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Hydrogen/Deuterium Exchange Kinetics by a Silica-Supported Zirconium Hydride Catalyst: Evidence for a σ-Bond Metathesis Mechanism

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Silica-supported molecular zirconium hydride species have been the subject of numerous investigations and have been identified as highly active olefin polymerization catalysts. Recently it has been shown that these materials catalyze hydrogenolysis of paraffins by activating carbon−hydrogen bonds under relatively mild conditions. Uncertainties regarding the nature of the hydrocarbon activation mechanism led us to study several H/D exchange processes. The rate and temperature dependence of H/D exchange between H_2 and D_2 and between CH_4 and D_2 was determined utilizing a glass recycle reactor in which reactants and products were repeatedly passed over the catalyst. A sequential, single-atom exchange process was observed for both exchange processes. More specifically, H_2/D_2 exchange to an equilibrium distribution was instantaneous even at liquid nitrogen temperatures. We estimate the upper bound for the activation energy to be about 2 kcal/mol. Moreover, the exchange kinetics between CH_4 and D_2 are characterized by a large negative entropy of activation (−27 ± 3 eu) and relatively low energy of activation (∼7 ± 1 kcal/mol), consistent with a σ-bond metathesis pathway.

Introduction

The development of heterogeneous analogs to organometallic catalysts is of ongoing interest. The desire is to develop catalysts that preserve (or even enhance) the activity and selectivity of homogeneous catalysts while adding the benefits of improved stability and ease of process control of heterogeneous catalysts. For example, organometallic catalysts anchored on solid supports are expected to have longer lifetimes because bimolecular decomposition reactions are eliminated and to be much more readily separable from product streams.

Tetra-alkyl zirconium complexes anchored on refractory metal oxide supports have received considerable attention.[1−5] In the hydride form, these materials are active catalysts for olefin polymerization,[2,3] hydrogenation,[4] and isomerization.[4] Recently, a number of studies on *well-defined* surface Ti, Zr, Hf, and Ta anchored alkyl and hydride species have been reported by Basset and co-workers.[5] The reactivity of these catalysts with paraffins has been described, including C−H activation, C−C activation, hydroisomerization, and hydrogenolysis.[5] The reactions of paraffins with these catalysts, to undergo either C−H or C−C bond activation, is assumed to proceed by a σ-bond metathesis mechanism.[5] To gain a greater understanding of the nature of these catalysts and obtain mechanistic information regarding the activation mechanism, we examine here the detailed kinetics of several H/D exchange reactions with silica-supported zirconium hydride species. Qualitative information on related H/D exchange reactions have been previously reported for this catalyst system;[6] herein we report on the rate and temperature dependence of these reactions and determine the associated kinetic parameters.

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Experimental Section

All manipulations were performed under an inert atmosphere of nitrogen or argon using either standard Schlenk techniques or a Vacuum Atmospheres glovebox. Dry, oxygen-free solvents were employed throughout. Elemental analyses were performed by Quantitative Technologies Inc. Tetraneopentylzirconium was prepared according to literature preparations.[7] Davison 62 silica gel with a surface area of 280 m^2/g was purchased from Aldrich Chemical Co. and partially dehydroxylated at 500 °C under vacuum prior to use. Preparation of the supported neopentyl catalyst was carried out in a similar manner, as reported by Collette and co-workers,[3i] with the exception that hexanes was used as the solvent. Typically, the supported neopentyl catalyst was washed several times with hexanes, in order to remove any residual tetraneopentylzirconium, and dried on a high-vacuum line (10^{-6} Torr) prior to hydrogenation. Hydrogenation (1000 Torr of H_2) was typically carried out on ~100 mg samples at 100 °C for 1 h. The hydrogenation was conducted, and monitored by gas chromotagraphy, in situ and the resultant catalyst used immediately.

Kinetic experiments were conducted in a glass recycle reactor in which reactants and products are repeatedly passed over the catalyst with a circulation time of about 0.5 min. The total loop volume was 157 cm^3, and 100 mg of catalyst at 1% Zr loading was used. The initial reactant charge was 40 kPa of CH_4 and 80 kPa of D_2. Thus, to achieve an equilibrium distribution of hydrogens, more than 1000 turnovers is required. Experimental conditions were selected to ensure that the conversion per pass over the catalyst was lower than 10%. Thus, the reactor has the properties of a fully mixed batch reactor. Doubling the circulation rate had no effect on the observed kinetics. The characteristic reaction time was found to scale inversely with the amount of the catalyst. Reactant and product concentrations were determined with a mass spectrometer by monitoring 12 masses with a sampling period of about 2000 ms. The overall time resolution is better than 0.1 min. Species concentrations were determined by adjusting the mass traces for the fragmentation patterns of each of the isotopic species. Total concentrations of methane and hydrogen are confirmed periodically during each run by GC analysis.

Results and Discussion

Two synthetic approaches have been utilized to prepare these supported zirconia catalysts: solution impregnation and sublimation.[1−5] In both approaches molecular tetraalkyl complexes of the general formula MR_4 (M = Ti, Zr, Hf; R = alkyl, allyl, benzyl) are contacted with a partially dehydroxylated silica surface prepared by thermal pretreatment. For our work, we synthesized anchored zirconium neopentyl and neophyl species by the solution impregnation route. The IR and NMR spectra of the complexes we prepared were similar to the spectra reported for materials obtained by sublimation techniques.[5] Titration experiments in which the surface-anchored Zr−neophyl species were treated with excess methanol produced 2.7 ± 0.2 *tert*-butylbenzenes per Zr. This is close to the mono(siloxy)/tris(neophyl) stoichiometry expected. Hydrogenation of the neopentyl or neophyl material (100 °C, 1 h) afforded the desired zirconium hydride material. The spectrum of our hydride was similar to that previously reported.[5] Titration experiments on the hydride material produced 1.0 ± 0.1 hydrogen per Zr, consistent with a tris(siloxy)/mono(hydrido) structure (eq 1). Thus, the structures of the supported zirconium materials are consistent with recent reports.[5]

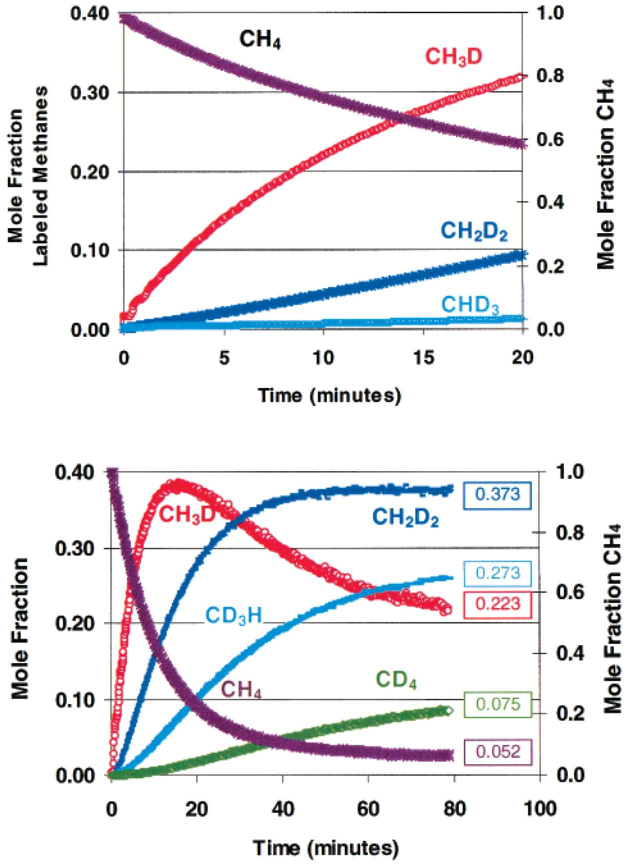

Figure 1. (A, top) Mole fraction of methanes vs time for exchange at 50 °C: initial CH_4 pressure, 40.5 kPa; initial D_2 pressure, 77.9 kPa. (B, bottom) Mole fraction of methanes vs time for exchange at 100 °C: initial CH_4 pressure, 54.0 kPa; initial D_2 pressure, 118.4 kPa. The labels at the right-hand side of the figure indicate the mole fraction expected at equilibrium for the relative H and D concentrations used in this experiment.

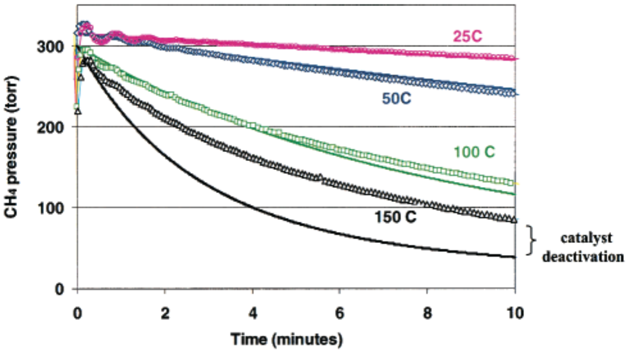

Figure 2. Pressure of unlabeled methane vs time at several temperatures: (symbols) experimental data; (solid lines) calculated rates.

Initial kinetic measurements focused on the deuterium/hydrogen exchange. An equimolar mixture of H_2 and D_2 was circulated over the catalyst at room temperature. An "instantaneous" conversion to an equilibrium distribution (1:2:1 H_2:HD:D_2 ratio) was observed. Even at liquid-nitrogen temperatures we found that the exchange was too fast for us to measure with our tech-

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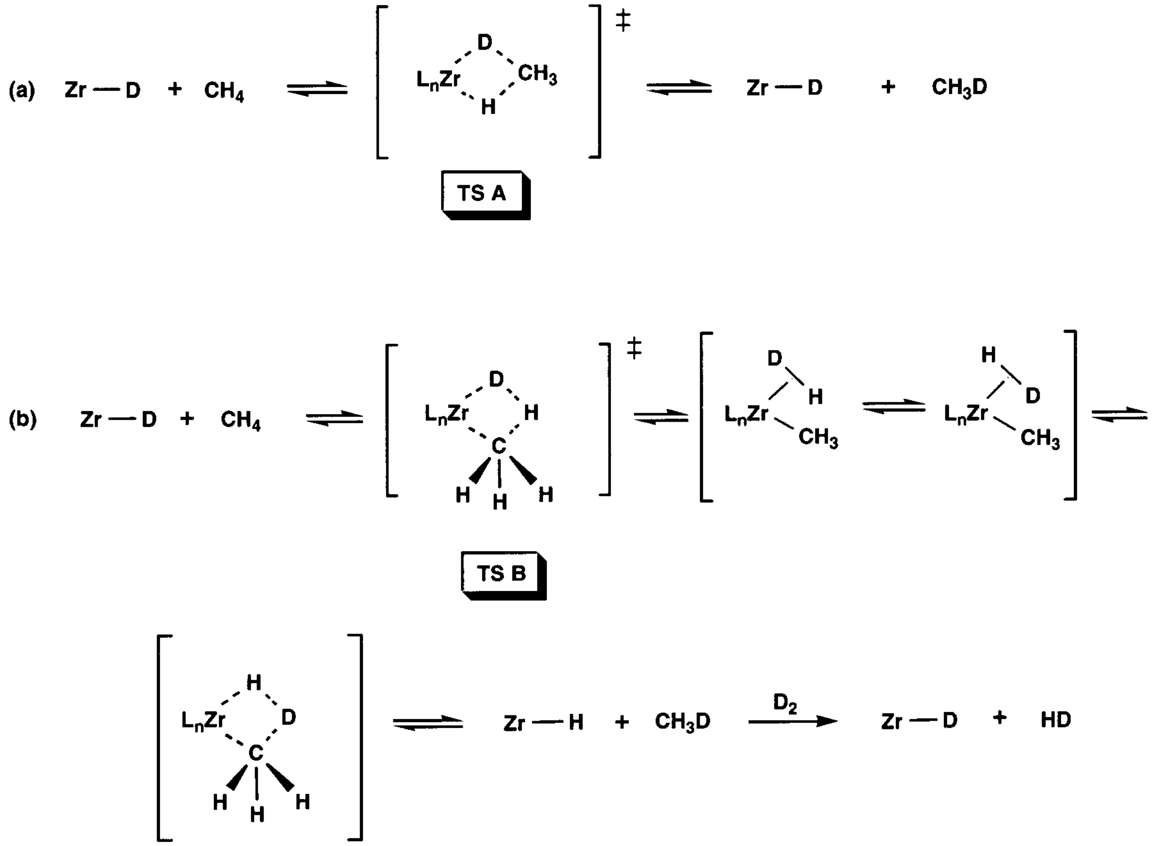
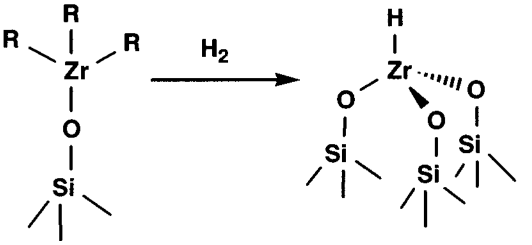


Figure 3. Transition states/reaction pathways for paraffins.



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nique. This indicates that there is an extremely small energy of activation for this exchange process. We estimate the upper bound for the activation energy to be about 2 kcal/mol.[8]

We next investigated the exchange kinetics between methane and deuterium. Deuterium and CH_4 were mixed in a 2:1 ratio and allowed to react with the catalyst. We observed that the H/D exchange rate was slow at room temperature but occurred readily at elevated temperatures. Data from experiments performed at 50 and 100 °C are shown in Figure 1. At early times, CH_3D is the exclusive product. Multiply labeled methanes appear only after CH_3D builds up. The data are well represented by a kinetic model involving multiple, single-atom exchange reactions between CH_xD_y and MD(H). (solid lines in Figure 2). The model is described in more detail below.

The methane/hydrogen isotope exchange was measured at a variety of temperatures. The decline of CH_4 as a function of time at each temperature is shown in Figure 2 (the appearance of the labeled products was also measured but is not shown here). The time dependence for all species can be fit to a simple reaction network model. In this model, we assume two reaction pathways shown in eqs 2 and eq 3. Each pathway can occur in either the forward or reverse direction.

$$\mathrm{R{-}H + M{-}D} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{R{-}D + M{-}H} \tag{2}$$

$$\mathrm{R} = \mathrm{CH_3, CH_2D, CHD_2, CD_3}$$

$$\mathrm{H{-}H + M{-}D} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{H{-}D + M{-}H}\ (\text{similar for } \mathrm{D_2}) \tag{3}$$

To a first approximation, we take the kinetic isotope effect to be small so that the forward and reverse rate constants are the same (e.g., $k_1 \approx k_{-1}$ in eq 2).[9] As noted above, the metal-catalyzed exchange between H_2 and D_2 is very fast compared to methane/hydrogen exchange. This indicates that $k_2 \gg k_1$. We arbitrarily take $k_2 = 10k_1$; however, any "high" value for k_2 would produce equivalent results. With this, we can describe the time dependence of all of the various species in terms of a single rate constant, k_1. The rate constant for a given methane isotope is taken to be the product of k_1 times

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[8] This estimate is made as follows. For the exchange rate to be faster than the 0.1 min response time of the experimental method, we have the following lower bound on the rate constant, k: $k \geq {}^1/_6\ \mathrm{s^{-1}}$, at $T = 77$ K. Using $k = (kT/\hbar)(e^{-\Delta S/R})(e^{-E_a/RT})$, and taking the same value for the entropy of activation as that found here for exchange with methane, i.e. −27 eu, the energy of activation is calculated to be less than about 2 kcal/mol.

[9] (a) The rate of hydrogen exchange at 80 °C for CD_4/H_2 mixtures was measured to be about 2.5 times slower than that for CH_4/D_2 mixtures. This kinetic isotope effect is sufficiently small that it has little influence on the rate parameters derived in the current analysis. A more detailed discussion of the kinetic isotope effect and implications concerning C−H activation will be published separately. (b) This is equivalent to assuming that the secondary kinetic isotope effect (KIE) is negligible, a reasonable assumption given the primary KIE noted above.

the statistical factor of that isotope (e.g., the rate constant for deuteration of CH_4 is 4 times that for deuteration of CHD_3).[9b] Finally, we assume an Eyring form for k_1.[8]

The reaction network (differential equations) includes all of the methane species (isotopes) and all of the hydrogen species, plus MH and MD. From the initial conditions (starting concentrations), the time evolution of all species is calculated by numerical integration using a Runga−Kutta method. Only the two parameters that describe k_1, the activation energy ΔS and the activation energy E_a, are varied in order to fit the experimental data. The calculated results for the concentration of CH_4 as a function of time at each temperature are shown in Figure 2 (solid lines).

From this analysis, we obtain an activation energy of $E_a^{\dagger} = 7.0\ (\pm 1)$ kcal/mol and a large negative entropy of activation $\Delta S^{\ddagger} = -27(\pm 3)$ eu. These observations are significant in that they imply that the reaction proceeds via a constrained transition state. A likely possibility is a four-center transition state (σ-bond metathesis), TS A and B, shown in Figure 3. These kinetic parameters are consistent with those reported by Bercaw for reactions of early metal systems postulated to involve a concerted four-center transition state (for the reaction of $Cp^*{}_2Sc-CH_3$ and styrenes $\Delta H^{\ddagger} = 12$ kcal mol^{-1} and $\Delta S^{\ddagger} = -36$ eu).[10]

At the highest temperature (150 °C) the calculated rate begins to deviate significantly from the observed rate. We attribute this deviation to catalyst deactivation. In support of this, we find the rate of exchange decreases if we hold the catalyst at 150 °C. In addition, ligand titration experiments indicate that the number of M−H groups declines if the catalyst is held at 150 °C. These same tests indicate that little or no deactivation occurs at temperatures below 130 °C. Only the data below 125 °C are used in deriving the values for the kinetic parameters.

Two transition states can be considered in the formation of deuterated methane involving σ-bond metathesis (Figure 3). The first transition state (TS A) places the carbon atom in a central position, which provides the most direct way to accomplish this exchange, avoids the formation of a Zr−Me intermediate (uphill in energy), and minimizes any potential steric interactions. Alternatively, the second transition state (TS B) places hydrogen in the central position which calculations suggest is the favored transition state due to the kite-shaped structure.[10] Thus, to produce a deuterated methane, this pathway (the microscopic reverse of the hydrogenolysis of a zirconium−alkyl bond) invokes the formation of a $Zr-CH_3(H-D)$ intermediate, followed by a very fast rotation of the Zr(H−D) bond and generation of the Zr−H and CDH_3.[10] Unfortunately, the current experiments cannot distinguish which of these transition states might be favored.

H/D exchange reactions between CH_4/CD_4 (and CD_4/H_2) catalyzed by a silica-supported Ta(3+) hydride system were recently reported.[6b] A sequential exchange process leading to the formation of a statistical distribution of all isotopomers of methane was observed, and a σ-bond metathesis mechanism was proposed. In addition to transition states involving metal hydride, a transition state involving metal−methyl groups exchanging with methane was postulated. The latter transition state was disfavored by the authors. We would also argue against a metal−methyl transition state, both on the basis of increased steric hindrance and on the kinetics we observe. We find that H_2/D_2 exchange is too fast for us to measure and that D_2/CH_4 exchange is much faster than exchange between CH_4 and CD_4 (results to be reported separately).

It is interesting to compare the relative activity of the Ta and Zr systems. The exchange reactions in the Ta system were reported at 150 °C, a temperature at which we observe a slow deactivation of the zirconium catalyst. Thus, a direct comparison is not possible. Despite this, it is clear that the rate of exchange in the Zr system is much faster than that of the Ta system. The rate of CH_4/D_2 exchange data of the tantalum at 150 °C is 10−100 times slower than the exchange rate for Zr at 100 °C. The rate differences may be attributed to the greater electrophilic character of zirconium due in part to the differences in d electron configuration (d^0 vs d^2). Alternatively, one could also argue that the structure of the zirconium center may be more open compared to that of the tantalum system, hence allowing easier coordination of methane to the zirconium center.

Conclusions

In conclusion, we have investigated the H/D exchange rates of hydrogen and methane with the silica-supported zirconium hydride catalyst. We have found that H/D exchange reactions between hydrogen and deuterium are rapid even at liquid nitrogen temperatures, thus putting an upper bound on the energy of activation for H_2/D_2 exchange at around 2 kcal/mol. Measured H/D exchange rates between methane and hydrogen support the view that these reactions proceed via σ-bond metathesis. Evidence for this mechanism is based on the low energy of activation and the high negative entropy of activation. These values are consistent with both theoretical and experimental studies of similar four-center processes.[10,11] Currently we are conducting kinetic studies with higher hydrocarbons and with a wider range of supported catalytic materials.

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