. Consequently, we infer that the initial reaction rates reported here characterize reaction between CD_4 and the clean solid acids. Consistent with this inference, the conversion vs. time plots for the initial periods were linear, indicating nearly constant initial rates. In contrast, data representing isomerization and disproportionation of alkanes catalyzed by SZ and FMSZ indicate induction periods suggesting that catalytic sites were formed from the reactants. This suggestion is consistent with data [12] showing slow conversion of methane (into ethane with traces of unsaturated products, ethylene and acetylene) in the presence of FMSZ, increasing with time on stream. The ethylene and/or acetylene might have been precursors of carbonaceous deposits incorporating catalytic sites.

4.3. Comparison of reactivities of solid acids for H–D exchange

It is tempting to seek a relationship between the acidities of the solid acids and the rates of their reactions with CD_4. At least roughly, there appears to be such a relationship for HZSM-5, FMSZ, and the $AlCl_3$/sulfonic acid resin; measurements of acid strengths of FMSZ by proton NMR and infrared spectra characterizing the adsorption of acetonitrile [13] indicate that it is similar in acid strength to zeolites. The $AlCl_3$/sulfonic acid resin, being analogous to a combination of $AlCl_3$ and sulfuric acid, is evidently a much stronger proton donor, one that has been compared with superacids [6,14]. Thus, the two solid acids with similar strengths indicated by the base probe molecules are similar in reactivity for the H–D exchange reaction and much less reactive than the much more strongly acidic resin. The indication that FMSZ does not have a very strong acidity weighs against the suggestion that it might have a minority of extremely strong acid sites, such as might be required for it to protonate an alkane [15].

According to the model of Kramer et al. [4], the H–D exchange reaction of CD_4 in HZSM-5 takes place at a Brønsted acid site associated with an aluminum center in the zeolite framework, which was modeled as the fragment (cluster) $H_3SiO(H)Al(OH)_2OSiH_3$. Kramer et al. [1,2] assumed a random distribution of Al over the twelve possible sites in the HZSM-5 framework. The mechanism of the reaction between the zeolite and CD_4 is represented as a concerted exchange involving transfer of a proton from a surface Brønsted acid site to CD_4 with the transfer of a deuteron from the CD_4 to a surface basic site. This mechanism does not involve an intermediate resembling a carbonium ion; the calculated intermediate was found to be more covalently than ionically bonded to the surface. Relaxation of the CD_4 molecule is energetically significant, and the important parameter representing the acidity of the surface was not the absolute acidity of a single Brønsted acid site, but rather the difference in acidity between an OH group and a neighboring basic oxygen atom, both of which participate in the reaction.

Recognizing that the apparent activation energies for the H–D exchange reaction are approximately the same for HZSM-5 and FMSZ (table 1, figure 2), we might speculate that the mechanisms are similar (concerted) for these two solid acids. Thus, the suggested redox role of Fe and Mn in alkane isomerization, giving alkenes [16,17], may not be important for the H–D exchange reaction.

The low reactivity of SZ relative to that of FMSZ remains to be explained. We might speculate that the concerted mechanism inferred for HZSM-5 and suggested for FMSZ may not be shared by SZ.

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