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# Reaction Network and Kinetics of Propane Oxydehydrogenation over Nickel Cobalt Molybdate

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**Reaction kinetics and a proposed mechanism for the oxydehydrogenation of propane over $Ni_{0.5}Co_{0.5}MoO_4/SiO_2$ are described. The reaction pathway proceeds by propane oxydehydrogenation yielding propylene as the exclusive primary product. The propylene thus formed oxidizes further primarily to acrolein, which oxides still further to waste products CO and $CO_2$, and acrylic acid. The relative rate of acrolein formation from propylene is 3.5 times that of propylene formation from propane, the rate of $CO_x$ formation from acrolein is 13 times that of acrolein formation from propylene, and the rate of $CO_x$ formation from acrolein is 46 times that of propylene formation from propane. Kinetic isolation of intermediates is therefore imperative for the recovery of practical amounts of useful products, and might be achievable through dioxygen limitation in the feed or utilization of cocatalysts to produce more stable intermediates. The selective oxidation of propane to propylene and propylene to acrolein are both zero order in oxygen and first order in hydrocarbon (propane and propylene, respectively). Deep oxidation of propane (to CO and $CO_2$) is half order in oxygen and first order in propane, while deep oxidation of propylene exhibits Langmuir type dependence on hydrocarbon and is half order in oxygen. Propane/propylene competition experiments reveal that propylene competes for the same metal oxide sites on which propane activation occurs. Their respective effectivenesses are of the same order of magnitude, with propylene being favored by a factor of 2.3 at equimolar concentration. These results are consistent with a direct pathway (i.e., surface mediated reaction) for the formation of useful products from both propane and propylene, and consecutive overoxidation of sorbed intermediates leading to deep oxidation. Kinetic isotope effects for both propane $(k_H/k_D)C_3^\circ = 1.7$) and propylene ($((k_H/k_D)C_3^= = 1.9$) activation reveal methylene hydrogen abstraction and allylic hydrogen abstraction, respectively to be the rate determining steps.** © 1997 Academic Press

## INTRODUCTION

Recent research aims in selective oxidation and ammoxidation catalysis are shifting toward the activation of the less expensive and abundantly available light alkanes for their conversion to the corresponding olefins, anhydrides, acids, and nitriles, rather than by starting with the more expensive and less abundant olefins of prior years. In an earlier study (1), we reported on the behavior of single and binary metal molybdates for the catalytic oxydehydrogenation of propane to propylene. From these systems we chose the composition $Ni_{0.5}Co_{0.5}MoO_4$, supported on 20 wt% $SiO_2$ for further study of the reaction network and kinetics involved in propane oxydehydrogenation which are reported here.

## EXPERIMENTAL

The preparation of Ni–Co-molybdate, supported on $SiO_2$, (80 wt% $Ni_{0.5}Co_{0.5}MoO_4$, 20 wt% $SiO_2$) and the experimental setup for evaluating its catalytic properties have been discussed previously (1).

Reaction network studies were conducted by following the selectivity of product formation at low conversions of propane and propylene, respectively, in a manner also described earlier (1). Kinetic studies for hydrocarbon (and oxygen) dependence were performed by feeding 25 cc/min of oxygen (hydrocarbon), varying the hydrocarbon (oxygen) concentration from 6 to 42 cc/min and diluting with nitrogen to keep the total flowrate at 100 cc/min. For propane oxidation, 1 g of catalyst/560°C was used, while for propylene oxidation, 0.5 g of catalyst/500°C was used. These conditions were chosen so as to operate the reactor in a differential mode, resulting in hydrocarbon and oxygen conversions typically between 2 and 10%. Although aging of these catalysts is not significant under the conditions utilized in this study, a catalyst line-out period of 8 h was used as a precaution prior to the start of the kinetic studies.

As defined earlier (1), conversion is the fraction of feed carbon or oxygen present in all reaction products, yield is the fraction of feed carbon present in a product, and selectivity is yield divided by conversion. The background reactivity of both propane and propylene with oxygen, measured in a reactor filled with quartz chips is insignificant

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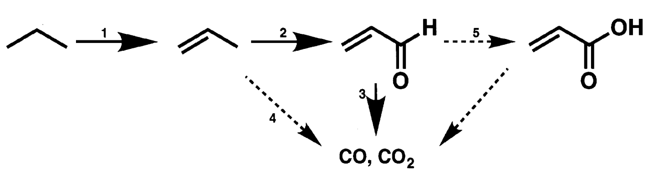
(less than 1.5% under the most severe conditions studied). Carbon and hydrogen closures were typically better than 97%, oxygen closures typically better than 95% (closures were calculated based on reaction stoichiometry, corrected for assumed water concentrations), and the results reported are then corrected for any carbon nonclosure.

## RESULTS AND DISCUSSION

### A. Reaction Network

The reaction network of propane ($C_3^{\circ}$) oxydehydrogenation over nickel-cobalt molybdate ($Ni_{0.5}Co_{0.5}MoO_4$ supported on $SiO_2$) was determined by following the selectivity of product formation at low (2 to 10%) propane conversions and, also, by examining the oxidation behavior of propylene ($C_3^{=}$) at low conversions. The observed products of propane oxidation were propylene, acrolein, acrylic acid, and carbon oxides (CO, $CO_2$); those of propylene were acrolein, acrylic acid and carbon oxides.

The selectivities of propane oxidation at 560°C to propylene, CO, and $CO_2$ are plotted as a function of propane conversion in Fig. 1a. It is observed that the selectivity to partial oxidation products (non-$CO_x$) decreases as $C_3^{\circ}$ conversion is increased (100% $C_3^{=}$ selectivity at 1.5% $C_3^{\circ}$ conversion → 76% $C_3^{=}$ selectivity at 10% $C_3^{\circ}$ conversion), but it is relatively insensitive to oxygen concentration, as 1 : 1 and 1 : 3.5 $C_3^{\circ}/O_2$ feed compositions yield similar useful product selectivities. The $C_3^{=}$ selectivity is 1 at 0% conversion, while the CO and $CO_2$ selectivities are 0 at 0% conversion. Propylene is therefore the exclusive primary product of propane oxidation, while both CO and $CO_2$ must be formed by at least one subsequent reaction step. This indicates that either propylene and/or a subsequent product derived from propylene (acrolein or acrylic acid) is unstable under the reaction conditions used in this study.



**SCHEME 1.** Reaction network of propane oxidation over $Ni_{0.5}Co_{0.5}MoO_4$.

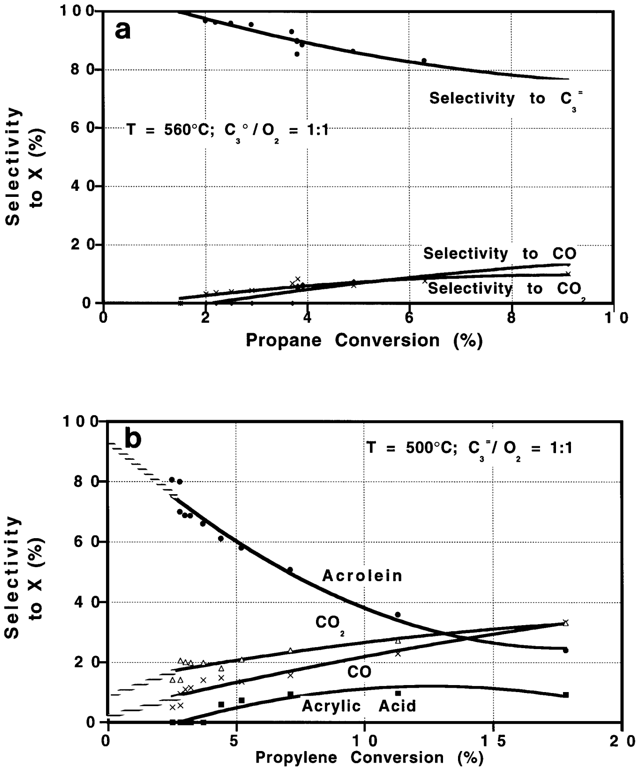


**FIG. 1.** Product selectivity profiles for propane (a) and propylene (b) oxidation over $Ni_{0.5}Co_{0.5}MoO_4/SiO_2$.

Propylene oxidation was also carried out over $Ni_{0.5}Co_{0.5}MoO_4/SiO_2$ with a 1 : 1 $C_3^{=}/O_2$ feed, at both 500 and 560°C. The results of selectivity to reaction products as a function of $C_3^{=}$ conversion at 500°C are summarized in Fig. 1b. Extrapolation to zero $C_3^{=}$ conversion indicates very high selectivity to acrolein (ca 90%), low but finite selectivities to CO and $CO_2$ (ca 3 and 7%, respectively), and zero selectivity to acrylic acid. Thus, acrolein, CO and $CO_2$ are primary products of propylene oxidation while acrylic acid is not a primary product. The relatively low selectivity to CO and $CO_2$ and high selectivity to acrolein at low $C_3^{=}$ conversion, coupled with the significantly higher selectivity to $CO_x$ (lower acrolein) at higher $C_3^{=}$ conversions, suggests that the vast majority of $CO_x$ is produced by sequential oxidation of propylene through acrolein, as opposed to a direct oxidation of $C_3^{=}$ to $CO_x$. There is only a minor direct route from propylene to $CO_x$. Acrylic acid is most likely formed by sequential oxidation of acrolein since it is a nonprimary product of propylene oxidation and its concentration increases as propylene conversion and, hence, acrolein production, increases.

The results of this study are consistent with the reaction network shown in Scheme 1. The primary reaction path is the oxidation of propane exclusively to propylene, which is then oxidized primarily to acrolein, and the acrolein thus formed is subsequently oxidized to CO and $CO_2$. Although the vast majority of waste is produced from acrolein overoxidation, minor amounts of $CO_x$ are also formed via the oxidation of propylene. Acrylic acid is produced from the oxidation of acrolein.

Selectivities to useful products from propane and propylene oxidation, respectively were also measured at higher hydrocarbon conversions (at 560°C), and the results are illustrated in Fig. 2. As is common for sequential reactions, propylene yield from propane oxidation, and acrolein yield

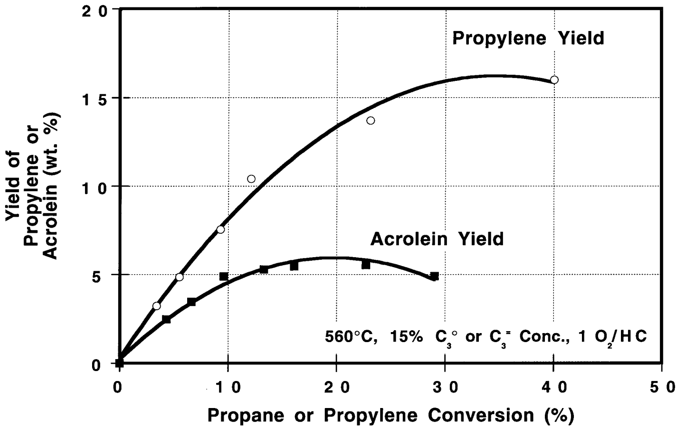


**FIG. 2.** Yields of propylene of acrolein from propane and propylene oxidation, respectively.

from propylene oxidation, increase with conversion, go over a maximum, and then decrease as hydrocarbon conversion is further increased. The maximum propylene yield achieved from propane oxidation is 16% (at 34% propane conversion), while the maximum acrolein yield from propylene conversion is 6% (at 9% propylene conversion). If we assume as a first approximation that the direct oxidation of propylene to $CO_x$ is negligible (as stated above, acrolein is nearly the exclusive primary product) and only insignificant amounts of acrylic acid are formed, we can write a simplified scheme of series reactions:

$$\text{A (propane)} \xrightarrow{k_1} \text{B (propylene)} \xrightarrow{k_2} \text{C (acrolein)} \xrightarrow{k_3} \text{D } (CO_x).$$

As will be seen below, reactions 1 and 2 are both first order in hydrocarbon disappearance. From the maximum yields reported above (16% propylene and 6% acrolein, respectively), and using equations from (16),[2] we can calculate the relative rates for the above reactions to be $k_2/k_1 = 3.5$, $k_3/k_2 = 13$, and $k_3/k_1 = 46$. Although only modest useful product yields are realized over $Ni_{0.5}Co_{0.5}MoO_4$ at these conditions, it is clear that in order to obtain high non-$CO_x$ product yields a combination of catalyst and process conditions must be found that limit both propylene and acrolein overoxidation. Although the relevant C–H bond strengths of propane and propylene are 89 and 95 kcal/mole, respectively, propylene is activated at a rate 3.5 times that of propylene. The observation is consistent with a facilitated α-hydrogen abstraction from propylene owing to the π-bond interaction of propylene with the catalyst surface, which is of course absent in propane. It is consistent with α-hydrogen abstraction being the rate limiting step in the oxidation of propylene, as is well documented in the literature (5), while the rate limiting step in the oxidation of propane is the abstraction of a methylene hydrogen.

## B. Kinetic Studies

### *Reaction Orders*

Kinetic studies of mapping reaction orders were carried out by studying the formation of useful and waste products as a function of hydrocarbon and oxygen concentrations under reaction conditions as close to a differential operating regime as possible (with propane conversions being less than 10%, and oxygen conversions less than 15%).

In the oxidation of propane at 560°C, propane disappearance is first order in propane at constant oxygen concentration (23%), and half order in oxygen at constant propane concentration (22%). The rate of partial oxidation of propane to propylene is zero order in oxygen (Fig. 3), a common behavior for hydrocarbon oxidation over metal oxide redox catalysts (2, 3), and consistent with a Mars–van Krevelen (4) mechanism. In this mechanistic scenario, if the rate of replenishment of lattice

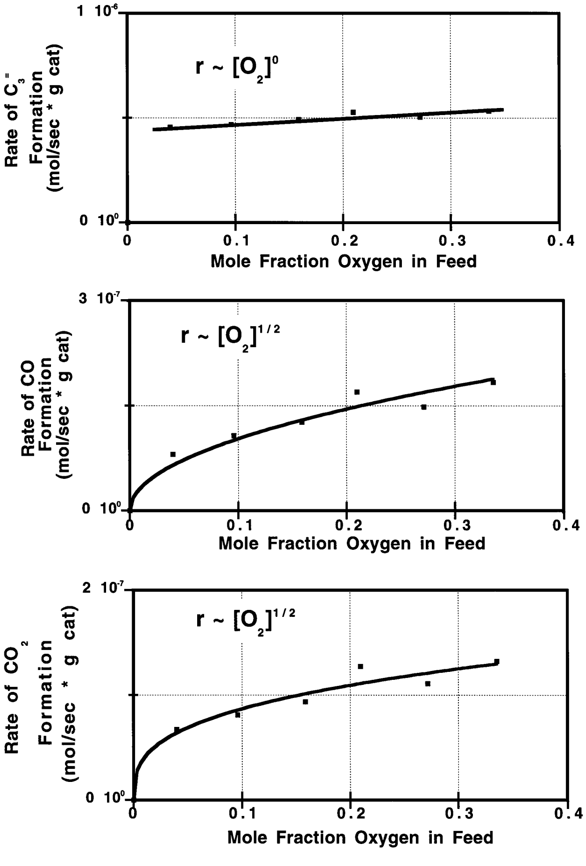


**FIG. 3.** Propane oxidation kinetics. Rates of propylene, CO, and $CO_2$ formation as a function of oxygen concentration.

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[2] For series first-order reactions, A → B → C, where the rate for these reactions is $k_1$ and $k_2$, respectively, $\beta$ is defined as $\beta \equiv [B]/[A_O]$, and $\kappa$ is defined as $\kappa \equiv k_2/k_1$. The maximum concentration of b is $\beta_{max} = \kappa^{\kappa/(1-\kappa)}$ (derivations may be found in (16, pp. 153–156)). Using numerical methods allows us to solve for $\kappa$ (3.5 and 13), from the $\beta_{max}$ of 16% and 6% maximum propylene and acrolein yields, respectively.

oxygen by gaseous oxygen is rapid, compared to the rate of removal, then the concentration of lattice oxygen at the catalyst surface is essentially constant and independent of the oxygen partial pressure in the gas phase, and the rate of hydrocarbon oxidation becomes zero-order in oxygen.

The partial oxidation of propane to propylene is first order in propane (Fig. 4) and, hence, consistent with a rate-limiting reaction between propane and a site on the catalyst surface. Therefore, propylene production from propane, over $Ni_{0.5}Co_{0.5}MoO_4$, is most likely achieved by a reaction between propane and lattice oxygen, as discussed earlier (1). The result is also consistent with that seen in selective allylic oxidation reactions (5).

Deep oxidation of propane to CO and $CO_2$ is also first order in propane, consistent with a reaction between propane and the catalyst surface (Fig. 4); however, it is half order in oxygen (Fig. 5). The data fit a half-order expression in oxygen substantially better than a Langmuir–Hinshelwood rate expression. Taking into account our results of the reaction network, where we find that $CO_x$ is produced from the consecutive oxidation of propane to propylene, which further oxidizes primarily to acrolein before acrolein is overoxidized to $CO_x$, a more complex kinetic scenario is at play in the formation of $CO_x$.

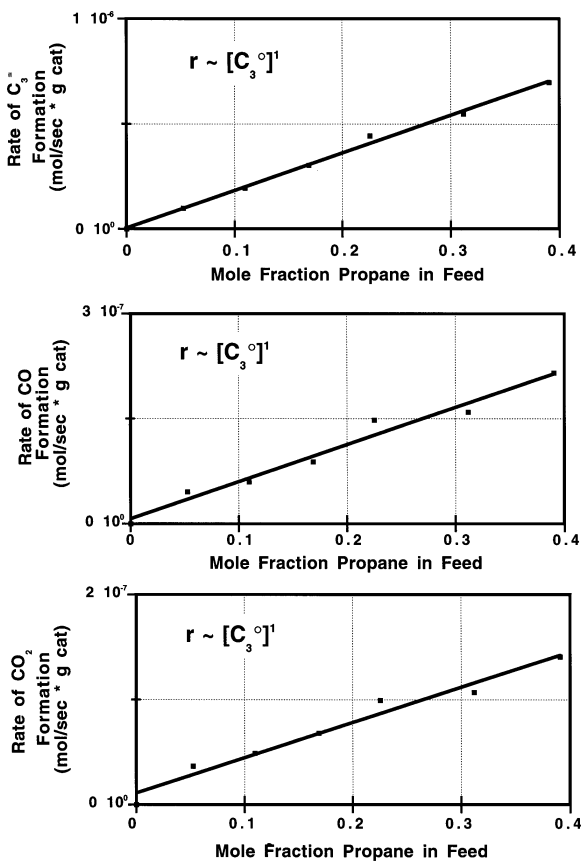

**FIG. 4.** Propane oxidation kinetics. Rates of propylene, CO, and $CO_2$ formation as a function of propane concentration.

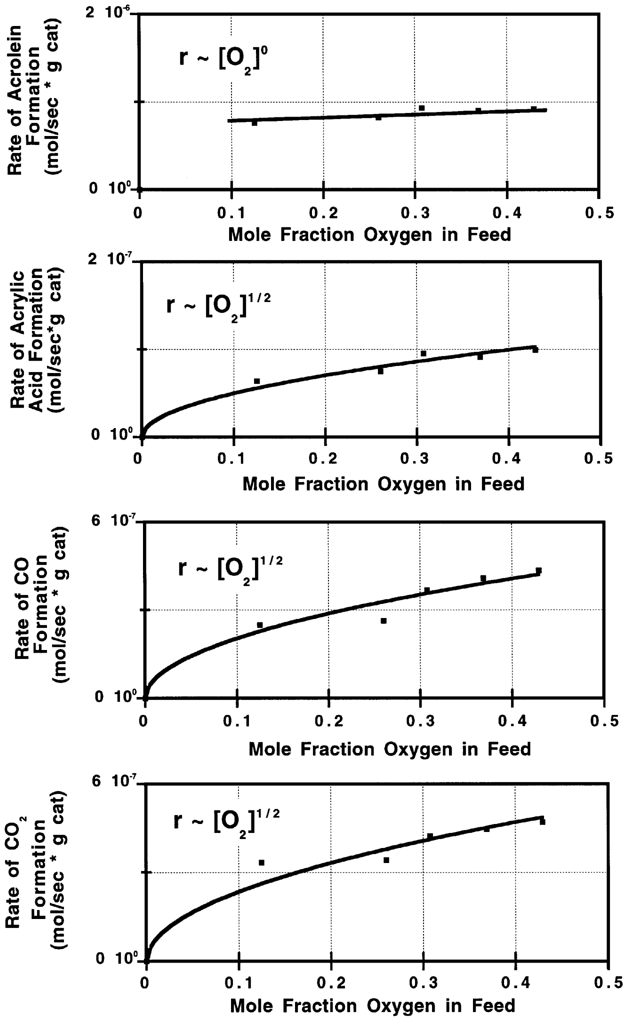

**FIG. 5.** Propylene oxidation kinetics. Rates of acrolein, acrylic acid, CO, and $CO_2$ formation as a function of oxygen concentration.

In order to gain further insights into the subsequent mechanistic steps of propane oxidation over the $Ni_{0.5}Co_{0.5}MoO_4$ system, we studied also the kinetics of propylene oxidation over this catalyst, the first formed product of propane oxidation. At 500°C, propylene disappearance is first order in propylene at constant oxygen concentration (26%) and half order in oxygen at constant propylene concentration (26%). The rate of partial oxidation of propylene to acrolein is zero order in oxygen (Fig. 5) and first order in propylene (Fig. 6). These results are consistent with those found above for the partial oxidation of propane to propylene and are common in hydrocarbon oxidation catalysis (5). The first-order dependence on propylene for acrolein formation is consistent with a rate-limiting reaction between propylene and the catalyst, and the zero-order oxygen dependence with a Mars–van Krevelen redox mechanism.

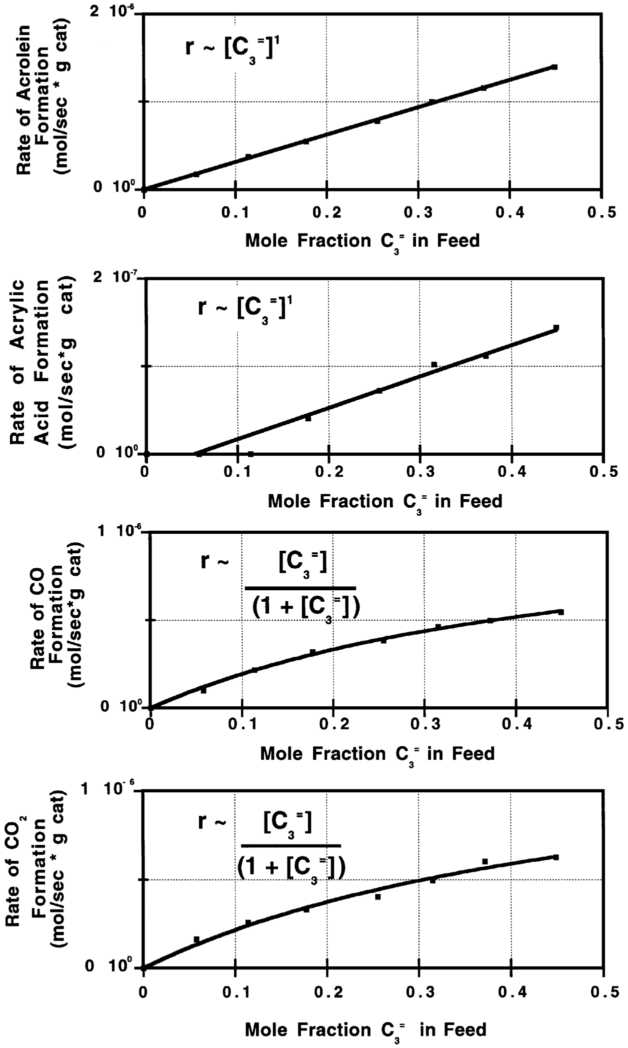

**FIG. 6.** Propylene oxidation kinetics. Rates of acrolein acrylic acid, CO, and $CO_2$ formation as a function of propylene concentration.

The rate data for waste formation from propylene to CO and $CO_2$, as a function of propylene concentration, can be fit to a Langmuir–Hinshelwood type rate expression (see Fig. 6),

$$\text{rate} \propto \frac{kx}{1 + Kx},$$

where $x =$ propylene mole fraction, $k =$ rate constant, and $K =$ adsorption equilibrium constant. The fit of our data to this rate expression is significantly better than to a half-order reaction. This typically indicates that the rate-determining step of a reaction involves a species that is in adsorption equilibrium with the gas phase. The first-order dependence found for propylene formation from propane is consistent with this rate expression as well, since as the mole fraction of propylene decreases (i.e., at low propane conversion), the denominator tends towards 1, thereby simplifying the expression to first-order hydrocarbon dependence. As was found above for propane oxidation, waste formation from propylene is half-order with respect to oxygen (Fig. 5).

The formation of acrylic acid, another secondary product of propylene oxidation, is half order in oxygen and appears to be first order in propylene (Figs. 5 and 6). The first-order fit in propylene concentration has a nonzero intercept, possibly owing to experimental difficulties in determining relatively small amounts of acrylic acid.

### *Propane/Propylene Competition Experiments*

As described above, propane oxidation is first order in hydrocarbon and zero order in oxygen, consistent with a bimolecular reaction between the hydrocarbon and the metal oxide surface. Given the finite number of metal oxide sites on which propane oxidation can occur and assuming that hydrocarbon oxidation involves an interaction between the hydrocarbon and the metal oxide sites, different hydrocarbons will compete for the same metal oxide activating sites with different degrees of success. We probed for this competition by cofeeding a mixture of propane, oxygen, and nitrogen over the catalyst, replacing portions of the nitrogen with propylene while keeping propane and oxygen partial pressures and contact times constant.

The results of these competition experiments are presented in Fig. 7. Propane conversion declines as propylene is cofed, from 8.4% to 3.6% as the propylene/propane ratio is increased from 0 : 1 to 1 : 1. The first-order rate constant for propane disappearance declines from 63 to 27 $h^{-1}$. The observed decline is consistent with propane and propylene competing for the same catalytic sites. The magnitude of the decline (by a factor of 2.3 in favor of propylene, for an equimolar propylene dilution) is consistent with propane and propylene competing with at least grossly similar effectiveness for the same sites, albeit as expected, propylene competes more effectively than propane.

It can be reasoned that the similar, rather than dissimilar, effectiveness of propane competition with propylene for the same metal oxide sites is in large measure due to the relatively high reaction temperature employed. At 560°C, the contribution from thermal C–H bond activation becomes substantial, and the effect of olefin chemisorption through the $\pi$-bond and its concomitant weakening of the $\alpha$-hydrogen bond becomes less important than at lower temperatures (e.g., 350 to 500°C).

### *Kinetic Isotope Effect*

Primary deuterium isotope effects for the activation of propane and propylene over $Ni_{0.5}Co_{0.5}MoO_4$ were determined. The measurements consisted of establishing relatively low, steady state hydrocarbon conversions over the catalyst with the proteo-hydrocarbon ($C_3H_8$ or $C_3H_6$), then switching to the respective per-deuterated hydrocarbon ($C_3D_8$ or $C_3D_6$) and again establishing steady state conversions. Relative rate constants for the disappearance of

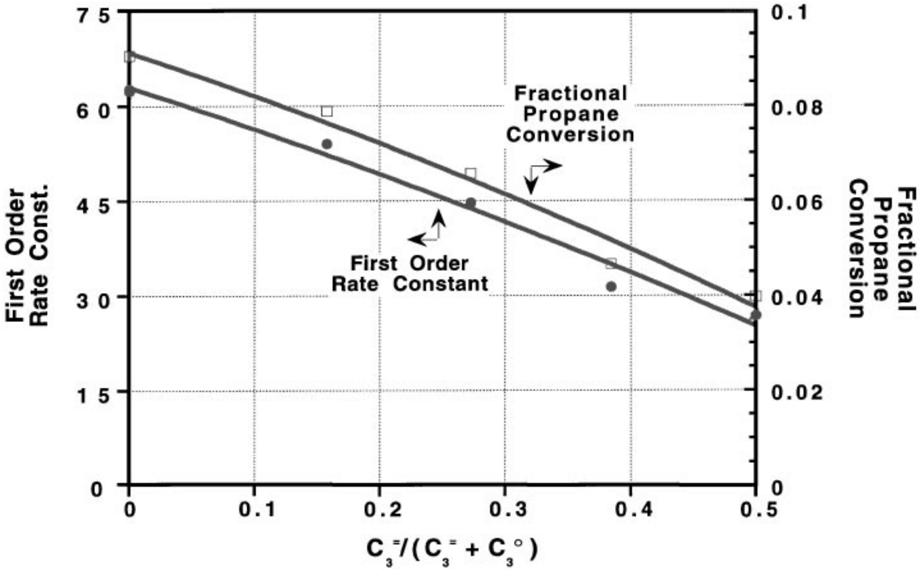

**FIG. 7.** Propylene/propane competition experiment.

hydrocarbon, and the theoretical primary kinectic isotope effects, are as follows[3]:

| Catalyst | Propane disapp. $k_H/k_D$ | Propylene disapp. $k_H/k_D$ |
|---|---|---|
| $Ni_{0.5}Co_{0.5}MoO_4$ | 1.7(1) | 1.9(3) |
| $Mg_4V_2Sb_2O_x$ | 2.3(1) | 1.1(3) |
| Theoretical maximum primary KIE | 1.95 (at 560°C) | 2.06 (at 500°C) |

For both propane and propylene oxidation over $Ni_{0.5}Co_{0.5}MoO_4$, the large KIE's are consistent with C−H bond breaking being the rate-determining step for both propane and propylene oxidation and with a relatively symmetric transition state. The relatively large KIE observed for propylene activation is consistent with data reported previously for effective olefin oxidation catalysts, over which propylene is oxidized very selectively to acrolein (6).

The activation of alkanes over many vanadium-based systems is thought to involve the homolytic cleavage of a C−H bond to yield an alkyl radical species (8). The large KIE observed for propane activation over $Mg_4V_2Sb_2O_x$ (9), a vanadium-based, light alkane upgrading catalyst, is consistent with this hypothesis. For propylene activation over $Mg_4V_2Sb_2O_x$, the KIE is close to unity. The observed differences in KIE's for these hydrocarbons are consistent with activation of the allylic C−H bond in propylene being facile, readily leading to overoxidation over $Mg_4V_2Sb_2O_x$, relative to the homolytic C−H bond cleavage for propane (i.e., vanadium sites are too proficient in their radical-like character). This may be one of the reasons why nickel-cobalt molybdates are more selective than vanadium-based systems for propylene production from propane.

### *Kinetic Model*

The kinetics of propane and propylene oxidation over $Ni_{0.5}Co_{0.5}MoO_4$ suggest that the partial and deep oxidation of the hydrocarbons occur by two distinctly different mechanisms.

The partial oxidation of propane to propylene, and propylene to acrolein can be described by a Mars–van Krevelen mechanism in which adsorbed hydrocarbon reacts with lattice oxygen:

(a) For propane:

$$C_3H_8 + \sigma_{HC} \Leftrightarrow C_3H_8\,(a) \qquad [1]$$

Fast, reversible

$$C_3H_8\,(a) + O_L \rightarrow C_3H_6 + H_2O + V_L \qquad [2]$$

Rate-determining

$$O_2 + 2\,V_L \rightarrow 2\,O_L \qquad [3]$$

Fast

(b) For propylene:

$$C_3H_6 + \sigma_{HC} \Leftrightarrow C_3H_6\,(a) \qquad [4]$$

Fast, reversible

$$C_3H_6\,(a) + 2\,O_L \rightarrow C_3H_4O(a)\ (\text{acrolein}) + H_2O + 2\,V_L \qquad [5]$$

Rate-determining

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[3] All KIE measurements were carried out at 500°C, except for propylene oxidation over $Mg_4V_2Sb_2O_x$, which was carried out at 440°C. Estimates for certainties are shown in parentheses (3-sigma values; 95% confidence limits). Derivations of the primary KIE's listed are described in (12).

$$C_3H_4O\,(a) \Leftrightarrow C_3H_4O + \sigma_{HC} \qquad [6]$$

Fast, reversible

$$O_2 + 2\,V_L \rightarrow 2\,O_L \qquad [3]$$

Fast.

Conversely, deep oxidation of propylene to $CO_x$ may be described by a Langmuir–Hinshelwood mechanism in which adsorbed hydrocarbon reacts with dissociatively adsorbed oxygen:

$$C_3H_6 + \sigma_{HC} \Leftrightarrow C_3H_6\,(a) \qquad [4]$$

Fast, reversible

$$O_2 + 2\,\sigma_O \Leftrightarrow 2\,O\,(a) \qquad [7]$$

Fast, reversible

$$C_3H_6\,(a) + 3(x+1)O\,(a) \rightarrow 3\,CO_x + 3\,H_2O \qquad [8]$$

Rate-determining

and

$$C_3H_6 + \sigma_{HC} \Leftrightarrow C_3H_6\,(a) \qquad [4]$$

Fast, reversible

$$C_3H_6\,(a) + 2\,O_L \rightarrow C_3H_4O(a)\ (\text{acrolein}) + H_2O + 2\,V_L \qquad [5]$$

Rate-determining

$$O_2 + 2\,V_L \rightarrow 2\,O_L \qquad [3]$$

Fast

$$C_3H_4O\,(a) \Leftrightarrow C_3H_4O + \sigma_{HC} \qquad [6]$$

Fast, reversible

$$O_2 + 2\,\sigma_O \Leftrightarrow 2\,O\,(a) \qquad [7]$$

Fast, reversible

$$C_3H_4O + \sigma_{H^+} + O\,(a) \rightarrow [C_3H_4O_2]\,(a) \qquad [9]$$

Rate-determining

$$[C_3H_4O_2]\,(a) + 3x\,O\,(a) \rightarrow 3\,CO_x + 3\,H_2O + \sigma_{H^+} \qquad [10]$$

Fast, irreversible.

In the above equations, (a) denotes an adsorbed species; $\sigma_{HC}$ and $\sigma_O$ hydrocarbon and oxygen adsorption sites, respectively; $O_L$ and $V_L$ lattice oxygen and lattice oxygen vacancy, respectively; $\sigma_{H^+}$ a strongly acidic site; and $[C_3H_4O_2]$ (a) an oxygenated, surface-adsorbed intermediate on its way to be further oxidized to $CO_x$ waste products.

In our studies of the propane oxidation network, we found that $CO_x$ is produced exclusively by the sequential oxidation of propane to propylene, which then further oxidizes primarily to acrolein before deep oxidation to $CO_x$ occurs. Thus, both sets of reactions [4]–[8] and [4]–[10] describe the deep oxidation of propylene, with reactions [4]–[10] being the predominant pathway for $CO_x$ production.

Simple rate expressions can be derived from these two mechanisms under the following assumptions: First, the rate-determining steps are assumed to be first order in each reactant. Second, propylene and oxygen are assumed to be in adsorption equilibrium, and their surface coverage's are assumed to be small. Third, reoxidation of the catalyst surface is rapid enough for the surface to remain fully oxidized during the reaction; therefore the concentration of lattice oxygen remains constant and is independent of the prevailing gas phase composition. Finally, under the differential reaction conditions used in this study, the concentrations of all products in the gas phase are small; therefore their surface coverages are assumed to be negligible. Under these constraints, the partial oxidations of propane to propylene, and propylene to acrolein, are described by

$$r_{C_3^=} = k_{C_3^=}\, x_{C_3^\circ}\, (O_2)^\circ \qquad [11]$$

$$r_{\mathrm{Acrolein}} = k_{\mathrm{Acrolein}}\, x_{C_3^=}\, (O_2)^\circ. \qquad [12]$$

The deep oxidation rates of propylene to CO and $CO_2$ (abbreviated as $CO_x$) are both described by the rate expression:

$$r_{CO_x} = \frac{k_{CO_x}\, x_{C_3^=}\, x_{O_2}^{1/2}}{(1 + K_{C_3^=}\, x_{C_3^=})} \qquad [13]$$

In these expressions, $x_{C_3^\circ}$, $x_{C_3^=}$ and $x_{O_2}$ are the mole fractions of propane, propylene, and oxygen in the gas phase, $k_{C_3^=}$ $k_{\mathrm{Acr.}}$, and $k_{CO_x}$ are the rate constants of propylene, acrolein, and $CO_x$ production, $K_{C_3^=}$ is a propylene adsorption equilibrium constant, and $(O_2)^\circ$ denotes the zero-order oxygen dependence.

These rate equations best describe our observations. Since we studied only the rate of acrolein formation from propylene and not, also, the rate of acrolein disappearance to waste products starting with acrolein, we cannot unequivocally close the loop of the rate of acrolein disappearance and the rate of waste formation from acrolein. Nonetheless, our data support a first-order dependence on propylene for the formatin of acrolein (Eq. [12]) and a Languimir–Hinshelwood dependence (Eq. [13]) for the formation of waste from propylene. We can reason that at the higher concentrations of propylene, i.e., when starting with propylene as feed, the formation of acrolein is first order in propylene as observed, because the $\alpha$-hydrogen abstraction of propylene is, as customary (5), the rate-determining step. The subsequent step, the disappearance of acrolein, probably involves a site other than the propane and/or propylene adsorption site ($\sigma_{HC}$), most likely a strong surface acid site ($\sigma_{H^+}$), for which propylene also competes favorably. Hence, at high propylene concentrations its competition for this site helps inhibit waste formation, with the result that a Langmuir–Hinshelwood relationship is observed for waste formation. At low propylene concentrations, a condition prevailing when propane is the feed material, the formation of acrolein is also deemed to be first order in propylene (i.e., there is no a priori reason for it to be anything else). However, the Langmuir–Hinshelwood relationship for waste formation reduces to a first-order dependence (Fig. 4), since the concentration of the first-formed product propylene is low, with the consequence that the above-postulated acrolein reaction sites are much less likely blocked by propylene and acrolein readily combusts to waste products, as our experiments indicate (i.e., only minor amounts of acrolein are observed when starting with propane as feed; Fig. 1 and Ref. (1)). Additional studies involving the exact fate of acrolein combustion are needed to further confirm our kinetic deductions, as well as in situ spectroscopic studies to assess the nature of the adsorbed, waste forming, oxygenated intermediate(s).

The rate of propylene formation from propane, as well as the formation of acrolein from propylene, are both zero order in oxygen, consistent with a Mars–van Krevelen mechanism (Figs. 3 and 5). The rate of waste products ($CO_x$) from propane and propylene are half-order in oxygen, consistent with a reaction of chemisorbed hydrocarbon intermediates with dissociatively adsorbed oxygen on the catalyst surface (Figs. 3 and 5).

### C. Mechanistic Implications

The effective functioning of olefin upgrading catalysts centers on their ability to efficiently activate the olefinic substrate, abstract hydrogen from it, insert oxygen and/or nitrogen into the sorbed organic moiety or remove a second hydrogen from it, provide for rapid electron exchange and lattice vacancy migration, efficiently regenerate the active catalytic sites (i.e., to achieve rapid metal oxide lattice regeneration), and allow for the desorption of desired products prior to their overoxidation by the catalyst to undesired products (5). For example, catalysts for the production of butadiene from 1-butene are extremely effective, e.g., yields of butadiene of 99+% have been achieved with selected catalysts (10), because they efficiently activate the olefinic substrate to form a $\pi$-allyl sorbed butenyl species, abstract a second hydrogen to form sorbed butadiene, and allow for the release of butadiene into the gas phase before further oxidation to waste products can occur. Since the vinylic C–H bonds of the product butadiene are significantly stronger than the allylic ones of the reactant butene (108 vs 89 kcal/mol), a catalytic system sufficiently effective to activate the weaker allylic C–H bond but not efficient enough to activate the relatively strong vinylic C–H bonds, allows butadiene desorption to occur without its overoxidation to $CO_x$. Catalysts employed industrially for the selective oxidation of propylene to acrolein and ammoxidation to acrylonitrile, are chemically relatively similar to butadiene synthesis catalysts. They are also effective at allylic C–H activation, but also at oxygen and/or nitrogen insertion (11). They are not effective at the overoxidation of the aldehyde and nitrile intermediate products to $CO_x$, because among others they allow for ready desorption of these formed products before overoxidation can occur. The presence of cofed and/or coproduced bases (water, ammonia) aids also the displacement of the sorbed desired intermediates.

In contrast to these systems, the activation of paraffins requires a relatively proficient site on which paraffinic C–H activation can occur. Therefore, many catalytic systems investigated have relied upon an inorganic radical for the alkane activation process. In particular, vanadium has the ability to homolytically activate C–H bonds proficiently, allowing for the low temperature, selective oxidation of butane to maleic anhydride over vanadyl pyrophosphate (12), the ammoxidation of propane over V-Sb-based catalysts to acrylonitrile (3, 8), and the activation of substituted aromatics (13) and heteroaromatics (14) over variously supported vanadium-containing catalysts to form, in the presence of ammonia, the corresponding nitriles. In all of these systems, a critical parameter in their effective functioning is that the product is oxidatively quite stable—that is, the proficiency of vanadium sites to oxidatively activate C–H bonds is constrained to the reactant because the product has C–H bonds significantly more difficult to activate than the reactant (e.g., maleic anhydride vs *n*-butane; acrylonitrite vs propane). Another important factor for the efficiency of the above catalysts is structural site isolation of paraffin activating sites (17). This prerequisite needs still to be worked out for Ni–Co-molybdates in the future, through compositional modifications.

Our study of propane oxidation kinetics and its reaction network, taken in the context of the requirements and effectiveness of selective olefin oxidation catalysts, sheds some light on why the yields of useful products from paraffins (e.g., propylene from propane) are modest. The activation of propane to form propylene is completely selective, as determined in our network study, and the activation of propylene to acrolein is also highly selective. These two reactions follow a Mars–van Krevelen mechanism, where the rate-limiting step involves a bimolecular reaction between lattice oxygen (i.e., nucleophilic oxygen) of the catalyst and the hydrocarbon, as is the case for the vast majority of the selective olefin oxidation catalysts. In contrast, deep oxidation reactions from acrolein follow a mechanistic pathway whereby the rate-limiting step is a reaction between adsorbed hydrocarbon and chemisorbed oxygen (i.e., electrophilic oxygen). In our present study we observed that propylene and propane sorption are competitive, as is presumably also the sorption of acrolein. Thus, hydrocarbon desorption from the catalyst surface may severely limit ultimate useful product selectivities; i.e., under the conditions used for propane upgrading, the residence time of the formed propylene and particularly that of acrolein is long relative to the time required for propane activation. Slow desorption of acrolein concomitant with it being attacked by adjacently adsorbed electrophilic oxygen, or its readsorption on some strongly acidic catalyst site (probably associated with molybdenum) and subsequent attack by adsorbed oxygen, are particularly implicated as the primary cause of waste $CO_x$ formation from propane, since the Langmuir–Hinshelwood rate dependence for $CO_x$ formation from propylene implies its formation from a later-formed product, i.e., acrolein.

Two ways may be envisioned to improve product selectivities under such circumstances: one is to form oxidatively more stable products (i.e., acids, anhydrides, nitriles); the other is to sacrificially add auxiliary bases (i.e., water, methanol, pyridine, thiophene, ammonia) which may effectively displace the product, or prevent its undesirable readsorption prior to its overoxidation. For example, acrylonitrile and acrylic acid (possible products starting from propane as feed) are oxidatively much more stable than propylene or acrolein, the first and second formed products from propane. Thus, combining and temperature matching (1) a paraffin activating catalyst such as Ni–Co-molybdate with an olefin ammoxidation catalyst such as a mixed metal multicomponent molybdate (11), and cofeeding ammonia with propane and air (or oxygen) should lead to desirable yields of acrylonitrile directly from propane.

## CONCLUSIONS

**1.** The primary reaction path of propane oxydehydrogenation is exclusively to propylene. The formed propylene oxidizes subsequently primarily to acrolein, which oxidizes further to waste products, CO and $CO_2$. Although the majority of waste is produced from acrolein overoxidation, $CO_x$ is also formed in small quantities from propylene. Acrylic acid is produced from further oxidation of acrolein.

**2**. Propane conversion to propylene is first order in propane, and the conversion of propylene to acrolein is first order in propylene. Both are zero order in oxygen.

**3**. Deep oxidation of propane to $CO_x$ is first order in propane and half-order in oxygen. Deep oxidation of propylene to $CO_x$ has Langmuir–Hinshelwood dependence in propylene and half-order in oxygen.

**4**. From conclusions 2 and 3 it follows that propane and propylene are converted to propylene and acrolein, respectively by (nucleophilic) lattice oxygen of the catalyst and that the replenishment of the lattice oxygen by gaseous dioxygen is fast, compared to the hydrogen abstraction from propane and propylene, respectively (i.e., Mars–van Krevelen mechanism). Deep oxidation of propane and propylene to $CO_x$ occurs by chemisorbed (electrophilic) oxygen on the catalyst surface, implied by the half-order dioxygen dependency and, particularly, by the sharp increase of $CO_x$ with an increase in dioxygen concentration.

**5**. Propane/propylene competition experiments reveal similar reaction efficiencies for both propane and propylene on the $Ni_{0.5}Co_{0.5}MoO_4$ catalyst surface.

**6**. The large primary kinetic isotope effects ($k_H/k_D$) of 1.7 for propane disappearance and 1.9 for propylene disappearance confirm that methylene hydrogen abstraction is the rate-limiting factor in propane activation and $\alpha$-hydrogen abstraction in the propylene activation.

**7**. Conclusions 2 through 6 are consistent and support the mechanistic scheme (conclusions 1) that propane is activated by surface sites on the $Ni_{0.5}Co_{0.5}MoO_4$ catalyst via methylene hydrogen abstraction, yielding propylene as the sole primary product. The so-formed propylene desorbs and competes for the same sites as propane, whereby $\alpha$-hydrogen is abstracted from the propylene and nucleophilic oxygen (probably lattice oxygen associated with Mo=O) is inserted from the catalyst surface to form acrolein. Acrolein and propylene can react further on the surface with chemisorbed (electrophilic) oxygen to give waste products $CO_x$, and some acrylic acid (the latter coming exclusively from acrolein).

**8**. The relative reaction rates are $k_{acr}/k_3^{=} = 3.5$, $k_{CO_x}/k_{acr} = 13$ and $k_{CO_x}/k_3^{=} = 46$, implying that kinetic isolation of intermediates is imperative for the recovery of practical amounts of useful products. This could be achieved in at least two possible ways:

a. Based on our kinetic analysis, secondary products, $CO_x$ and acrylic acid, are derived from the intermediately formed propylene and acrolein, and since their yield increases with the half-power of oxygen concentration it is likely that higher yields of propylene and/or acrolein could be obtained from propane in the absence of cofed oxygen, i.e., in a redox mode utilizing the lattice oxygen of $Ni_{0.5}Co_{0.5}MoO_4$ alone, with periodic dioxygen regeneration after depletion of the available lattice oxygen of the catalyst. This could be realized in practice by employing multiple reactors or a transfer line reactor configuration (i.e., moving bed).

b. Since reaction efficiencies for both propane and propylene are of the same order of magnitude on $Ni_{0.5}Co_{0.5}MoO_4$, combining the paraffin activating catalyst $Ni_{0.5}Co_{0.5}MoO_4$ (preferably Cr modified) with a temperature matched, multicomponent molybdate catalyst, efficient in olefin and/or acrolein selective oxidation and/or ammoxidation, should lead to good recoverable yields of desirable products such as unsaturated acids (e.g., acrylic acid) or nitriles (e.g., acrylonitrile).

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