Thermodynamic Isotope Effect in Partial Oxidation of Methane to Syngas

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Thermodynamic deuterium substitution effects on reactant conversion and product selectivity were investigated by computer simulation for the stoichiometric partial oxidation of methane. Methane conversion shows a normal deuterium isotope effect, whereas CO selectivity shows an inverse deuterium isotope effect. H_2 selectivity exhibits a large normal deuterium effect. Moreover, deuterium isotope effects are dependent on reaction temperatures and pressures. When reaction pressure is very low, such as 0.001 MPa, all thermodynamic deuterium isotope effects are negligible at 650°C or above. Three criteria, based on the deuterium-isotope effects, were proposed to determine whether a partial oxidation reaction of methane is kinetically controlled without accurately measured reaction temperatures.

Introduction

The upgrading of natural gas, which consists mostly of methane, to value-added products, such as easily transportable fuels, is driven by the abundance of natural gas discoveries in remote areas. Over the past 20 years, extensive efforts have been focused on both the direct and indirect conversion of methane to value-added products (Ashcroft et al., 1990, 1991; Boucouvalas et al., 1994; Bradford and Vannice, 1999; Choudhary et al., 1993; Dissanayake et al., 1991; Foster, 1985; Gadalla and Bower, 1988; Hickman and Schmidt, 1992, 1993; Hu and Ruckenstein, 1996, 1998a,b,c; Keller and Bhasin, 1982; Lunsford, 1994; Periana et al., 1998; Pitchai and Klier, 1986; Rostrup-Nielsenand and Hansen, 1993; Ruckenstein and Hu, 1996, 1998, 1999; Yamazaki et al., 1996). The direct conversion routes involve some form of selective oxidation of methane to olefins, methanol, or formaldehyde (Foster, 1985; Keller and Bhasin, 1982; Lunsford, 1994; Periana et al., 1998; Pitchai and Klier, 1986). These are difficult approaches because, at the high temperatures that are necessary for high conversions, the formation of CO_2 is highly favorable. For this reason, interest in the indirect conversion of CH_4 has been renewed (Ashcroft et al., 1990, 1991; Boucouvalas et al., 1994; Bradford and Vannice, 1999; Choudhary et al., 1993; Dissanayake et al., 1991; Gadalla and Bower, 1988; Hickman and Schmidt, 1992, 1993; Hu and Ruckenstein, 1996, 1998a,b,c; Rostrup-Nielsenand and Hansen, 1993; Ruckenstein and Hu, 1998,1999,1996; Yamazaki et al., 1996). Indirect conversion involves methane conversion to methanol or other hydrocarbons via syngas.

Currently, synthesis gas is typically prepared by steam reforming (reacting CH_4 with H_2O at ~ 800°C) (Trimm, 1977):

$$CH_4 + H_2O \rightarrow CO + 3H_2, \quad \Delta H = 225.4 \text{ kJ/mol.}$$

This process, however, provides an uneconomic production of synthesis gas due to its endothermic nature, the requirement for low space velocity, and a high H_2/CO ratio that is unsuitable for methanol and long-chain hydrocarbon Fischer-Tropsch syntheses

Catalytic partial oxidation,

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2, \quad \Delta H = -22.6 \text{ kJ/mol}$$

offers a desirable alternative route for rapid, efficient, and economical conversion of methane to synthesis gas. In 1990, A. T. Ashcroft et al. (Ashcroft et al., 1990) reported that the reaction can take place at temperatures of only ~ 775°C over lanthanide ruthenium oxide catalysts. Nearly 90% conversion of methane and more than 90% selectivity to CO and H_2 was achieved at 770°C and at high GHSV of 4×10^4 h^{-1}, 1 atm of

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pressure. Schmidt et al. (Hickman and Schmidt, 1992, 1993) and (Choudhary et al., 1993) used even higher space velocities (residence time close to 10^{-3} s) for the reaction. In fact, those research works represent the beginning of a new kind of catalytic partial oxidation of methane, which is characterized by very short contact times between the reactants (methane and oxygen) and the catalyst. Over the past 10 years, partial oxidation of methane became one of the most active research topics in catalysis (Ashcroft et al., 1990; Boucouvalas et al., 1994; Choudhary et al., 1993; Dissanayake et al., 1991; Hickman and Schmidt, 1992, 1993; Hu and Ruckenstein, 1996, 1998a,b,c; Ruckenstein and Hu, 1998, 1999, 1996). Many articles related to reaction mechanisms of partial oxidation have been published (Dissanayake et al., 1991; Hickman and Schmidt, 1992, 1993; Hu and Ruckenstein, 1996, 1998a,b; Tsipouriari et al., 1998; van Looij and Geus, 1997). However, conclusions in the literature related to the reaction mechanisms are contradictory.

Kinetic deuterium isotope effects can be used as a guide to determine whether the isotopic site participates directly in the rate-determining step of a reaction, because, when a bond to hydrogen or deuterium is broken in the rate-determining step of a reaction, the rate constant, k_H, for the reaction of the hydrogen compound exceeds the constant, k_D, for the same reaction of the corresponding deuterium compound (Melander, 1960; Ozaki, 1977; Wiberg, 1955). On the other hand, the thermodynamic deuterium isotope effect, namely, the effect of isotopic substitution on the equilibrium constant, can be used to indicate important characteristics of reaction equilibriums (Goering and Paisley, 1987). Therefore, the kinetic deuterium isotope effect can be expressed by the rate-constant ratio of hydrogen compounds to corresponding deuterium compounds in a rate-determined step, while the thermodynamic deuterium isotope can be determined by the overall reaction equilibrium constant ratio of hydrogen compounds to corresponding deuterium compounds. Recently, isotope effects have been used to evaluate the rate-determining step (RDS) in the partial oxidation reaction (Au and Wang, 1997; Wang and Ruckenstein, 1999; Tang et al., 1998). However, it is important to know whether the isotope effect obtained from their experiments is kinetic or thermodynamic. An improbable explanation of isotope effects will result in a misleading practical reaction mechanism, because kinetic isotope effects and thermodynamic isotope effects provide different information about reactions.

In the partial oxidation of methane, it is very difficult to know whether the reaction is kinetically or thermodynamically controlled. This is because of the very large temperature heterogeneousity of the catalysts (Dissanayake et al., 1993; Hu and Ruckenstein, 1998c), hot spots (Dissanayake et al. 1993), and temperature oscillations, that are observed (Hu and Ruckenstein, 1998d). It is very difficult to get a representative temperature for the reaction (Hu and Ruckenstein, 1998c). Without a precise reaction temperature, one cannot judge whether the reaction reaches a thermodynamic equilibrium by the traditional method, in which reactant conversions obtained from the experiment are compared with thermodynamic conversions at a certain temperature. In this case, it is important to study the thermodynamic isotope effect, which can provide a basis by which to distinguish kinetic isotope effects and thermodynamic isotope effects. To the best of our knowledge, however, no research work for thermodynamic isotope effects in partial oxidation of methane has been published.

The objective of the present study is (1) to investigate thermodynamic deuterium isotope effects in the partial oxidation of methane, including isotope effects on reactant conversion and product formation and the relationship between the isotope effects and reaction conditions; and (2) to provide a new effective method based on the deuterium isotope effects to determine whether the partial oxidation reaction of methane is kinetically controlled without accurately measured reaction temperatures.

Modeling and Simulation

For two equilibria involving the isotopically substituted molecules A_1, A_2, C_1, and C_2

$$aA_1 + bB \overset{K1}{\leftrightarrow} cC_1 + dD \tag{1}$$

$$aA_2 + bB \overset{K2}{\leftrightarrow} cC_2 + dD \tag{2}$$

An equilibrium constant, K_{eq}, can be expressed in the usual notation (for pressure or concentration)

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{3}$$

and in statistical mechanical notation

$$K_{eq} = \frac{Q_C^c Q_D^d}{Q_A^a Q_B^b} \tag{4}$$

where Q_i is the partition function of species i. Therefore, the equilibrium deuterium isotope effect can be expressed in statistical mechanical notation

$$\frac{K_{eq1}}{K_{eq2}} = \left(\frac{Q_{C_1}}{Q_{C_2}}\right)^c \left(\frac{Q_{A_2}}{Q_{A_1}}\right)^a \tag{5}$$

and

$$\frac{Q_1}{Q_2} = \left(\frac{Q_{(D)}}{Q_{(H)}}\right)_{\text{Trans}} \left(\frac{Q_{(D)}}{Q_{(H)}}\right)_{\text{Rot}} \left(\frac{Q_{(D)}}{Q_{(H)}}\right)_{\text{Vib}} \left(\frac{Q_{(D)}}{Q_{(H)}}\right)_{\text{Elec}} \tag{6}$$

where $Q_{(H)}$ and $Q_{(D)}$ are partition functions of hydrogen compounds and corresponding deuterium compounds, respectively.

Furthermore, Eq. 6 can be expressed as follows (Ozaki, 1977; Wiberg, 1955)

$$\frac{Q_1}{Q_2} = \left(\frac{M_1}{M_2}\right)_{\text{Trans}} \left(\frac{(I_A I_B I_C)_1}{(I_A I_B I_C)_2}\right)_{\text{Rot}} \left(\frac{\left(\sum_{\upsilon=0}^{\infty} e^{-\upsilon\theta_\upsilon/T}\right)_1}{\left(\sum_{\upsilon=0}^{\infty} e^{-\upsilon\theta_\upsilon/T}\right)_2}\right)_{\text{Vib}}$$

Table 1. Partition Functional Ratio of Isotopomer

Molecules	$\left(\frac{Q_{(D)}}{Q_{(H)}}\right)_{Trans}$	$\left(\frac{Q_{(D)}}{Q_{(H)}}\right)_{Rot}$	$\left(\frac{Q_{(D)}}{Q_{(H)}}\right)_{Vib}$	$\left(\frac{Q_{(D)}}{Q_{(H)}}\right)_{Elec}$
CD_4/CH_4	1.3975	2.8284	≈ 1	$e^{3528/T}$
D_2O/H_2O	1.1712	2.8284	≈ 1	$e^{1706/T}$
D_2/H_2	2.8284	2	≈ 1	$e^{841/T}$

Source: Ozaki, 1977; Au-Yeung et al., 1999.

$$\left(\frac{(e^{-E_0/RT})_1}{(e^{-E_0/RT})_2}\right)_{\text{Elec}} \tag{7}$$

where M is the mass of molecules; I_A, I_B, and I_C are the moment of inertia; υ is a quantum number; θ_υ is the characteristic temperature for vibration; T is the temperature; E_o is the zero-point energy.

Table 1 lists the partition functional ratios of the hydrogen compounds to the corresponding deuterium compounds, which are involved in the partial oxidation of methane. One can see that the thermodynamic deuterium isotope effect would mainly originate from the difference in zero-point energy (involved in electronic partition functions) between hydrogen compounds and the corresponding deuterium compounds in the partial oxidation of methane.

Equilibrium isotope effects, which lead to a difference in isotopic composition in reaction reagents and products, in terms of classic thermodynamics, arises from their free-energy differences. Therefore, the equilibrium isotope effects can be studied by chemical equilibrium calculations based on basic thermodynamic data, such as Gibbs free energy and enthalpy, which are available for both regular compounds and isotopic compounds. In this work, chemical equilibrium for the partial oxidation of methane, in which reactants are CH_4 (or CD_4) and O_2 and products are CO, CO_2, H_2 (or D_2) and H_2O (or D_2O), was calculated by Gibbs free-energy minimization. The objective function of the Gibbs free energy, which is to be minimized, is composed of two parts (SIMSCI, 1994). The first is the total Gibbs free energy of the mixture in all phases

$$G = RT \sum_{p=1}^{NP} \sum_{j=1}^{NC} \frac{G_{jp}}{RT} n_{jp} \tag{8}$$

where NP is the number of fluid phases; NC is the number of fluid components; G_{jp} is the Gibbs free energy of fluid component at reaction temperature and pressure; T is the reaction temperature; and n_{jp} is the number of moles of fluid component.

The second part of the objective function is the conservation of element groups and mass-balance equations created from the constraints on chemical equilibrium. For each element group, the output flow rate from the reaction system has to be equal to the feed flow rate into the reaction system, that is

$$b_k = \sum_{p=1}^{NP} \sum_{j=1}^{NC} m_{jk} n_{mp} \quad k = 1, \ldots, NE \tag{9}$$

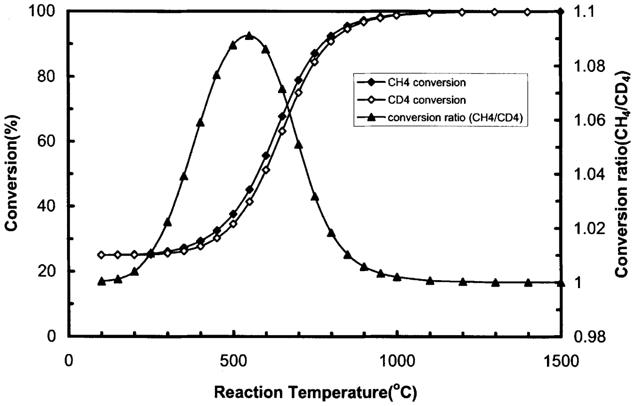

Figure 1. Deuterium substitution effect on equilibrium methane conversion in partial oxidation of methane at various temperatures [reaction conditions: CH_4(or CD_4)/O_2 = 2; pressure = 0.1 MPa].

where b_k is the feed quantity of element group k; NE is the number of element groups; and m_{jk} is the number of element groups, k, contained in component j.

All thermodynamic equilibrium process simulations for the stoichiometric partial oxidation of methane (that is, $CH_4/O_2 = 2$ in feed), at different temperatures and pressures, were carried out by using the PRO II software (Simulation Sciences Inc.). Thermodynamic data used in the simulations are from the PRO II database.

Results

Thermodynamic deuterium isotope effects on reactant conversion and product selectivities in the stoichiometric partial oxidation of methane (that is, $CH_4/O_2 = 2$ in feed) are obtained from our equilibrium process simulations at atmospheric pressure (0.1 MPa). The simulation results show that O_2 equilibrium conversions are always 100% at various reaction conditions both in $CH_4 + O_2$ and in $CD_4 + O_2$. This indicates that deuterium substitution does not affect O_2 equilibrium conversions. However, as shown in Figure 1, methane conversion has a normal deuterium isotopic effect in the temperature range of 200°C to 900°C, that is, deuterium substitution results in a decrease in methane conversion. The largest effect is observed at 550°C, where the ratio of CH_4 conversion to that of CD_4 is 1.09. This effect decreases with increasing temperature above 550°C and disappears above about 1,000°C.

Figure 2 shows the deuterium effect on CO selectivity. At temperatures below 550°C, CO selectivity has an inverse deuterium isotope effect. The ratio of CO selectivity in the $CH_4 + O_2$ system to that in the $CD_4 + O_2$ system is less than 1, that is, deuterium substitution results in an increase in CO selectivity. The ratio of CO selectivity in the $CH_4 + O_2$ system to that in the $CD_4 + O_2$ system becomes 1 at 550°C and then remains unchanged with increasing temperature. This indicates that no deuterium isotope effect on CO selectivity exists above about 550°C.

Deuterium substitution provides a normal isotope effect on hydrogen selectivity. In Figure 3, a large normal deuterium

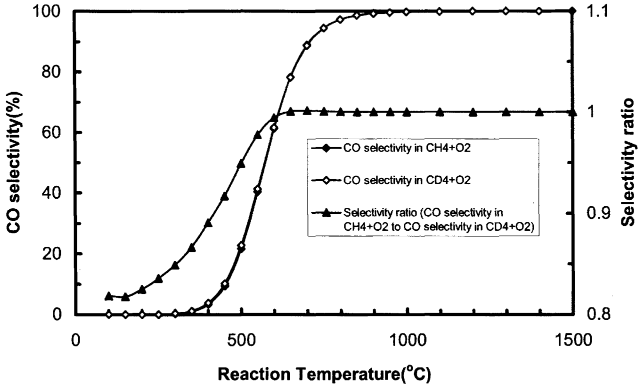

Figure 2. Deuterium substitution effect on equilibrium CO selectivity in partial oxidation of methane at various temperatures [reaction conditions: CH_4(or CD_4)/O_2 = 2, pressure = 0.1 MPa].

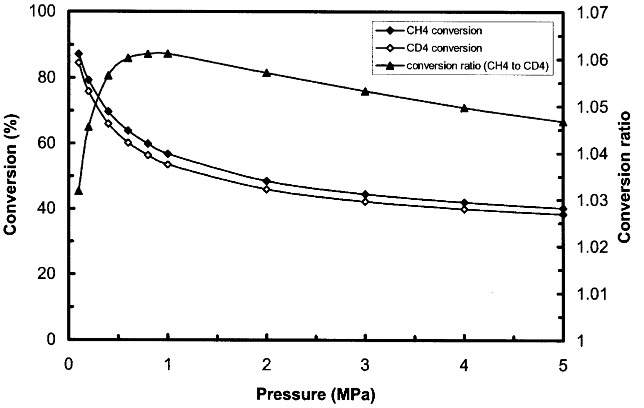

Figure 4. Deuterium substitution effect on equilibrium methane conversion in partial oxidation of methane at various pressures [reaction conditions: CH_4(or CD_4)/O_2 = 2; temperature = 750°C].

effect on hydrogen selectivity is observed at low temperatures. This effect decreases with increasing reaction temperature and disappears at temperature of 850°C or above.

Deuterium isotope effects on reactant conversions and product selectivities depend on total reaction pressures. As shown in Figure 4, at 750°C, the normal deuterium effect on methane conversion increases with increasing pressure from 0.1 MPa to 1 MPa, and then decreases at higher pressures. Figure 5 shows that when the reaction pressure is higher than 0.1 MPa, CO selectivity has an inverse deuterium isotope effect, that is, deuterium substitution results in an increase in CO selectivity. Moreover, this inverse deuterium effect increases with increasing pressure. This is different from the results at atmospheric pressure (0.1 MPa) (Figure 2), which show no deuterium isotope effects on CO selectivity at 550°C or above. For hydrogen selectivity, increasing pressure results in an increase in the normal deuterium isotope effects (See Figure 6).

Deuterium isotope effects at pressures below 0.1 MPa were also evaluated. As shown in Figures 7 and 8, deuterium isotope effects are smaller at pressures below 0.1 MPa than at 0.1 MPa. Moreover, when the pressure is decreased to 0.001 MPa at 650°C and 750°C, all deuterium effects disappear.

In addition, it is worth noting that the CO and H_2 (or D_2) selectivities decrease with decreasing temperature and reach almost zero at about 500°C (Figures 2 and 3). This indicates that a complete oxidation reaction is dominant in the equilibrium reaction between CH_4 (or CD_4) and O_2 at temperatures below 500°C. On the other hand, the increase in pressure leads to the decrease in the CO and H_2 (D_2) selectivities (Figures 5 and 6). This happens because the partial oxidation of methane ($CH_4 + 1/2O_2 \rightarrow CO + 2H_2$) is a volume-increase reaction, which is dependent on pressure, whereas the complete oxidation ($CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$) is a volume-constant reaction, which is independent of pressure. Therefore, the increase in pressure reduces the partial oxidation, but does not affect the complete combustion. As a result, the increase in pressure reduces methane conversion. Furthermore, the ratio of CH_4 conversion to CD_4 conversion is also dependent on pressure (Figure 4). This happens be-

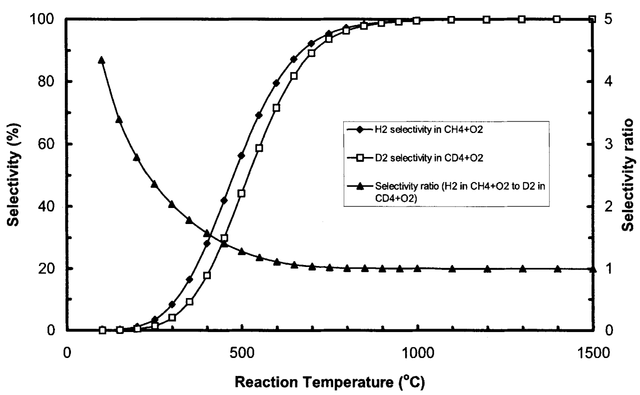

Figure 3. Deuterium substitution effect on equilibrium H_2 selectivity in partial oxidation of methane at various temperatures [reaction conditions: CH_4(or CD_4)/O_2 = 2; pressure = 0.1 MPa].

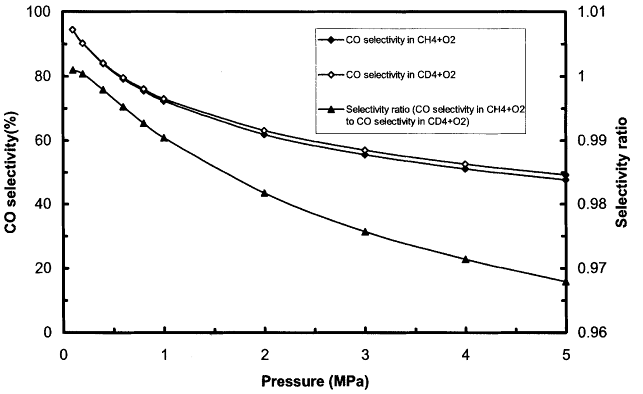

Figure 5. Deuterium substitution effect on equilibrium CO selectivity in partial oxidation of methane at various pressures [reaction conditions: CH_4(or CD_4)/O_2 = 2; temperature = 750°C].

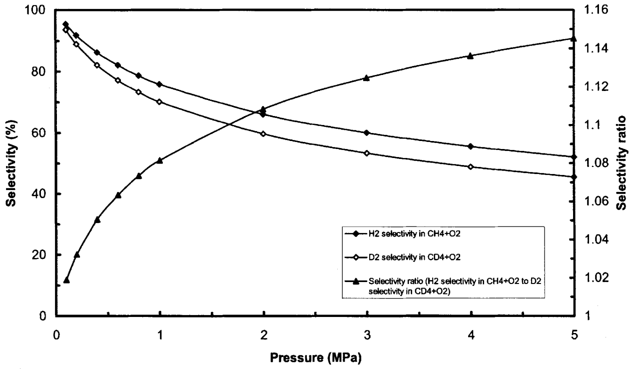

Figure 6. Deuterium substitution effect on equilibrium H_2 selectivity in partial oxidation of methane at various pressures [reaction conditions: CH_4(or CD_4)/O_2 = 2; temperature = 750°C].

cause the decrease in the methane conversion with increasing pressure is different for CH_4 and CD_4 due to their different reaction equilibrium constants.

Discussion

In many reports in the literature where isotope experiments are performed, it is unclear whether deuterium isotope effects are kinetic or thermodynamic equilibrium effects. Although the magnitude of kinetic isotope effects cannot be predicted reliably, the magnitude of thermodynamic equilibrium isotope effects, which are calculated in this article, can be used to judge whether the isotope effect obtained in an experiment is kinetic or thermodynamic.

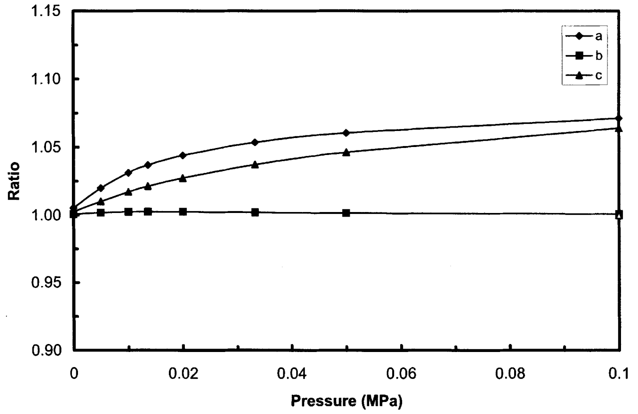

Figure 7. Deuterium substitution effect on equilibrium reactant conversion and product selectivities in partial oxidation of methane at various pressures [reaction conditions: CH_4(orCD_4)/O_2 = 2; temperature = 650°C].

(a) Ratio of CH_4 conversion to CD_4 conversion; (b) ratio of CO selectivity in $CH_4 + O_2$ to that in $CD_4 + O_2$; (c) ratio of H_2 selectivity in $CH_4 + O_2$ to D_2 selectivity in $CD_4 + O_2$.

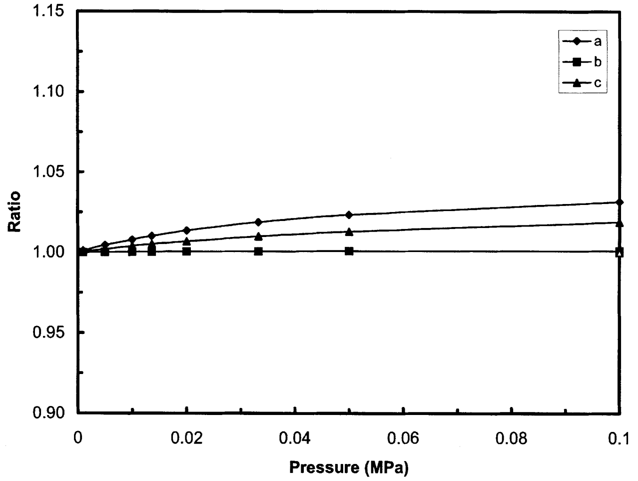

Figure 8. Deuterium substitution effect on equilibrium reactant conversion and product selectivities in partial oxidation of methane at various pressures [reaction conditions: CH_4(or CD_4)/O_2 = 2; temperature = 750°C].

(a) Ratio of CH_4 conversion to CD_4 conversion; (b) ratio of CO selectivity in $CH_4 + O_2$ to that in $CD_4 + O_2$; (c) ratio of H_2 selectivity in $CH_4 + O_2$ to D_2 selectivity in $CD_4 + O_2$.

For the stoichiometric partial oxidation of methane (that is, $CH_4/O_2 = 2$ in feed) at atmospheric pressure, the characteristics of the deuterium isotope effects are: (1) methane conversion has a normal deuterium isotope effect, the maximum of which is 1.09 (ratio of CH_4 conversion to that of CD_4); (2) CO selectivity has an inverse deuterium isotope effect below 550°C and no deuterium at 550°C or above; (3) H_2 selectivity has normal deuterium effects. If the stoichiometric partial oxidation of methane at atmospheric pressure reaches thermodynamic equilibrium, it must have all of those deuterium isotope effect characteristics. In other words, if one of the following occurs in a stoichiometric methane partial oxidation experiment at atmospheric pressure, the reaction does not reach thermodynamic equilibrium, that is, it is kinetically controlled: (1) methane conversion in experiments shows a reverse deuterium isotope effect or a much greater normal isotope effect than 1.09; (2) CO selectivity shows a normal deuterium isotope effect; (3) H_2 selectivity has a reverse deuterium isotope effect. These three criteria can be used without accurately measured reaction temperatures to determine whether over a particular catalyst a stoichiometric partial oxidation of methane is thermodynamically or kinetically controlled in atmospheric pressure experiments. For example, it was reported that a normal deuterium effect of 1.04 ~ 1.29 (the ratio of CO selectivity in $CH_4 + O_2$ to that in $CD_4 + O_2$) was observed for CO selectivity in the partial oxidation of methane over a Pt/Al_2O_3 catalyst in the temperature range of 550–650°C (Tang et al., 1998). This normal deuterium effect on CO selectivity is totally different from the corresponding thermodynamic isotope effect, which is a reverse deuterium isotope effect. According to item 2 in the preceding criteria, the experiments in that research obviously are kinetically controlled, and the deuterium isotope effects observed were kinetic. In another report (Au and Wang, 1997), over Rh-based catalysts at 700°C, normal deuterium isotope effects were observed on methane conversion, but no effect on CO selectivity. These observations are very similar to the thermodynamic deuterium effects calculated in this article. The magnitudes of these effects reported in the article (Au and Wang, 1997) are not much higher than the thermodynamic effects we calculated, but all the trends are the same, so it is likely that the experiments performed in that work are close to thermodynamic equilibrium.

To get reliable information for reaction mechanisms, one should operate under conditions that experimental deuterium effects are kinetic and have no thermodynamic effect contributions. As shown in Figures 7 and 8, when pressures are below 0.1 MPa, deuterium thermodynamic effects, on reactant conversion and product selectivities in the partial oxidation of methane, decrease with reducing pressure. When the pressure is very low, such as 0.001 MPa, these deuterium thermodynamic effects can be negligible at 650°C or above. Therefore, for the stoichiometric partial oxidation of methane, the deuterium isotope effects obtained in very low-pressure systems, such as a vacuum system, would be likely kinetic at 650°C or above.

Conclusion

Deuterium substitution in the stoichiometric partial oxidation of methane at atmospheric pressure (0.1 Mpa) has effects on equilibrium methane conversion and product selectivity: (1) methane conversion shows normal deuterium isotope effects; (2) H_2 selectivity has a large normal deuterium effect; (3) CO selectivity has an inverse deuterium isotope effect below 550°C and no deuterium at 550°C or above. Moreover, it was found that deuterium isotope effects also depend on reaction pressure. When reaction pressure is very low, such as 0.001 MPa, all deuterium isotope effects are negligible at 650°C or higher.

According to the characteristics of calculated thermodynamic deuterium isotope effects, the following three criteria were proposed to determine if a reaction is kinetically or thermodynamically controlled. If one of the following occurs in a stoichiometric partial oxidation of a methane experiment at atmospheric pressure, the reaction is most likely kinetically controlled: (1) methane conversion in experiments shows a reverse deuterium isotope effect or a much larger normal isotope effect than 1.09; (2) CO selectivity shows a normal deuterium isotope effect; and (3) H_2 selectivity has a reverse deuterium isotope effect.

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