

Isotopic Tracer Studies of Reaction Pathways for Propane Oxidative Dehydrogenation on Molybdenum Oxide Catalysts

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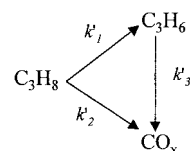
Kinetic analysis and isotopic tracer studies were used to identify the elementary steps and their reversibility in the oxidative dehydrogenation of propane over ZrO_2 -supported MoO_x catalysts. Competitive reactions of C_3H_6 and $\text{CH}_3^{13}\text{CH}_2\text{CH}_3$ showed that propene is the most abundant primary product, and that CO and CO_2 are formed via either secondary combustion of propene, or by direct combustion of propane. A mixture of C_3H_8 and C_3D_8 undergoes oxidative dehydrogenation without forming $\text{C}_3\text{H}_8-x\text{D}_x$ mixed isotopomers, suggesting that steps involving C–H bond activation are irreversible. Normal kinetic isotopic effects ($k_{\text{C-H}}/k_{\text{C-D}}$) were measured for propane dehydrogenation (2.3), propane combustion (1.6) and propene combustion (2.1). These data indicate that the kinetically relevant steps in propane dehydrogenation and propene combustion involve the dissociation of C–H bonds in the respective reactant. H–D exchange occurs readily between C_3H_6 and D_2O or C_3D_6 and H_2O , suggesting that OH recombination steps are reversible and quasi-equilibrated. Reactions of $^{18}\text{O}_2/\text{C}_3\text{H}_8$ on supported Mo^{16}O_x species lead to the preferential initial appearance of lattice ^{16}O atoms in H_2O , CO , and CO_2 , indicating that lattice oxygen is required for C–H bond activation and for the ultimate oxidation of the adsorbed products of this reaction. $^{18}\text{O}^{16}\text{O}$ was not detected during reactions of $\text{C}_3\text{H}_8-^{18}\text{O}_2-^{16}\text{O}_2$ mixtures, consistent with irreversible O_2 dissociation steps. These isotopic tracer results are consistent with a Mars–van Krevelen redox mechanism in which two lattice oxygens participate in the irreversible activation of C–H bond in propane. The resulting alkyl species desorb as propene, and the remaining O–H group recombines with neighboring OH groups to form water and reduced Mo centers. The reduced Mo centers finally reoxidize by irreversible dissociative chemisorption of O_2 . The proposed reaction mechanism leads to a complex kinetic rate expression that accurately describes the observed dependences on the partial pressure of propane, oxygen, and water.

Introduction

The oxidative dehydrogenation (ODH) of propane has been investigated as a potential route to propene.^{1–7} Extensive evaluations of catalyst compositions have shown that the most active and selective ones contain V or Mo oxides as the active component.³ Over these catalysts, it has been proposed that the oxidation of propane occurs via parallel and sequential oxidation steps (Scheme 1).³

Propene is the primary product and carbon oxides (CO_x) form as byproducts via propane and propene combustion. Several studies have addressed the primary and secondary reactions occurring during propane ODH,^{8–15} but only a few of them have provided descriptions of the elementary steps involved or evaluations of the rate coefficients for the elementary steps. By analogy with other oxidation reactions, propane ODH has been proposed to proceed via a Mars–van Krevelen mechanism,^{9,12–15} in which propane reacts with lattice oxygen in the catalyst and the resulting vacancies then react by dissociative adsorption of O_2 . This mechanistic interpretation has been based largely on agreement between proposed sequences of elementary steps and experimental reaction kinetics. Only limited independent evidence for specific elementary steps has been reported.¹³ Although kinetic rate expressions for oxidative dehydrogenation and combustion pathways can provide a basis for developing

SCHEME 1: Reaction Network for the Propane Oxidation Reactions



mechanistic inferences, they are insufficient to establish the identity and reversibility of individual elementary steps. Isotopic tracer studies, however, can discriminate among various mechanistic proposals that may describe with similar accuracy the measured rate expressions. Such studies can also confirm the assumptions required in order to obtain a given rate expression from a sequence of elementary steps.^{15,16}

Vanadium-based catalysts have been widely studied as selective oxidation catalysts.³ Reaction mechanisms and detailed elementary steps for propane ODH on VO_x species have been proposed, and the reversibility of proposed elementary steps has been confirmed by isotopic tracer studies.¹⁵ Molybdenum-based catalysts have also been widely studied, but less thoroughly than vanadium-based catalysts, because of their lower ODH reaction rates.³ Some Mo-based catalysts, however, show very high propene selectivity.^{3,4} Only a few studies have addressed the mechanism for alkane ODH reactions on Mo-based catalysts but, to our knowledge, the detailed elementary steps have not been examined using isotopic methods or detailed

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TABLE 1: Characteristics of Various Mo–Zr Catalysts

catalyst	MoO ₃ loading (wt %)	treatment temp (K)	Mo species structure ^a
MoO _x /ZrO ₂	11	773	MoO _x oligomers
MoO ₃ /ZrO ₂	37	673	bulk MoO ₃
ZrMo ₂ O ₈ /ZrO ₂	37	873	bulk ZrMo ₂ O ₈

^a Obtained by XRD, Raman, XAS, and UV–vis spectroscopy characterization.

kinetic studies of the individual primary and secondary reactions involved.^{13,14}

The structure and propane ODH properties of molybdate species supported on ZrO₂ have been recently reported.⁴ The structure of MoO_x species on ZrO₂ depends on the MoO_x surface density and on the temperature of thermal treatments. For Mo surface densities below 5 Mo/nm², two-dimensional MoO_x oligomers form on ZrO₂ surfaces, irrespective of treatment temperature. For higher MoO_x surface densities, treatment at low temperatures (~673 K) leads to the formation of MoO₃ crystallites, while treatment at high temperatures (~873 K) causes the formation of ZrMo₂O₈ crystallites. Propane ODH turnover rate are widely different on MoO₃ and ZrMo₂O₈ because of apparent differences in the strength and accessibility of active Mo=O bonds. On both structures, the pseudo-first-order rate constant for the combustion of propene is significantly higher than for propane ODH.⁴

The objective of this study is to determine the identity and reversibility of elementary steps involved in propane ODH on Mo-based catalysts and to infer the nature of the active surface species required to catalyze the rate-determining elementary steps. Isotopic tracer methods are combined with measurements of the concentration dependence for each reaction in Scheme 1. Most of the reported results were obtained on a MoO_x/ZrO₂ sample with a surface density of 3–4 Mo/nm² and containing predominately two-dimensional MoO_x oligomers as the active species. Rate expressions were also obtained on two other MoO_x/ZrO₂ samples containing predominately either MoO₃ or ZrMo₂O₈ crystallites.

Experimental Section

Three MoO_x/ZrO₂ catalysts were used in the present study. These samples were prepared by incipient wetness impregnation of precipitated zirconium oxyhydroxide with an ammonium dimolybdate (99%, Aldrich, Inc.) solution, followed by drying and thermal treatment in dry air.⁴ One sample contained 11 wt % MoO₃ and it was treated in air at 773 K. Structural characterization of this sample by X-ray diffraction and by X-ray absorption, Raman, and UV–visible spectroscopies indicated that Mo species exist predominantly as MoO_x oligomers.⁴ The other two samples contain 37 wt % MoO₃. One sample was treated in air at 673 K and the other at 873 K. After treatment at 673 K this sample contains predominately MoO₃ crystallites, while treatment at 873 K leads to the preferential formation of crystalline ZrMo₂O₈ structures.⁴ Table 1 shows the structural properties and designation for each of the MoO_x/ZrO₂ samples used in this study.

Reaction rates were measured using a quartz microreactor containing 0.02–0.1 g samples.⁵ C₃H₈ and O₂ conversions were varied by changing reactant flow rates between 0.8 and 3.5 cm³ s⁻¹. C₃H₈ and O₂ conversions were typically below 2% and 20%, respectively. Propane reaction rates were extrapolated to zero residence time in order to obtain initial dehydrogenation and combustion reaction, while propene combustion were obtained from the observed changes in propene selectivity with

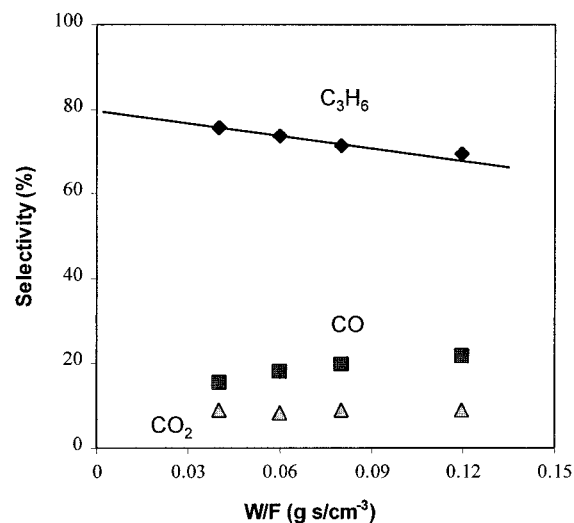


Figure 1. Dependence of products selectivity on bed residence time during ODH of propane (MoO_x/ZrO₂, 703 K, 14 kPa of C₃H₈, 1.7 kPa of O₂, balance He).

residence time.⁵ Water was introduced into the C₃H₈–O₂ reactants by reacting a metered 20% H₂/Ar side stream with CuO (150 g of CuO) at 623 K to form the desired amount of H₂O. All transfer lines located down stream of the point of water introduction were kept above 393 K in order to prevent condensation.

All isotopic tracer studies were carried out in a gradientless batch reactor contained within a gas recirculation loop.¹⁷ Reactants and products were recirculated at 3.3 cm³ s⁻¹ using a graphite gear micropump in order to maintain low propane conversions per pass (<1%). The reactor was evacuated by mechanical and diffusion pumps isolated from the system by liquid nitrogen traps. The chemical and isotopic composition of reactants and products were measured by mass spectrometry after capillary gas chromatography (Hewlett-Packard model 5972 GC-MS). The deuterium and carbon-13 contents in the products were determined from mass spectrometric data using matrix techniques that correct for ion fragmentation and natural ¹³C abundance.¹⁸ Undeuterated propane (Matheson, instrument purity >99.5%), perdeuterated propane (Isotec, chemical purity >99.0%, isotopic purity >99.0%), 2-¹³C-propane (Cambridge Isotopes, chemical purity >98.0%, isotopic purity >99.0%), propane-2,2-*d*₂ (Isotec, chemical purity >99.0%, isotopic purity >99.0%), ¹⁸O₂ (Isotec, isotopic purity >99.0%), ¹⁶O₂ (research grade, >99.999%), and propene (Matheson, C. P., >99.0%) were used as reactants without further purification. Perdeuterated water (D₂O; Isotec, chemical purity >99.0%, isotopic purity >99.0%) and distilled water (H₂O) were purified by several freeze–thaw evacuation cycles before use. Helium (research grade, >99.999%) was used as an inert diluent in all studies.

Results and Discussion

Reaction Network. Isotopic tracer and residence time studies have shown that propane reactions occur via a combination of parallel and sequential oxidation steps (Scheme 1) on VO_x-based catalysts.¹⁵ Similar reaction pathways are suggested by residence time effects on propene selectivity observed on MoO_x/ZrO₂ (Figure 1). Propene selectivity decreases with increasing contact time, as it converts to CO_x via secondary combustion pathways. Propene selectivities extrapolated to zero residence time are less than 100%, indicating that direct propane combustion reactions occur in parallel with ODH. Propene forms as the primary ODH product and CO_x forms via propene or propane combustion

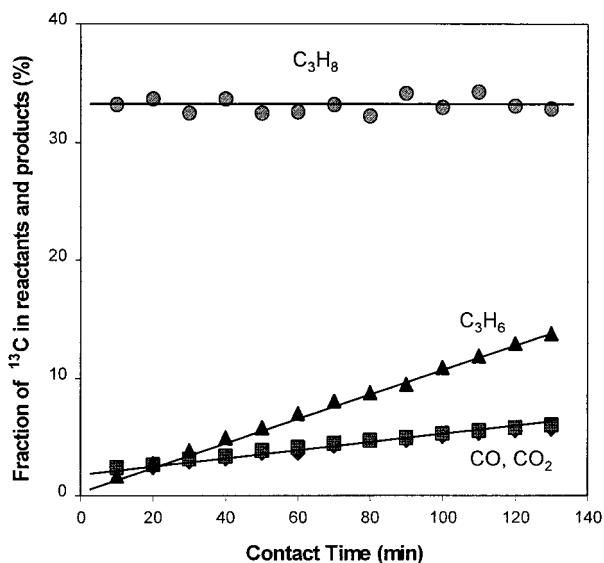


Figure 2. ¹³C content in reaction products of propene/2-¹³C propane/O₂ mixtures on MoO_x/ZrO₂ (688 K, 2.5 kPa of C₃H₈-2-¹³C, 0.5 kPa of C₃H₆, 1.7 kPa of O₂, balance He, gradientless batch reactor).

steps. The rates of propane and propene reactions in Scheme 1 can be determined from the ¹³C content in the products formed from mixtures of unlabeled propene and propane-2-¹³C.^{15,19–22} The ¹³C content in the reactants and products is shown in Figure 2 for reactions of propane-2-¹³C/propene/oxygen mixture on MoO_x/ZrO₂. The ¹³C fraction in propane remained at its initial value (0.33) throughout. Thus, the isotopic content in propane is not diluted by propene hydrogenation, as expected from the irreversible nature of the overall ODH reaction at the conditions of our study. The ¹³C fraction in propene increases with contact time, because propene-2-¹³C is gradually formed from propane-2-¹³C via dehydrogenation, at the same time as the propene isotopomers are consumed by combustion. The ¹³C fractions in CO and CO₂ were very similar, suggesting that the CO₂/CO selectivity ratios in primary propane combustion and secondary propene combustion were very similar. However, the ¹³C fraction in CO_x extrapolated to zero contact time is greater than 0, suggesting that CO_x forms via both propane and propene combustion reactions. The reaction rate constant ratio (k'_3/k'_2) for propene combustion (k'_3) to propane combustion (k'_2) can be calculated from the initial value of ¹³C in CO_x. The calculated k'_3/k'_2 value is 80 (based on the initial ¹³C fraction in CO_x). This value is very similar to the value of 87 calculated from the data in Figure 1 using the kinetic analysis procedures reported previously.⁴ Thus, these isotopic tracer results are consistent with the observed effects of reactor residence time on propene and CO_x selectivities,^{4,5,10–13} they confirm the parallel and sequential oxidation steps in ODH of propane over Mo-based catalysts.

Kinetic Dependence of Propane ODH Rates on C₃H₈, O₂, and H₂O Concentrations. The effects of varying the concentrations of C₃H₈, O₂, and H₂O on the initial rate of propene formation were determined. One kinetic rate expression was able to describe propane ODH rates on the three samples used in this study. This suggests that the elementary steps required for propane ODH reactions are similar on the surfaces of two-dimensional MoO_x oligomers (MoO_x/ZrO₂), bulk MoO₃ (MoO₃/ZrO₂), and bulk ZrMo₂O₈ (ZrMo₂O₈/ZrO₂). Here, we show detailed data on MoO_x/ZrO₂. Figure 3 shows initial propene formation rates as a function of propane partial pressure at a given value of O₂ partial pressure. Propene formation rates increased linearly with increasing propane partial pressure, in

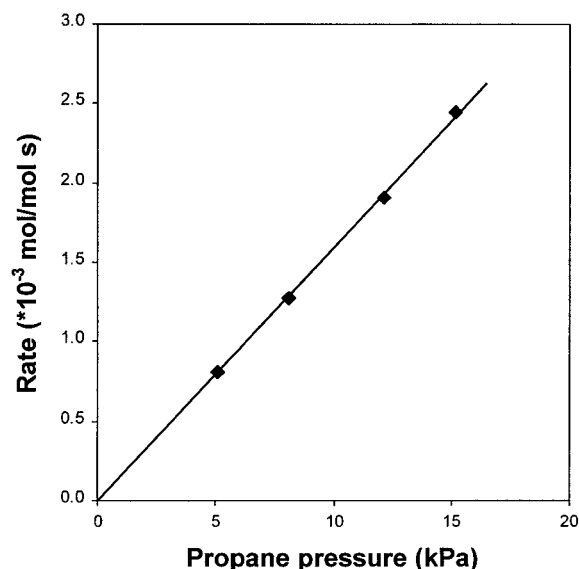


Figure 3. Effect of C₃H₈ pressure on C₃H₆ formation rate on MoO_x/ZrO₂ (703 K, 1.3 kPa of O₂, balance He).

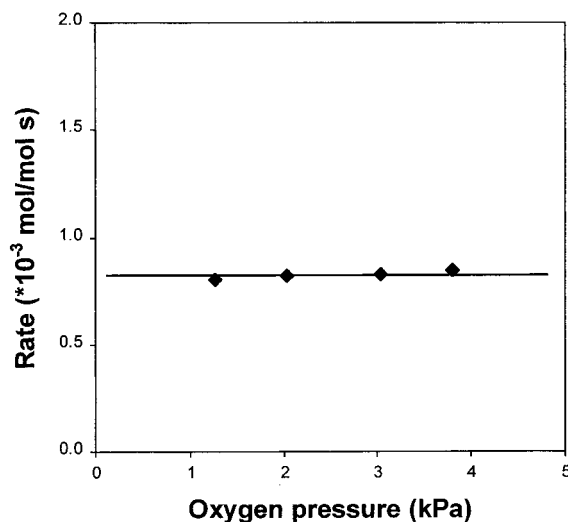


Figure 4. Effect of O₂ pressure on C₃H₆ formation rate on MoO_x/ZrO₂ (703 K, 5.1 kPa of C₃H₈, balance He).

agreement with previous reports.^{11,13–15} Figure 4 shows that initial propene formation rates are independent of O₂ partial pressure at a given propane partial pressure when H₂O is not present in the C₃H₈/O₂ feed, also in agreement with previous reports^{11–15} and suggesting a zero-order dependence on oxygen partial pressure. The effect of H₂O partial pressure on initial propane ODH rates is shown in Figure 5 at constant C₃H₈ and O₂ partial pressures. Water inhibits the rate of propane ODH, in a manner similar to that reported previously for propane and ethane ODH over V₂O₅-based catalysts.^{15,23}

Analysis of Elementary Steps. By analogy with our previous proposal on supported vanadia,¹⁵ the set of elementary steps below is used in order to describe the kinetic dependence of propene formation rates on O₂, C₃H₈, and H₂O for MoO_x catalysts. Propane ODH can be proposed based on the obtained kinetic power law rate expressions.

1. Nondissociative adsorption of propane by interaction on a lattice oxygen (O*)



2. C–H bond activation by abstraction of H atom from adsorbed propane using a neighboring lattice oxygen atom

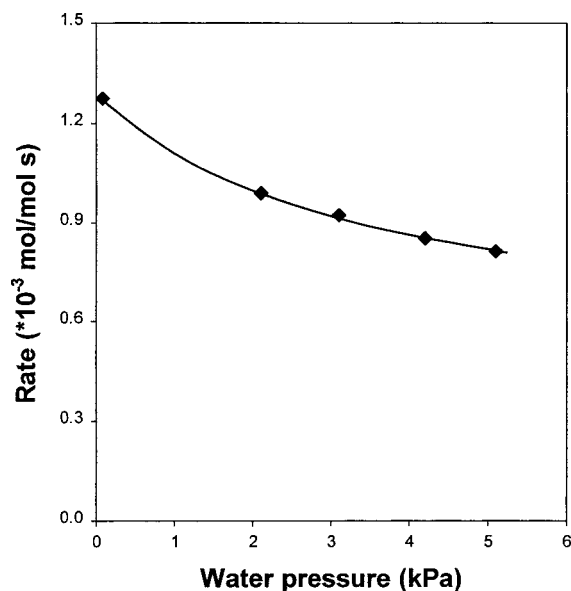
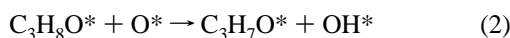


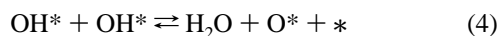
Figure 5. Effect of H₂O pressure on C₃H₆ formation rate on MoO_x/ZrO₂ (703 K, 8.1 kPa of C₃H₈, 1.3 kPa of O₂, balance He).



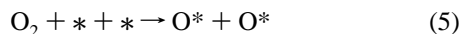
3. Desorption of propene by β -hydride elimination



4. Recombination of OH groups to form water and a reduced Mo center (*)



5. Reoxidation of Mo centers via dissociative chemisorption of O₂



In this scheme, O* is a lattice oxygen in Mo=O or Mo–O–Mo structures, OH* is a hydroxyl group in Mo–O–H, C₃H₇O* represents an adsorbed propoxide species bonded to a Mo cation through one of its O atoms (Mo–O–C₃H₇), and * represents a surface vacancy associated with either one Mo⁴⁺ or two Mo⁵⁺ cations in the MoO_x lattice.

The assumption of pseudo-steady state for all reaction intermediates leads to a complex rate expression, which can be made simpler by additional assumptions about the reversibility of specific elementary steps. Step 1 involves weak nondissociative adsorption of propane; the small expected binding energy of molecularly adsorbed propane is likely to lead to rapid reversible adsorption–desorption and to quasi-equilibration during propane ODH. Step 2 is assumed to be irreversible based on the low C₃H₈–C₃D₈ isotopic scrambling rates during ODH (shown below). The recombination of OH groups is assumed to be reversible and quasi-equilibrated, based on the observed inhibition by H₂O, which would not be possible if step 4 were irreversible, and on the results of C₃H₈–D₂O exchange rate measurements during ODH reactions (shown below). O₂ chemisorption is assumed to be irreversible based on the negligible rate of isotopic scrambling of ¹⁶O₂–¹⁸O₂ mixtures during ODH reactions (shown below). Both in situ X-ray absorption and UV–visible spectroscopy showed that MoO_x/ZrO₂ catalysts remain essentially oxidized state during propane ODH and that concentration of oxygen vacancies is very low.²⁴ The vacancy (*) concentration is likely to be much smaller than those of

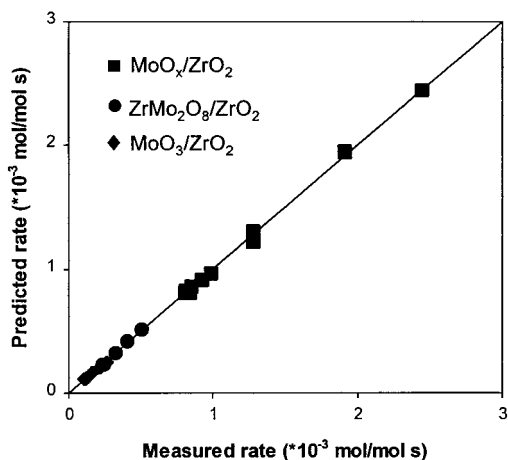


Figure 6. Comparison of predicted (from eq 6) and experimental C₃H₆ formation rates.

(O*) and (OH*) during propane ODH. These assumptions lead to the kinetic rate expression

$$r = \frac{K_1 k_2 [\text{C}_3\text{H}_8]}{[1 + K_1^{0.25} k_2^{0.25} K_4^{-0.5} k_5^{-0.25} [\text{H}_2\text{O}]^{0.5} [\text{C}_3\text{H}_8]^{0.25} [\text{O}_2]^{-0.25}]^2} \quad (6)$$

in which k_i is the rate coefficient and K_i is the equilibrium constant for reaction i . This equation predicts that the rate of propane ODH is first order in C₃H₈ concentration and zero order in the concentration of O₂ at very low H₂O concentrations. As the concentration of H₂O increases, propane ODH rate decreases, and the apparent orders in C₃H₈ and O₂ become smaller than unity and larger than zero, respectively. Figure 6 compares propane ODH rates predicted by this expression with rate data at various C₃H₈, O₂, and H₂O concentrations. The estimated rate coefficients are different for the three molybdena catalysts of this study, because these coefficients depend on the dispersion of the Mo oxide species and on the number of accessible sites. The excellent agreement shown in Figure 6 for all three catalysts, however, confirms the mechanistic resemblance of propane ODH reactions on MoO_x oligomers, bulk MoO₃, and bulk ZrMo₂O₈. This is consistent with our previously proposed kinetic equivalence of MoO_x species at polymolybdate and bulk MoO₃ surfaces.⁴ Alternate elementary steps, including propane interactions with surface vacancies and irreversible OH recombination steps, did not lead to rate expressions in satisfactory agreement with experimental rates.

Irreversible Initial C–H Bond Activation in Propane. At very low H₂O concentrations, the rate of propene formation depends linearly on C₃H₈ concentration, suggesting that propane activation is a kinetically relevant step. The reversibility of C–H bond activation steps can be probed by measuring the rate of H–D isotopic scrambling in “unreacted” propane during reactions of C₃H₈/C₃D₈–O₂ mixtures.¹⁵ If the C–H bond activation is reversible, C₃H_xD_{8–x} (0 < x < 8) isotopomers can form via the microscopic reverse of the C–H bond activation step.^{19,20} If C–H bond activation is irreversible, however, the formation of C₃H_xD_{8–x} (0 < x < 8) isotopomers will be much slower than propane conversion to propene and CO_x.¹⁵

Figure 7 shows the deuterium distribution in propane during the reaction of a C₃H₈/C₃D₈/O₂ mixture over MoO_x/ZrO₂ at ~4% propane conversion. At all propane conversions, only C₃H₈ and C₃D₈ were detected in the unreacted propane pool. No cross-exchange C₃H_xD_{8–x} isotopomers were detected by mass spec-

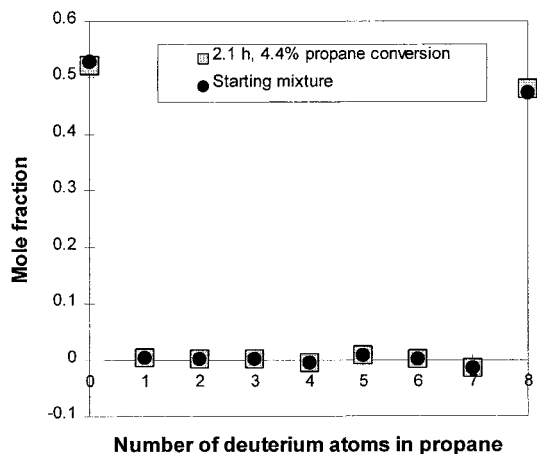


Figure 7. Deuterium cross exchange for $C_3H_8/C_3D_8/O_2$ reactant mixture on MoO_x/ZrO_2 . Deuterium distributions in reactant mixture and in “unreacted” propane (688 K, 7.1 kPa of C_3H_8 , 7.1 kPa of C_3D_8 , 1.7 kPa of O_2 , balance He, gradientless batch reactor).

trometry, suggesting that C–H bond activation is an irreversible step in the ODH reaction sequence. The isotopomer distributions were determined using deconvolution methods that neglect secondary kinetic isotope effects in the fragmentation process.¹⁸ This deconvolution procedure can lead to very small negative values of some isotopomer mole fractions (e.g., C_3D_7H in Figure 7). The mole fractions of all mixed propane isotopomers are zero within the accuracy of the measurements and the reliability of the deconvolution procedures. These conclusions are similar to those reached for propane ODH reactions on VO_x/ZrO_2 .¹⁵

The kinetic relevance of C–H (and C–D) bond dissociation steps can also be inferred from the effect of deuterium substitution on the rate of propene and CO_x formation. The reaction rate constants for ODH reactions of undeuterated (C_3H_8) and perdeuterated (C_3D_8) propane (k'_{C-H} and k'_{C-D} , respectively) were obtained from the initial rates of propene formation using $C_3H_8-O_2$ or $C_3D_8-O_2$ mixtures. Kinetic isotope effects for propane direct combustion and for secondary propene combustion can also be measured from the initial rates of CO_x formation and from the effect of residence time on propene selectivity for $C_3H_8-O_2$ and $C_3D_8-O_2$ mixtures.²⁵

A rigorous analysis of the kinetic isotope effects requires that we treat the system using the reaction network of Scheme 1. At relatively low conversions and without external H_2O addition, the rate of each of these reactions is well described by

$$r_1 = k'_1[C_3H_8] \quad (7)$$

$$r_2 = k'_2[C_3H_8] \quad (8)$$

$$r_3 = k'_3[C_3H_6] \quad (9)$$

where k_i is the apparent first-order rate coefficient for reaction i . The propene selectivity at relatively low conversions in a batch reactor is given by⁵

$$S = S^0(1 - k'_3C_v t/2) \quad (10)$$

where C_v is the concentration of Mo atoms per unit reactor volume, t is the reaction time in the batch reactor, and $S^0 = k'_1/(k'_1 + k'_2)$ is the initial propene selectivity (as t goes to zero). The initial rate of propene conversion (as $t \rightarrow 0$) gives the value of k'_1 . The initial propene selectivity (S^0) depends on the k'_1/k'_2

TABLE 2: Kinetic Isotope Effects over 11 wt % MoO_x/ZrO_2 Catalyst (688 K, 14.2 kPa of Propane, 1.7 kPa of O_2 , Balance He)

isotope	$CH_3CH_2CH_3$ $CD_3CD_2CD_3$	$CH_3CH_2CH_3$ $CH_3CD_2CH_3$	$CH_3CD_2CH_3$ $CD_3CD_2CD_3$
primary dehydrogenation $k'_{1,C-H}/k'_{1,C-D}$	2.3	1.7	1.4
secondary combustion $k'_{3,C-H}/k'_{3,C-D}$	2.1	1.1	1.8
primary combustion $k'_{2,C-H}/k'_{2,C-D}$	1.6	1.3	1.2

ratio which can then be used to calculate k'_2 . Finally, k'_3 is obtained from the dependence of selectivity on time predicted by eq 10.

Reaction rate constants ($k'_{i,C-H}$ and $k'_{i,C-D}$) for ODH of undeuterated propane, perdeuterated propane, and propane-2, 2- d_2 , were obtained from the rate of initial propene formation using reaction mixtures containing $CH_3CH_2CH_3/O_2$, $CD_3CD_2CD_3/O_2$, or $CH_3CD_2CH_3/O_2$. Kinetic isotope effects (defined as $k'_{i,C-H}/k'_{i,C-D}$ ratios) for the three reactions in Scheme 1 are shown in Table 2. When using C_3H_8 and C_3D_8 as reactants, the kinetic isotope effect is greater than unity for all reactions, suggesting the involvement of C–H bonds in kinetically relevant steps. Propane ODH and propene combustion show similar kinetic isotope effects (2.3 and 2.1, respectively) consistent with rate-determining initial C–H bond activation steps for both reactions. These similar kinetic isotope effects suggest a kinetic resemblance between these two reactions that may include the requirements for similar active surface oxygen species. The kinetic isotope effect for propane combustion (1.6) is slightly lower than for propane dehydrogenation, suggesting that the formation of propene and CO_x from propane involves different active sites, as proposed previously.^{4,5,13,25}

Propane and propene reactions involve the cleavage of C–H bonds in kinetically relevant steps. There are two kinds of C–H bonds in propane. The methyl C–H bonds have a dissociation enthalpy of 420 kJ/mol, and the methylene C–H bonds have a dissociation enthalpy of 401 kJ/mol.²⁶ Kinetic isotope effect measurements using $CH_3CH_2CH_3$ and $CD_3CD_2CD_3$ cannot determine which C–H bond is involved in the initial activation step. However, $CH_3CD_2CH_3$ is expected to react more slowly than $CH_3CH_2CH_3$ if methylene C–H bonds are involved in the initial activation step. A similar rate for $CH_3CD_2CH_3$ and $CD_3CD_2CD_3$ would indicate that only methylene C–H bonds are involved in the rate-determining step and that the isotopic identity of the rest of the propane molecule does not influence reaction rates. In turn, similar rates for $CH_3CD_2CH_3$ and $CH_3CH_2CH_3$ would indicate that only methyl C–H bonds are involved in the rate-determining step. The data in Table 2 show that $CH_3CD_2CH_3$ exhibits a normal KIE (with respect to $CH_3CH_2CH_3$) for both propane dehydrogenation (1.7) and combustion (1.3). These values are smaller than those obtained when using $CD_3CD_2CD_3$ and $CH_3CH_2CH_3$ as isotopes (2.3 and 1.6, respectively), but greater than unity, suggesting that C–H bonds in both methyl and methylene groups can be involved in the rate-determining steps required for both propane dehydrogenation and combustion at these reaction conditions. These results differ from those obtained for VO_x/ZrO_2 at 593 K (propane dehydrogenation KIE of 2.8 for $CD_3CD_2CD_3$, and KIE 2.7 for $CH_3CD_2CH_3$ vs $CH_3CH_2CH_3$).²⁵ On VO_x/ZrO_2 , KIE values clearly showed that only methylene C–H bonds are involved in the rate-determining C–H bond activation step. These differences in KIE values for MoO_x and VO_x catalysts may reflect mechanistic differences or merely the different reaction temperatures required for the two catalysts to reach

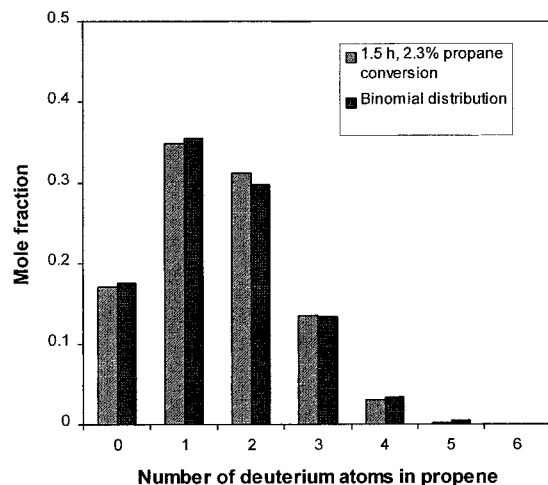


Figure 8. Deuterium distribution in propene formed from C₃H₈/C₃D₈/O₂ mixtures on MoO_x/ZrO₂ (688 K, 7.1 kPa of C₃H₈, 7.1 kPa of C₃D₈, 1.7 kPa of O₂, balance He, gradientless batch reactor).

measurable turnover rates. As a result of the lower reactivity of MoO_x catalysts, the temperature of the KIE measurements was higher (688 K) than on VO_x catalysts (593 K). Such higher temperatures would tend to decrease the selectivity for activating one specific C–H bond in propane, because bond energy difference for the two types of C–H bonds in propane is only 19 kJ mol⁻¹. Recent DFT calculations²⁷ show that C–H bonds in both methyl and methylene groups in propane can be activated on V₂O₅ species, but the activation energy for methyl C–H bond reactions was much higher (9.4 kcal mol⁻¹) than for the methylene C–H bond (14.5 kcal mol⁻¹). As a result, propene conversion pathways involving methyl C–H group activation are much more sensitive to reaction temperature than the more facile paths involving methylene C–H bonds. This would imply, in turn, that KIE values for CH₃CD₂CH₃ vs CH₃CH₂CH₃ should decrease with increasing temperature and the KIE observed for CH₃CD₂CH₃ vs CD₃CD₂CD₃ should rise with increasing temperatures. This is exactly the trend observed when KIE values on Mo-based catalysts at 688 K are compared with those the V-based catalysts at 593 K. Thus, it appears unnecessary to propose a different activation selectivity for the two types of C–H bonds in VO_x and MoO_x catalysts.

Kinetic isotopic effects for propene combustion on MoO_x/ZrO₂ catalysts were also measured; they are shown in Table 2. Propene molecules contain three types of C–H bonds.²⁶ It is not possible, however, to determine which specific C–H bond is cleaved in the rate-determining step for propene conversion to CO_x by simple inspection of KIE values using CH₃CD₂CH₃/O₂ reactants. Figure 8 shows the deuterium distribution in propene during reactions of C₃H₈/C₃D₈/O₂ mixtures. The binomial distribution of deuterium observed in propene at all chemical conversions shows that H is mobile on the catalyst surface and that multiple exchange of C₃H₆ and C₃D₆ with the surface adsorbed hydrogen (OH*/OD*) pool occurs rapidly during ODH reactions, leading to a statistical distribution of D atoms in propene molecules, irrespective of the isotopic locations in the starting mixture. Therefore, propene formed from CH₃CD₂CH₃/O₂ contains CH₃CD₂CH₃, as well as all other isotopomers (C₃H_{6-x}D_x), and as a result the measured KIE reflects an average value for all possible propene isotopomers.

H/D ratios in the propene formed from C₃H₈/C₃D₈/O₂ mixtures confirm the relative rates of C–H and C–D bond activation. The H/D ratio in the reactant mixture is approximately 1, but initial propene products have an H/D ratio

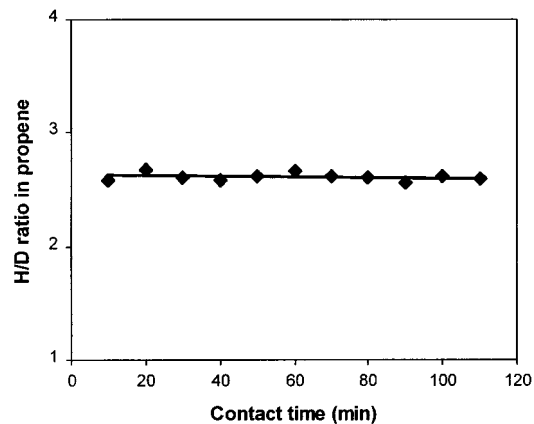


Figure 9. H/D ratio in propene formed from C₃H₈/C₃D₈/O₂ mixtures on MoO_x/ZrO₂ (688 K, 7.1 kPa of C₃H₈, 7.1 kPa of C₃D₈, 1.7 kPa of O₂, balance He, gradientless batch reactor).

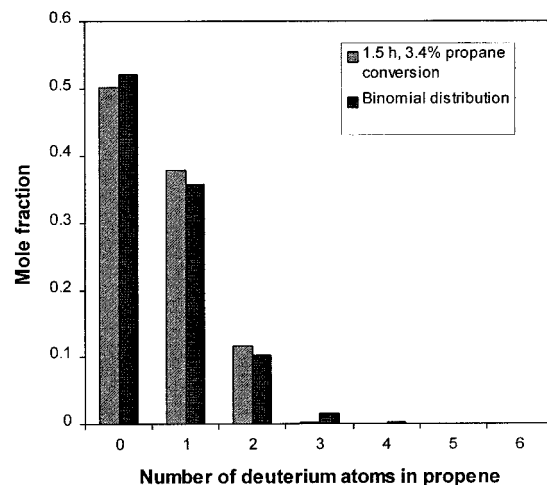


Figure 10. Deuterium distribution in propene formed from C₃H₈/D₂O/O₂ mixtures on MoO_x/ZrO₂ (688 K, 14.2 kPa of C₃H₈, 0.5 kPa of D₂O, 1.7 kPa of O₂, balance He, gradientless batch reactor).

of 2.6 on MoO_x/ZrO₂ at all contact times between 0.1 and 2 h (Figure 9). This value is very similar to that obtained for the kinetic isotope effect (2.3) from the conversion of separate C₃H₈–O₂ and C₃D₈–O₂ mixtures to propene (Table 2).

Reversible Recombinative Desorption of OH Groups To Form Water. Water forms during propene ODH reactions and it inhibits propene reaction rates (Figure 5); therefore, the formation of water must involve a reversible elementary step. This effect of water is similar to that observed for propene reactions on VO_x/ZrO₂¹⁵ and for ethane reactions on V₂O₅/SiO₂.²³ The reversible nature of the recombinative desorption of OH groups to form water was confirmed from the D-distribution in propene molecules formed on MoO_x/ZrO₂ from C₃H₈/D₂O/O₂ or C₃D₈/H₂O/O₂ mixtures. Neither mixture led to the formation of C₃H_xD_{8-x} (0 < x < 8) isotopomers in unreacted propane even at ~2 h contact times (~4% propane conversion); this confirms that C–H bond activation steps are irreversible. Binomial D-distributions were detected at all contact times in the propene molecules formed from either C₃H₈/D₂O/O₂ or C₃D₈/H₂O/O₂ (Figure 10). These data show that water dissociatively adsorbs on MoO_x surfaces during propene ODH, and that its microscopic reverse, the recombination of OH groups to form water during ODH, is therefore a reversible step. The binomial D-distributions in propene from C₃H₈/D₂O/O₂ or C₃D₈/H₂O/O₂ mixtures also suggest that H atoms formed from C–H bonds in propane and from O–H in water are mobile and that

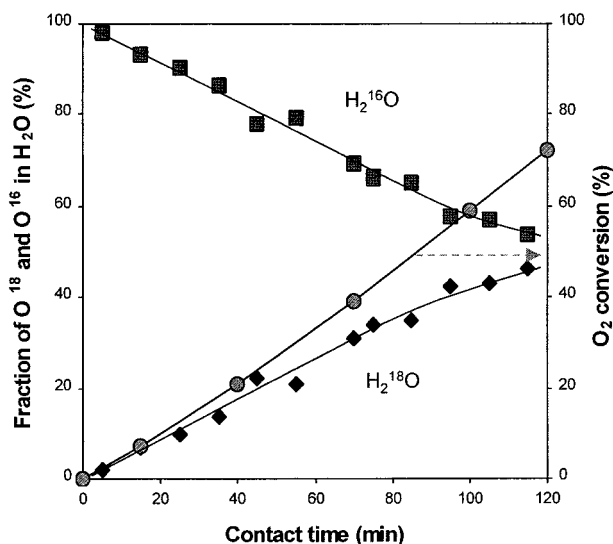


Figure 11. Fraction of ^{18}O and ^{16}O in H_2O formed during reactions of $^{18}\text{O}_2\text{-C}_3\text{H}_8$ mixtures on $\text{Mo}^{16}\text{O}_x/\text{Zr}^{16}\text{O}_2$ (688 K, 14.2 kPa of C_3H_8 , 1.7 kPa of $^{18}\text{O}_2$, balance He, gradientless batch reactor).

multiple exchange of C_3H_6 or C_3D_6 with this surface OH^*/OD^* pool occurs during propane ODH. These results are consistent with the assumption of quasi-equilibrated, recombinative desorption of OH groups (reaction 4), which was used in order to describe the inhibition of propane ODH by water. The form of the kinetic rate expression measured for propane ODH on MoO_x is more specifically consistent with the quasi-equilibration of this step.

Irreversible Oxygen Dissociation and Involvement of Lattice Oxygen Atoms. The rate of propane ODH over $\text{MoO}_x/\text{ZrO}_2$ (in the absence of added water) is independent of the O_2 concentration, suggesting that lattice oxygen atoms on a saturated surface are involved in this reaction, as also proposed by others.^{11–15} The involvement of lattice oxygen atoms was confirmed by carrying out propane ODH using $^{18}\text{O}_2$ on Mo^{16}O_x measuring the relative concentrations of ^{18}O and ^{16}O in the H_2O and CO_x products initially formed. Figure 11 shows the isotopic content in the H_2O formed from $^{18}\text{O}_2\text{-C}_3\text{H}_8$ mixtures on 11 wt % $\text{Mo}^{16}\text{O}_x/\text{Zr}^{16}\text{O}_2$. Initially, water consists predominately of H_2^{16}O , as expected if C_3H_8 reacted with lattice ^{16}O atoms in Mo^{16}O_x . As contact time increased, the H_2^{18}O concentration increased because ^{16}O atoms in the lattice are gradually replaced by ^{18}O from the $^{18}\text{O}_2$ in the gas phase. Figure 12a shows the isotopic distribution in CO_2 . Initially, the predominant isotopomer is C^{16}O_2 , suggesting that lattice oxygen atoms are also required for the combustion reactions that form CO_x . These results are consistent with those reported in the literature.^{15,28,29} Figure 12b shows the isotopic content of CO_2 as a function of reaction time. Similar to what is seen for H_2O , the percentage of ^{16}O decreases with the increase of contact time, while that of ^{18}O increases.

The reversibility of dissociative O_2 chemisorption steps was probed by using $^{18}\text{O}_2\text{-}^{16}\text{O}_2\text{-C}_3\text{H}_8$ reactant mixtures and measuring the rate of formation of $^{18}\text{O}^{16}\text{O}$ molecules, which can only arise from a reversible dissociation event. Reversible dissociative chemisorption of O_2 would lead to rapid isotopic equilibration of $^{16}\text{O}_2$ and $^{18}\text{O}_2$ during ODH reactions; irreversible chemisorption steps would preserve the isotopic purity of the reactant mixture. Figure 13 shows the rates of propane and oxygen chemical conversion and the rate of formation of $^{16}\text{O}^{18}\text{O}$ isotopomers on $\text{Mo}^{16}\text{O}_x/\text{Zr}^{16}\text{O}_2$ as a function of contact time. $^{18}\text{O}^{16}\text{O}$ molecules are formed at a rate about 100 times smaller

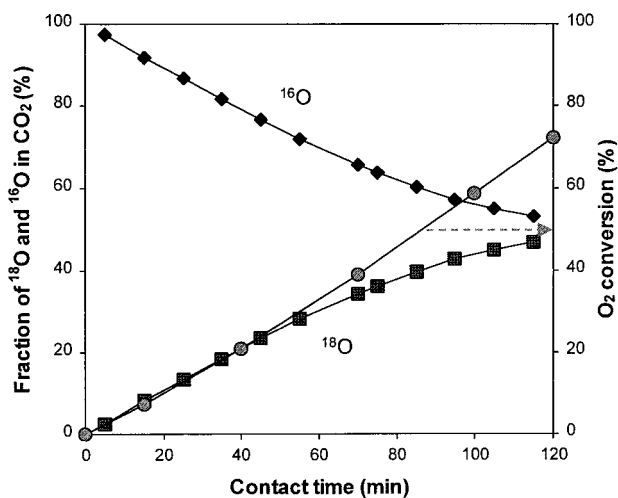
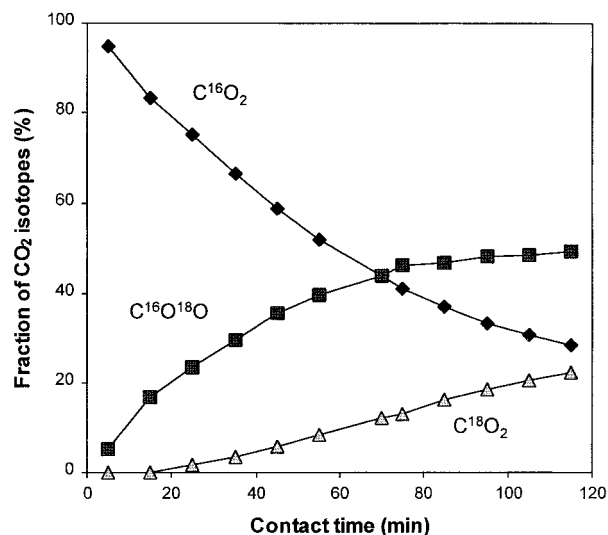


Figure 12. (a, top) Fraction of CO_2 isotopes formed during reactions of $^{18}\text{O}_2\text{-C}_3\text{H}_8$ mixtures on $\text{Mo}^{16}\text{O}_x/\text{Zr}^{16}\text{O}_2$ (688 K, 14.2 kPa of C_3H_8 , 1.7 kPa of $^{18}\text{O}_2$, balance He, gradientless batch reactor). (b, bottom) Fraction of ^{18}O and ^{16}O in CO_2 formed during reactions of $^{18}\text{O}_2\text{-C}_3\text{H}_8$ mixtures on $\text{Mo}^{16}\text{O}_x/\text{Zr}^{16}\text{O}_2$ (688 K, 14.2 kPa of C_3H_8 , 1.7 kPa of $^{18}\text{O}_2$, balance He, gradientless batch reactor).

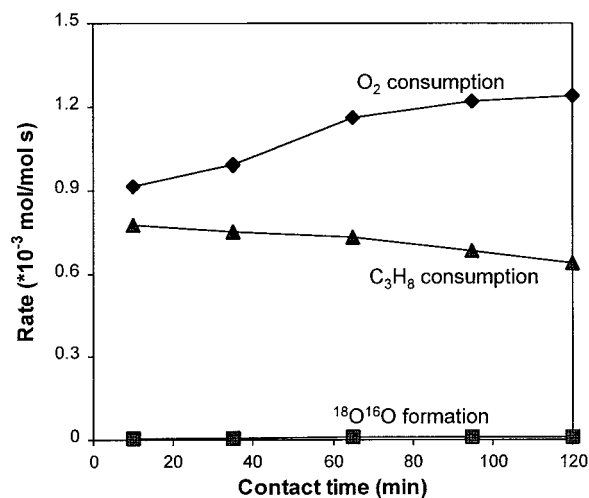


Figure 13. C_3H_8 and O_2 consumption rates, and $^{16}\text{O}^{18}\text{O}$ formation rates from $^{18}\text{O}_2\text{-}^{16}\text{O}_2\text{-C}_3\text{H}_8$ mixtures on $\text{Mo}^{16}\text{O}_x/\text{Zr}^{16}\text{O}_2$ (688 K, 14.2 kPa of C_3H_8 , 0.85 kPa of $^{18}\text{O}_2$, 0.85 kPa of $^{16}\text{O}_2$, balance He, gradientless batch reactor).

than the rate at which propane or oxygen are consumed by chemical reactions. Trace amounts of $^{18}\text{O}^{16}\text{O}$ are only observed

after a contact time of ~2 h (at ~70% O₂ conversion). This suggests that dissociative O₂ chemisorption steps (step 5) required in propane ODH are irreversible at the conditions of these experiments.

Since O₂ dissociation is irreversible and ¹⁶O¹⁸O molecules do not form during reactions of ¹⁸O₂-C₃H₈ mixtures on Mo¹⁶O_x/Zr¹⁶O₂, the amount of ¹⁶O coming from lattice oxygen can be calculated from O₂ conversion and ¹⁶O concentration in products CO_x and H₂O. The total amount of ¹⁶O in the Mo¹⁶O₃ phase supported on ZrO₂ is 80 μmol (calculated from MoO₃ concentration and amount of catalyst used). At 70% O₂ conversion, the ¹⁶O fraction in water and CO_x products is 0.5; this corresponds to 191 μmol ¹⁶O in the products, which must have come from the lattice. This value exceeds the number of lattice oxygens in the supported MoO_x phase (80 μmol), but it is much smaller than the total amount of ¹⁶O available in the MoO₃ and ZrO₂ (587 μmol) components of the catalyst. Therefore, lattice oxygens in both the MoO_x active phase and the ZrO₂ support exchange rapidly during propane ODH reactions at 688 K. Consequently, lattice oxygens from both MoO₃ and ZrO₂ support are ultimately used in propane reactions.

Conclusions

Oxidative dehydrogenation of propane on MoO_x/ZrO₂, MoO₃/ZrO₂, and ZrMo₂O₈/ZrO₂ catalysts occurs via parallel and sequential oxidation steps. Propene is the most abundant primary product. CO and CO₂ form via either secondary combustion of propene, or by direct combustion of propane. The dependences of reaction rates on C₃H₈, O₂, and H₂O concentrations are identical on supported MoO_x, MoO₃, and ZrMo₂O₈ powders, suggesting that similar active centers are present on these catalysts surfaces. The reaction kinetics are consistent with a Mars-van Krevelen redox sequence in which lattice oxygen atoms participate in the irreversible activation of C-H bonds in propane. The resulting alkyl species desorb as propene and the remaining OH groups recombine to form water and reduced Mo centers. These reduced Mo centers reoxidize by irreversible dissociative chemisorption of O₂. The recombination of OH groups to form water is reversible. The assumption that surface oxygen and OH groups are the most abundant surface intermediates leads to a rate expression that describes accurately the measured kinetics of propane ODH reactions. Isotopic tracer studies fully confirm the assumptions required in order to

describe the observed effects of reactant and product concentrations on the rate of propane ODH reactions.

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