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The structure–function relationships in selective oxidation reactions over metal oxides

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Abstract

Oxidation catalysis over metal oxide surfaces continues to pose major challenges for catalysis researchers. The surface of a metal oxide catalyst under reaction conditions is a dynamic one, with multiple adsorption–desorption, reduction–oxidation steps taking place. Lattice oxygen diffusion, formation of defects and surface restructuring may all be important molecular processes that play a role in determining the catalytic performance. Although, catalytic activity is often thought of in terms of a single active site, the determining factor for activity and selectivity may be a combination of several competing phenomena, involving multiple active sites and/or their interaction and proximity to each other. Some of the earlier work that addressed the questions regarding structural specificity, synergy, role of promoters, and support effects are reviewed in an effort to provide examples of structure–function relationships of metal oxide catalysts in oxidation reactions.

Keywords: Alkali promoter; Halide promoter; Silica–titania support; Molybdenum oxide catalysts; Use of methyl iodide in coupling reactions; Structural specificity; Oxygen spillover

1. Introduction

Many important industrial processes are centered on catalytic selective oxidation reactions. About one quarter of the value produced worldwide via catalytic reactions stems from partial oxidation processes. The contribution of these processes to the national economies of industrialized countries is very significant [1]. It is therefore highly important to acquire a fundamental understanding of selective oxidation catalysis while continuing to improve the performance of existing catalysts while developing new ones. Oxidation catalysts can be quite complex, often with multiple phases and with different active sites to fulfill multiple functions, hence requiring the study of the role of each phase and their interaction under working conditions. Multiple functions the selective oxidation catalysts need to perform may include activation of the organic molecule, hydrogen abstraction, oxygen activation, oxygen insertion, and regeneration of the active site(s). During selective oxidation and oxidative dehydrogenation (ODH) of hydrocarbons, non-selective mechanisms can also exist, in which oxygen, from the lattice or activated from the gas phase, can be inserted into the hydrocarbon, and several reaction steps advance ultimately to form carbon oxides. For selective catalysts, an optimal balance should exist between the oxygen activity, acid–base characteristics, and lattice diffusivity. It is therefore essential for an oxidation catalyst to possess a certain degree of structural and/or phase complexity. Intermediate reducibility, weak Lewis acid centers, and oxygen mobility represent the characteristics determined to be essential for selective oxidation. However, quantitative correlations between these properties and catalytic performance cannot easily be obtained and these characteristics are therefore usually expressed as a ‘‘good-mix’’ or ‘‘favorable balance’’ between acid–base characteristics and redox behavior. The ‘‘favorable’’ oxygen that can provide this requirement is that which binds strongly enough to the surface to have oxidizing strength but weakly enough to oxidize the reactant molecule selectively. Over supported transition-metal oxides, the species of interest exist in the form of M=O, M–O–M, or M–O-support bonds, where M is

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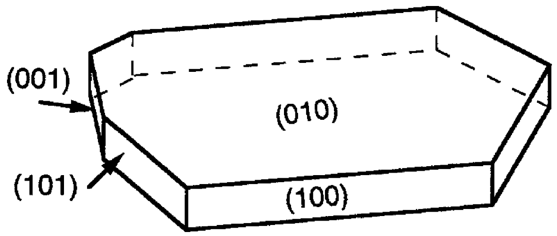
the supported transition-metal. The nature of the active oxygen can be tuned by variations in transition-metal loading, dispersion, support effects, and by the addition of modifiers. Since different organic molecules of interest may possess different reactivities, a finely tuned oxidation catalyst for one hydrocarbon may not be optimized for another. Hence, control of selectivity requires that not only the rate limiting step (hydrocarbon activation) be studied but that the rates of all intermediates from the start of hydrocarbon activation up to the final product be coordinated in such a way as to avoid the accumulation of intermediates that can give rise to non-selective oxidation pathways. The development of methods for independent control and optimization of these non-rate limiting, single step reaction rates by modifying the surface catalyst characteristics would be a breakthrough in the control of selectivity in selective oxidation [2].

Transition metal oxides may exhibit very different behavior when supported compared to their performance in unsupported form. When supported, transition metal oxides often exist as isolated species at low loading levels. However, as loading increases, poly-aggregates or clusters form, and crystalline domains can appear above monolayer coverage. The strength of the M–O-support bonds can be altered by the type of oxide support and can serve as a basis for the structure–function relationship over supported metal oxide catalysts. The structure of supported metal oxide species can be significantly altered by addition of a promoter, or dopant. Doping is a frequently used method to modify the physical–chemical properties of a transition metal oxide catalyst. Dopants may act as structural promoters by enhancing surface area or promoting a certain supported metal oxide structure or may be directly involved in the surface catalysis due to additional acid–base or redox properties they introduce. Additionally, the activity of M–O–M and M–O bonds (or reduced M ± O centers) can differ significantly under reaction conditions. The extent of reduction and resulting coordination of the metal cations can be a function of the hydrocarbon of interest and this degree of reduction can affect the state of bound oxygen during operating conditions. In this article specific examples from our work in selective oxidation are cited to address some of these issues.

2. Structural specificity of crystalline metal oxides

Studies on the reactivity of highly oriented crystalline MoO_3 catalysts have given insight into the structure–function relationship in the transformation of hydrocarbons due to specificity of reactions over different crystal planes preferentially exposing different abundances of transition metal–oxygen bonds.

The structure of orthorhombic molybdenum oxide can be described as being made up of heavily distorted octahedra or tetrahedra in which there are five different Mo–O bond distances [3]. Many studies have shown that the basal facets (the (0 1 0) surfaces) favor the deep oxidation of hydrocarbons through participation of strongly basic, electrophillic oxygen [4–7], while the side planes (the (1 0 0) and (1 0 1) surfaces) show a higher selectivity to partial oxidation products (Fig. 1). Additionally, studies of the conversion of propene to acrolein, methanol to formaldehyde, 1-butene and isobutene oxidation, and the oxidation of ethanol indicates that selective and unselective oxidation pathways require specific Mo–O bonds on both the side and the basal planes [8]. Intuitively, nucleophilic oxygen groups on the catalyst surface are necessary for C–H bond activation while weaker and longer metal–oxygen bonds favor the insertion of oxygen into organic molecules.



(010) Basal Plane
(100) Side Plane
(001), (101) Apical Planes

Fig. 1. Orthorhombic MoO_3 crystal faces.

We have studied [9,10] the partial oxidation of methane to formaldehyde on molybdenum oxide crystals with differing amounts of basal (0 1 0) and side (1 0 0) plane areas. The samples were prepared by differing thermal treatments and verified by X-ray diffraction (XRD), Raman spectroscopy, and scanning electron microscopy (SEM). X-ray diffraction yielded the relative intensity ratios of the sum of intensities of the d-spacing related to the side and basal planes. Raman spectroscopy has shown relative intensity changes of bands at $818\ cm^{-1}$ and $996\ cm^{-1}$, which are associated with the stretching vibrations of Mo–O–Mo bonds and Mo=O stretching vibrations, respectively. Catalysts which had a higher (0 1 0)/(1 0 0) plane ratios also had higher relative intensities for the M–O–M bands with respect to M=O bands. Stereo SEM images were used to accurately determine the crystallographic areas of the samples for correlation to reaction performance. Steady-state reaction studies verified the existence of structural specificity of molybdenum trioxide in partial oxidation of methane. In addition to methane, possible reaction intermediates and products were also used as feed materials, including methanol, formaldehyde, and carbon monoxide. The reaction experiments were performed at a temperature range of 550–650 °C and at slightly above atmospheric pressures. The feed composition was varied to assess the effect of oxygen concentration on the formaldehyde selectivity. The molybdenum trioxide crystals which preferentially exposed the (1 0 0) planes were shown to be much more selective to partial oxidation products as in the case of methane oxidation to formaldehyde. Intermediate oxidation studies showed that methanol could not be ruled out as an intermediate in the reaction scheme; however any methanol that was produced was likely to react further into other reaction products under the reaction conditions used. Additional studies on the structural specificity of molybdenum oxide crystallites in C_4 hydrocarbon oxidation revealed a similar behavior. Oxidation studies performed by using four different hydrocarbons (1-butene, 1,3-butadiene, furan, and maleic anhydride) showed a pronounced difference in behavior related to crystal structure [11]. The catalysts with a higher percentage of the (0 1 0) plane promoted complete oxidation, whereas with the lower percentage of basal plane, catalyzed selective oxidation more readily. The (1 0 0) plane was found to have sites that are capable of incorporating a limited amount of oxygen into the hydrocarbon molecules.

The studies of this structural specificity have led to interesting observations, not only on involvement of each specific site in the hydrocarbon conversion process, but to the oxidation–reduction process occurring at each. The role of lattice versus gas phase oxygen was investigated using a transient isotopic labeling technique under steady-state reaction conditions. This technique involved switching from a feed stream that contained $^{16}O_2$ to a second stream that contained $^{18}O_2$ without disturbing the steady-state. Isotopic labeling technique was also utilized in conjunction with laser Raman spectroscopy using isotopically labeled gas phase oxygen for identifying active sites. These studies led us to suggest that formaldehyde formation takes place over Mo=O sites and uses lattice oxygen. The Mo–O–Mo sites, on the other hand, appeared to be involved in the complete oxidation step. These results also indicated that the re-oxidation of these sites could take place by both gas phase oxygen and by diffusion of lattice oxygen through the solid, however, the replenishment of oxygen at the Mo=O sites by lattice diffusion seemed to be much faster as evidenced by the observation that 99% of all oxygen in formaldehyde long after the isotopic switch was still unlabeled. This conclusion was supported by Raman experiments in which partially reduced samples were exposed to $^{18}O_2$ for re-oxidation. Raman bands associated with Mo=O stretching vibrations were seen to re-gain their intensity without changing position or width while bands associated with Mo–O–Mo vibrations only partially re-gained their intensity but more interestingly experienced a slight band shift with a corresponding broadening. The combined results therefore have suggested that Mo–O–Mo bonds in the crystalline samples are more easily re-oxidized by gas phase oxygen.

Previous evidence of structural specificity has been revealed during the 1970s and 1980s using a wide variety of delicately prepared crystals and single crystal faces. Although we limit our discussion to molybdenum oxide, other structure function relationships have been reported for tungsten, vanadium, and several mixed molybdate and vanadate catalyst systems for a variety of hydrocarbon selective oxidations. For example, crystalline V_2O_5 catalysts preferentially exposing basal (0 1 0) planes were found to promote direct oxidation of NH_3 more readily than nitric oxide reduction during selective catalytic reduction (SCR) of nitric oxide with ammonia [12]. The difference in catalytic activity and selectivity to N_2 was related to the relative abundance of V=O sites exposed on the catalysts surface. However, a more complete description of the catalyst surface must include not only the crystal termination layer but the configuration and participation of defects. When equilibrium is established between oxygen atoms of the gas phase and the catalyst, the surface is populated by transient oxygen species (i.e., O^-, O_2^-), which are strongly electrophillic that can be responsible for complete oxidation [4]. It should also be anticipated that the relative surface concentration of these oxygen species will also depend on the degree of reduction of the oxide. Indeed it has been found [13] that oxygen migration through the crystalline bulk also exhibits a form of specificity. Thus, the surface can be covered by steps, point defects, and new sites created by the removal of oxygen atoms to form reduced metal cations, all of which can significantly affect catalytic activity [14]. These characteristics need not be initiated by reaction with a gas phase molecule as they may also form thermally.

3. Synergy effects and oxygen spillover phenomenon

Synergy in catalysis is defined as a mutually advantageous conjunction or compatibility of two distinct catalytic phases that creates an enhanced activity or selectivity greater than that achieved by the individual components. Early work on the catalytic activity of $NiMoO_4$ [15–17] and $CoMoO_4$ [18] has shown that these simple molybdate catalysts show a pronounced change in their selective oxidation performance when an excess of MoO_3 is present. When the Mo to metal ratios are larger than 1:1, the MoO_3 surfaces, which are in intimate contact with the simple molybdate phase, are the active component which determine the selectivity to maleic anhydride during C_4 oxidation. Our previous studies on manganese molybdate-promoted molybdenum trioxide ($MnMoO_4/MoO_3$) [19–21] have shown a strong synergy effect between the two phases in the partial oxidation of C_4 hydrocarbons to maleic anhydride. Characterization was conducted over MoO_3, $MnMoO_4$, and several samples of MoO_3 impregnated with $MnMoO_4$ all calcined at 500 °C for 5 h. Scanning electron microscopy provided visual evidence of the coexistence of the MoO_3 and $MnMoO_4$ phases after impregnation. Raman spectroscopy showed an increase in bands associated with $MnMoO_4$ that corresponded to an increase in its percentage in the samples. However, no change in the Raman spectra was observed that would signal a lattice structure change in MoO_3 following impregnation. In the oxidation of 1-butene, a remarkable increase in the selectivity to maleic anhydride was observed over the mixed phases ($\sim$51%) as compared to the pure compounds of

MoO_3 (10.9%) and $MnMoO_4$ (0%) during reaction run with equal surface area. Additionally, the same phenomenon was observed in several experiments conducted over a wide range of temperatures, oxygen partial pressure, and conversions [22]. We have also investigated these phenomena over $CdMoO_4/MoO_3$ catalysts and observed a similar synergistic effect between the two phases [23]. Oxidations run with 1,3-butadiene and furan as the feed hydrocarbon showed the same trend [24]. In maleic anhydride oxidation experiments, $MnMoO_4$ was found to be the most active. The two-phase catalyst system showed a high sensitivity to gas-phase oxygen concentration, but the presence of excess O_2 seemed to favor the formation of maleic anhydride rather than the formation of complete oxidation products.

Subsequent studies on these mixed phase catalysts have revealed that pure MoO_3 used lattice oxygen almost exclusively for the formation of partial oxidation products, but had very low oxygen uptake. $MnMoO_4$, on the other hand, was not very efficient in utilizing lattice oxygen, but had a high oxygen uptake under reaction conditions [25]. Transient response experiments of 1,3-butadiene oxidation performed using isotopically labeled oxygen and high temperature oxygen uptake measurements performed over fresh and reduced catalysts suggested a catalytic job distribution between the two phases of the $MnMoO_4/MoO_3$ catalysts where oxygen from the MoO_3 lattice was incorporated into the hydrocarbon molecule, resulting in a partially oxidized product (i.e., furan, maleic anhydride), and the MoO_3 sites were regenerated through an oxygen spillover mechanism from the $MnMoO_4$ phase. In pulse experiments, molybdenum trioxide was seen to be much more active in the absence of gas-phase oxygen than in its presence. These findings suggest that there may be a competition between oxygen and the hydrocarbon for the same catalytic site over MoO_3 surface. The simple molybdate phase, on the other hand, had very little activity in the absence of gas-phase oxygen. If this is the case, then the synergy effect may be operating though an oxygen spillover process where an active form of oxygen for reoxidizing the sites on MoO_3 is provided by the $MnMoO_4$ phase.

Additional characterization using in situ Raman spectroscopy was performed over this catalyst to further examine the role of lattice and gas-phase oxygen [26]. Catalyst samples were reduced under a stream of 5% 1,3-butadiene in nitrogen at 450 °C for 1 h. The cell was then pressurized with a 10% $^{18}O_2/N_2$ mixture for 30 min, flushed, and re-pressurized with this mixture for three cycles. Raman spectra obtained over this two-phase catalyst system in fresh form and after reduction with 1,3-butadiene and re-oxidation with $^{18}O_2$ showed very distinct shifts in the MoO_3 band positions due to the isotope effect (Fig. 2). The band at 818 cm^{-1}, associated with Mo–O–Mo stretching, was shifted to 790 cm^{-1}, with only a shoulder remaining in the original position. The band located at 991 cm^{-1}, Mo=O stretching, was also split into two parts, one at 935 cm^{-1} and one at the original location. The bands corresponding to $MnMoO_4$ did not show any shift, providing further evidence to the use of lattice oxygen from MoO_3. Control experiments were performed in which the catalysts were reduced with 1,3-butadiene and re-oxidized with $^{16}O_2$. The band positions did not change, providing proof that the shifts observed following re-oxidation with $^{18}O_2$ were actually due to the isotope effect.

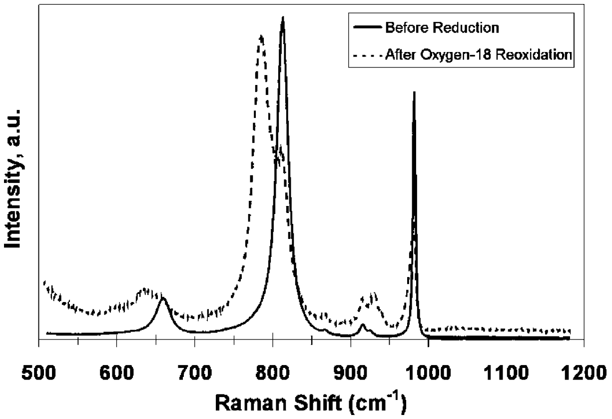


Fig. 2. Laser Raman spectra of $MnMoO_4/MoO_3$ before reduction and after reoxidation with $^{18}O_2$.

When the evaluation of the synergistic effect was extended to include *n*-pentane and 1-pentene oxidation to maleic and phthalic anhydrides [27], it was still observed that the mixed phase catalysts provided better selectivity to partially oxidized products than the pure phases. Temperature programmed desorption experiments of adsorbed C_5 molecules led to the conclusion that MoO_3 contains the sites for preferential activation of pentane. In addition, even though a complete characterization has not been performed on the effect that the mixed phases have on surface adsorption/desorption phenomena, the TPD data have suggested that the presence of the two phases (MoO_3 and $MnMoO_4$) in close proximity may also influence partially oxidized product desorption from the surface of these synergistic catalysts.

Synergistic effects have been observed in other metal oxide systems in both oxidation reactions and oxygen exchange capacity. Gaigneaux et al. [28] have observed increases in both the conversion of isobutene and the selectivity to methacrolein in a mixture of oriented (0 1 0) MoO_3 and α-Sb_2O_4. The antimony oxide phase was found to produce spillover oxygen, which flows onto the MoO_3 surface to reconstruct the (0 1 0) face into steps exposing the (1 0 0) faces. The oxygen "acceptor" sites on the (0 1 0) face of MoO_3 are likely reduced sites created by reaction with the hydrocarbon. Synergistic effects in the presence of antimony oxide have also been reported in the oxidative dehydrogenation of propane when using manganese vanadate catalysts [29]. These effects were observed to the highest degree, when the α-Sb_2O_4 present in the catalysts did not form additional phases with the manganese or vanadium. The authors explained the observed increases in propane conversion and propane yield effects through a oxygen spillover mechanism that inhibits the unselective mechanism. To explain the synergy effects between two or more oxides, Delmon and co-workers [30] have proposed a remote control effect based on three assumptions: (i) the catalyst is composed of two phases, an acceptor phase and a donor phase, (ii) the acceptor phase is the center for hydrocarbon activation and can have, when alone, a low activity in selective oxidation, and (iii) the donor phase generally has no selective oxidation activity. The role of the donor phase is to produce spillover oxygen species.

4. Suboxides of transition metals

It is accepted that the oxidative dehydrogenation of lower alkanes proceeds via an overall Mars–van Krevelen redox mechanism on many catalyst systems in which the alkane is activated by lattice oxygen of the catalyst to ultimately form an olefin through several possible intermediate surface structures. Gas-phase oxygen then serves the role of re-oxidizing the catalyst surface. However, while it has been found for many ODH reactions that the oxygen from the catalyst lattice can solely perform ODH in the absence of gas-phase oxygen, the exact role of gas-phase oxygen in the selectivity is often more complex. Thus, many ODH reactions are classified as having two different types of oxygen participating in the reaction. The first type is the lattice oxygen that reacts giving both olefins and carbon oxides. The second type of oxygen is adsorbed oxygen on the catalyst surface that reacts in a non-selective way to give CO_x [31]. This description is congruent to the idea of selective nucleophillic oxygen species and electrophillic non-selective species originally put forth by Haber et al. [32]. It is generally believed that gaseous oxygen must be converted to a more active form or be incorporated into an oxide matrix before it will appear in oxidation products [33]. Surface oxygen species can exist as mononuclear or molecular, neutral or charged. It is often assumed that adsorbed molecular oxygen can accept electrons one by one until ultimately forming O^{2-} lattice ions [34]. Thus, several kinds of active oxygen species such as O^-, O_2^-, and O^{2-} have been detected on the surface of oxidation catalysts and the nature of these active oxygen species depends not only upon reaction conditions, but strongly on the degree of reduction of the catalyst surface and the metal oxide structure.

The different forms of oxygen and their role in activation and partial oxidation of lower alkanes continue to pose a challenge for catalysis researchers. In the case of pentane oxidation to form phthalic anhydride, the challenge is even greater since the catalyst needs not only to activate the alkane molecule, but also promote the formation of C–C bonds in an oxidative medium. The earlier studies we performed in this area using 1-pentene as feed indicated that once the first oxidative dehydrogenation step is eliminated, alkene oxidation proceeds readily towards maleic and phthalic anhydride formation. Interestingly, the use of 1-pentene as the feed caused a bulk reduction of the catalyst from V_2O_5 to VO_2 despite the presence of excess gas-phase oxygen [35,36]. Vanadium oxides containing vanadium ions in lower oxidation states have not been significantly explored for their catalytic ability. Several characterization studies have been performed on these species, which indicate their potential for oxidation reactions. For instance, it has been theoretically and experimentally shown that the surface concentration of V=O species is higher on oxidized V_6O_{13} and V_2O_4 catalysts than on V_2O_5 [37,38]. Adsorption studies over V_2O_5 demonstrate that the V=O bonds are located on the (0 1 0) plane, while the (1 0 0) plane contains partially reduced vanadium ions.

Based on these results, a study was undertaken in our laboratory in an effort to further examine the activity of partially reduced vanadium oxide catalysts in pentene oxidation experiments [39]. It was hypothesized that suboxides of vanadium may give rise to better catalytic performance than oxidized states based upon different oxygen diffusion characteristics and/or structural specificity of the V–O bonds. Samples of vanadium oxide were subjected to an in situ, controlled reduction step before the catalyst was exposed to the reaction feed. The temperature of this reduction was varied over a range of 350–600 °C. The surface composition of these reduced samples was determined using controlled-atmosphere X-ray photoelectron spectroscopy (XPS) (Table 1). Fig. 3 presents the phthalic anhydride yield obtained as a result of different pre-reduction temperatures. The data are plotted as a function of surface vanadium-to-oxygen ratio. The optimum reduction temperature appears to be near 400 °C based upon the reaction results. At the higher reduction temperatures, 450 and 600 °C, a loss of activity is observed. The optimum oxygen to vanadium ratio appears to be significantly lower than 2.5, suggesting a sub-stoichiometric oxide surface.

Table 1
Suboxides of vanadia observed by XPS on catalysts reduced at different temperatures

Reduction temperature (°C)	Phases observed by XPS (%)
No reduction	V_2O_5: 100
350	V_2O_5: 23 V_4O_9: 60 VO_2: 17%
400	V_4O_9: 64 V_6O_{13}: 5 VO_2: 31
450	V_6O_{13}: 28 V_2O_3: 70 V: 2
600	V_6O_{13}: 26 V_2O_3: 67 V: 7

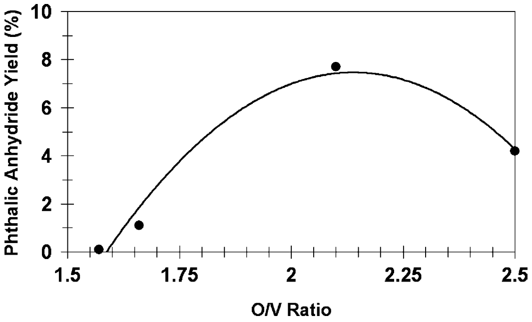


Fig. 3. Phthalic anhydride yield as a function of surface vanadium-to-oxygen ratio.

Molybdenum oxide based catalysts are also believed to operate effectively as oxidation catalysts under slightly reduced conditions where the presence of Mo(V) is essential [40,41]. Furthermore, it has been cited that Mo(V) is the active site in propane ODH and other oxidation reactions over MoO_x based catalysts [42–44]. While Mo(V) is, in all probability, related to the active sites of MoO_x catalysts, it seems more likely that the electronic structure of MoO_x domains (explicitly the nature of the oxygen atoms) is the underlying factor in determining "activity" over the supported Mo catalysts. Some of our previous work has focused on altering the electronic nature of supported MoO_x over Mo/Si:Ti 1:1 catalysts domains through the addition of low levels of halide promoters (chlorine). While many studies have shown the positive effects of halide introduction to the feed and its subsequent modification of the catalyst surface in order to enhance the homogeneous radical reaction in the ODH of ethane, there are significant environmental implications associated with the use of chlorinated compounds as feed materials. Furthermore, the stability of chlorine phases on the catalyst surface at high temperatures can also contribute to the release of chlorine. There have been previous reports in the literature citing effect of chlorine on the surface properties by creating active centers, improving dispersion, stabilizing chemical phases, adjusting reducibility, and modifying lattice oxygen mobility over different catalytic systems [45–50]. Our previous work focused on determining if molybdenum oxide based catalysts, modified with chlorine, operated at lower temperatures (<650 °C), are able to modify the nature of MoO_x domains and thus the redox mechanism of ethane and propane ODH. When altered in such a way, we have found not only a pronounced improvement in the ODH activity of these catalysts, but also significant change in the reducibility of the MoO_x domains [51,45].

To investigate the effect of chlorine on the interaction of propane with the catalyst surface after contact at high temperatures, samples were placed inside an atmosphere/vacuum quartz tube and contacted with 800 Torr of oxygen at 550 °C for 30 min, purged to 10^{-3} Torr for 30 min, and "reduced" with 500 Torr of propane at 400 °C for 30 min. This was followed by evacuation at 10^{-3} Torr and a backfill with helium. The samples were subsequently analyzed by XPS, ESR, and Raman spectroscopy. The post-reduction XPS spectra acquired over the Mo/Si:Ti 1:1 and (Cl/Mo = 1.0)/Si:Ti 1:1 catalysts are presented in Fig. 4. The Mo 3d region of the pre-reduction spectrum (not shown) exhibited one linked doublet, characteristic of Mo (VI) species in an oxide matrix. The spectrum taken following propane reduction, on the other hand, showed the co-existence of the Mo(VI)/Mo(V)/Mo(IV) oxidation states, corresponding to Mo $3d_{5/2}$ and $3d_{3/2}$ binding energy values at 235.6/234.6/232.2 and 232.4/231.4/228.9 eV, respectively. Different from Mo-only catalyst, the spectrum over Cl-doped catalyst only showed the co-existence of the Mo(VI)/Mo(V) oxidation states after reduction with propane. In agreement with our previous results from temperature programmed reduction with hydrogen [51], in which the major reduction peak shifts to higher temperature range with the addition of chlorine, this shows that the incorporation of chlorine could modify the reducibility of the MoO_x species. The total extent of reduction of Mo(VI) species is larger over the Mo-only catalyst, and it mainly comes from further reduction to Mo(IV). For both Mo-only and Cl-doped catalysts after propane reduction, the change of *g*-tensor values calculated from ESR spectrum (not shown) indicated that reductions with propane are accompanied by a coordination state change of the $Mo(V)O_x$ domains from hexa- to penta-coordinated, indicating the loss of an oxygen from Mo(V) species [52].

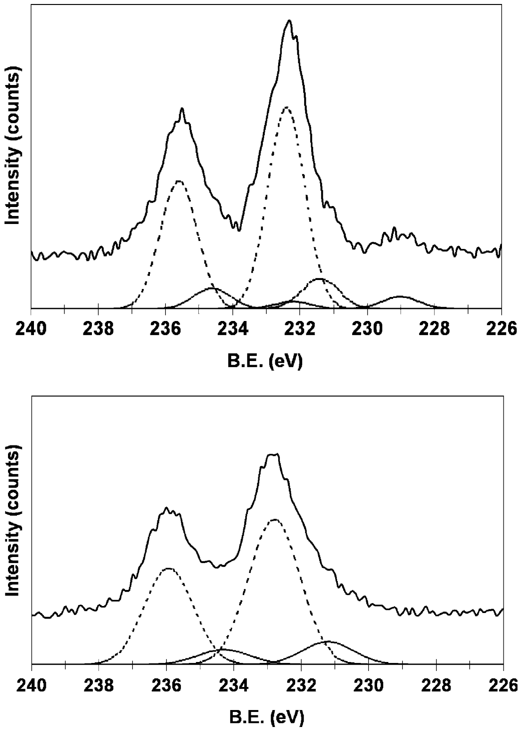


Fig. 4. Post-propane reduction X-ray photoelectron spectra of 10% Mo/Si:Ti = 1:1 (top) and 10% (Cl/Mo = 1.0)/Si:Ti = 1:1 (bottom) catalysts.

The Raman spectra for 10% Mo/Si:Ti = 1:1 and 10%(Cl/Mo = 1.0)/Si:Ti 1:1 catalysts before and after reduction with propane are plotted in Fig. 5 in the molybdenum–

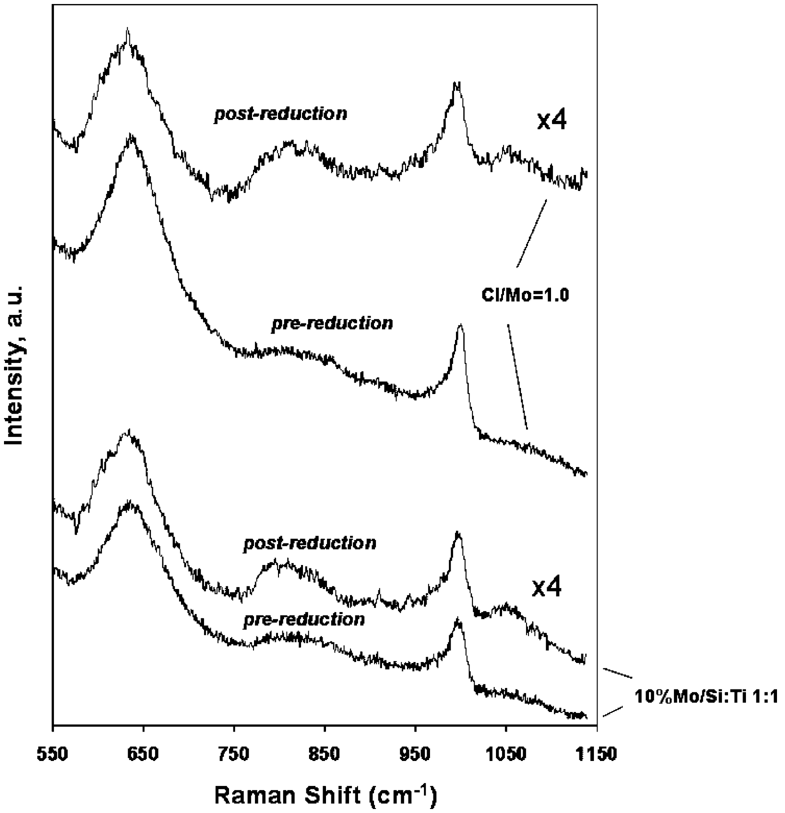


Fig. 5. Pre- and post-propane reduction Raman spectra of 0% Mo/Si:Ti = 1:1 and 10% (Cl/Mo = 1.0)/Si:Ti = 1:1 catalysts.

oxygen (Mo=O and Mo–O–Mo) vibration region. Broad bands associated with crystalline TiO_2 limit the detection of MoO_x species below 640 cm^{-1}. Since the band intensities decreased after propane reduction, the post-reduction spectra were multiplied by four to give a better comparison with pre-reduction spectra. The feature located at 1066 cm^{-1} for reduced catalysts is indicative of Ti–O–Si bonds [53,54], and this band could also have the contribution from the asymmetric Si–O–Si stretching vibration, which is located at 1050 cm^{-1} for pure silica [55]. Considering this feature intensified for post-reduction samples, it is possible that there might be an agglomeration of surface Mo species associated with the reduction process, which might either decrease Mo species attached to Si–O or Ti–O ligands in favor of Ti–O–Si or Si–O–Si bridging oxygen sites or leave more of these sites exposed on the surface. As a result, the contribution from bridging oxygen bonded to support becomes more pronounced. Another change observed in the reduced samples is an increase in the intensity of a broad band in the range of 750–950 cm^{-1}.There could be multiple contributions to this band, including antisymmetric stretching of Mo–O–Mo bonds in polymolybdate structures [56,57], and symmetric mode of Si–O–Si stretching [58]. This increase in the intensity observed following reduction may be due to enhanced vibrations created by the presence of oxygen vacancies present within MoO_x domains, similar to what has been observed on reduced crystalline MoO_3 samples [3]. The bands associated with terminal Mo=O stretching vibrations are present in the 970–1005 cm^{-1} region and the contributions to isolated terminal Mo=O bond can come from molybdena species supported solely on silica or titania domains of the support, or from species sharing mixed support-O ligands [51]. After reduction with propane, the intensity of this band relative to the Mo–O–Mo bands decreases indicating a preferential interaction of the hydrocarbons with this bond.

Incorporation of Cl into Mo/Si:Ti catalysts has been found to improve hydrocarbon conversion rate and olefin yield in ODH reactions of both ethane and propane. Characterization results have shown that the Cl incorporation affects the support structure through increased titania crystallinity, preferential surface concentration of Si compared to Ti, and increased density of Mo centers with Si–O ligands. With experiments designed to determine the structure–function relationship of reduced metal oxide species we are beginning to understand the way these structural characteristics are responsible for the observed interactions with hydrocarbons. They seem strongly dependant on the type of hydrocarbon used, which may be related to the C–H bond strength and the effectiveness of the hydrocarbon as a reducing agent. Future research should focus on elucidating the distribution of oxidation states on the catalyst surface in the presence of oxygen, hydrocarbons, and water (ODH conditions) and on determining the influence of structure on these characteristics.

5. Supported metal oxides

The metal–oxygen bond structure of common partial oxidation catalysts (based on Mo, V, W, Sb) have been well characterized on a variety of supports as a function of surface coverage, degree of hydration, and in the presence of dopants. The surface dispersed species are stabilized or ‘‘anchored’’ by their interaction with the hydroxyls of the support surface, and the surface coverage and reactivity of hydroxyl sites determines monolayer coverage of the supported oxide. Thus, the monolayer coverage is considered the maximum loading at which the supported oxide is deposited as isolated surface species, free of 3-dimentional aggregates or crystal structure formation [59]. Similar structures are observed for other supported oxides. Such structures are affected by ambient humidity, which can hydrolyze the M–O-support bond, resulting in an ‘‘aqueous solution’’ of the supported oxide. The chemistry of these species has been studied by several authors and many factors that influence the coordination and extent of polymerization of the supported species and their reactivities toward selective oxidation have been characterized.

Our earlier work has focused on molybdenum oxide catalysts supported on silica for the partial oxidation of methane to formaldehyde [60]. Catalysts were characterized using TPR, X-ray diffraction, ambient and in situ laser Raman spectroscopy, and X-ray photoelectron spectroscopy. The catalysts with loading levels below monolayer coverage were seen to contain silicomolybdic species with terminal oxygen sites as confirmed with Raman spectroscopy. The maximum rate of formation of HCHO was obtained on the most highly dispersed sample containing silicomolybdic acid species (0.5 wt.% Mo). As loading level increased, polymeric species with bridging oxygen sites began to form at the expense of the silicomolybdic species with chain lengths further increasing with increasing loading. Further increase in the loading level led to the formation of crystalline MoO_3. When reaction experiments were performed over these catalysts, the silicomolybdic species were found to be the most selective for formaldehyde formation.

Impregnation methods to support MoO_x over high surface area silica are limited by several factors such as choice of precursor and low reactivity of surface silanols [61]. Thus, in literature, detailed preparation methods have been reported to enhance silica affinity for supported MoO_x species. Several methods have been adopted such as preparation methods to increase the concentration or reactivity of surface silanol groups, Mo-complexes that directly react with the surface hydroxyl groups of silica, gas-phase grafting, non-aqueous impregnation, or sol–gel synthesis. Over the mixed oxides of silica and titania, a much better dispersion of MoO_x is obtained compared to the silica supported catalyst. Addition of TiO_2 into the silica matrix has been shown to lead to unique structural and chemical properties that can provide advantages that the respective single oxides cannot [62–69]. These benefits include stronger metal-support interactions, hindering reduction and segregation of the active metal, and smaller particle size that leads to better dispersion and higher surface area. Additionally, Klimova et al. [70] have achieved an enhanced dispersion of MoO_x over silica (MCM-41) by incorporating titania into the silica network. Much of these discussed properties are related to changes in surface acidity, porosity, Ti–O–Si connectivity, and phase segregations. Thermogravimetric analysis of SiO_2, TiO_2, and Si:Ti 1:1 supports prepared in our laboratory [71,72] revealed that the hydroxyl concentration per unit surface area was significantly increased on the mixed oxide sample. This allowed for an increase in the amount of molybdenum that could be loaded onto the support as dispersed species compared to SiO_2 or TiO_2 alone. Characteristic Raman bands from polymolybdate species (Mo–O–Mo) were visible over 10 wt.% Mo loaded SiO_2 and TiO_2 while the Si:Ti 1:1 support showed no evidence of these species until a weight loading of 15%.

The oxygenated ligands present around transition-metal centers play a crucial role in determining the reactivity of the surface species on these mixed-oxide supports. Our work in this area has been aimed at the characterization of molybdenum oxide supported on the silica-titania mixed oxides. We have prepared and characterized a series of molybdena catalysts (0–20 wt.% loadings) supported on the mixed oxides of silica and titania that have been prepared by a ‘‘one-pot’’ sol–gel synthesis that distributes the molybdenum precursor through the Si:Ti support network as it forms. In this method, we believe the one-pot preparation can allow for a greater possibility and a more even distribution of hetero-linkages M–O–M′, where M and M′ can be Si, Ti, or Mo. Raman spectra taken under dehydrated conditions coupled with XPS data has shown that surface supported molybdena species are supported preferentially on titania but still share a significant amount of bonding with the silica domains of the support. The Raman spectra taken under dehydrated conditions are shown in Fig. 6. The main Mo=O Raman frequency remains essentially unchanged with weight loading (1004–1006 cm^{-1}) until crystalline MoO_3 appears at 20%. Small shoulders are observed in the main Mo=O Raman band for 2 wt.% loading at 977 and 997 cm^{-1}. With increasing wt. loading, the shoulder at 977 cm^{-1} is no longer observed while higher wavenumber shoulders are still observed up to 15 wt.% (5% Mo: 990 cm^{-1}, 997 cm^{-1}, 10% Mo: 982, 998 cm^{-1}, 15% Mo: 987, 1001 cm^{-1}). The band present on 2% Mo/Si:Ti 1:1 at 977 cm^{-1} arises from Si–O–Mo bonds corresponding to a silicomolybdic acid species [57–61]. The silica band at 605 cm^{-1} is seen to decrease with 5 wt.% loading and become unresolved at 10 wt.% loading. The band at $\sim$1080 cm^{-1} shows the same trend. The broad band at 800 cm^{-1} disappears altogether at 5 wt.% loading. This is another indication that, as weight loading is increased over the support, the molybdena species interact more strongly with silica domains until the formation of crystalline MoO_3 above 15 wt.%. When the catalysts were tested for their

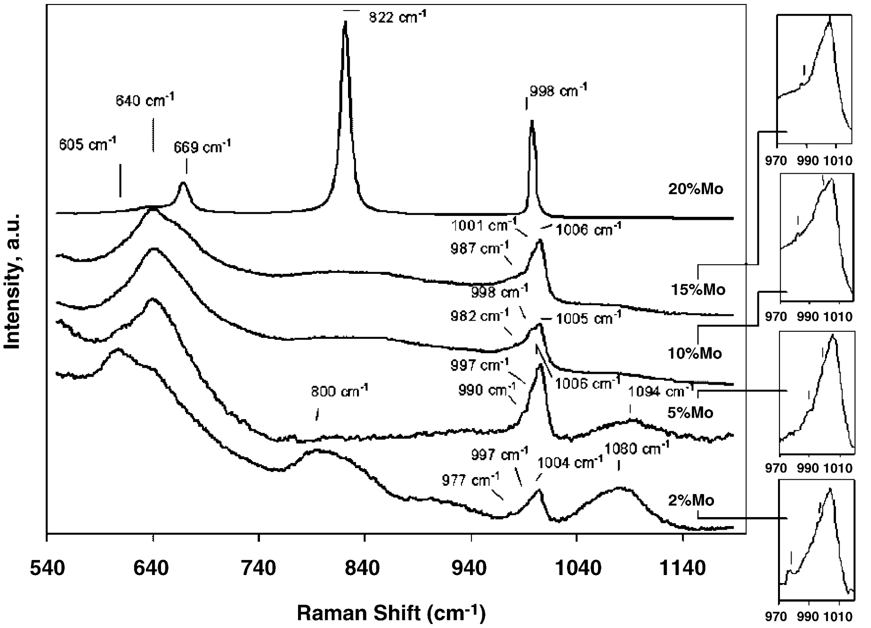


Fig. 6. Raman spectra (dehydrated conditions) of Mo/Si:Ti 1:1 catalyst with different Mo loadings. Spectra taken under 10% O_2/He at room temperature.

performance in both propane and ethane ODH, the highest olefin formation was observed over 10% Mo/Si::Ti 1:1. It is believed that this loading level provided MoO_x species that share several types of support linkages with differing electronegativities. Our results also indicate that, using this preparation method, Mo loading affects not only the structure of the surface MoO_x species, but also influences the nature of TiO_x/MoO_x concentrations over the silica domains. As molybdenum loading is increased, there is a greater degree of crystalline titania segregation. At the same time, there appears to be an increased interaction of the silica with MoO_x. By studying these types of metal-support interactions and the factors that determine the nature of supported metal oxide species, the tailoring of activities/selectivies of supported species could be accomplished. We have not performed extensive studies to determine the role metal-support interaction plays upon oxygen diffusion or oxygen spillover processes, but it seems likely that these characteristic can also be altered in a controlled manner by tailoring the support properties.

6. Promoted metal oxides

The accompanying increase in activity and/or selectivity in partial oxidation reactions with the use of alkali (Li, Na, K, Rb, and Cs) doping has been widely studied and offers another way to adjust the redox and acidic properties of supported transition metal oxides. The positive effects of alkali promotion arise from the alkali's ability to alter oxidation/reduction behavior, affect surface acidity, and/or cause a synergism between alkali and transition metal oxide phases.

We have previously studied the oxidative coupling of methane over alkali-promoted simple molybdate catalysts [73–76]. The investigations included synthesis of catalysts, characterization of catalysts using TPR, XRD, laser Raman spectroscopy and XPS. The alkali promoters were seen to affect the catalytic activity and selectivity very significantly, with K-promoted $MnMoO_4$ catalysts achieving the highest C_2 selectivity. Alternatively, the simple molybdate catalysts promoted by sodium or lithium showed an increase in the selectivity to formaldehyde. The oxygen exchange behavior and gas phase or lattice oxygen incorporation into the products was investigated using the transient isotopic labeling technique under steady-state conditions by switching from a feed mixture containing $^{16}O_2$ to a mixture containing $^{18}O_2$. The oxygen exchange behavior was found to change from that of pure simple molybdate due to the addition of an alkali promoter. The potassium-promoted catalyst, which gave the highest selectivity for C_2 hydrocarbons, was found to produce significantly greater amounts of mixed oxygen ($^{18}O^{16}O$) during oxygen exchange experiments than pure molybdate or catalysts promoted with other alkali metals. The rate of lattice oxygen incorporation into carbon dioxide and water was also found to be the lowest for potassium-promoted catalyst. The effect of carbon dioxide was also examined by introducing CO_2 into the feed stream. The product analysis showed no effect of carbon dioxide on catalytic activity or selectivity. Transient isotopic labeling studies aimed at comparing the residence time of methane and its intermediates on different catalyst surfaces by switching from $^{12}CH_4$ to $^{13}CH_4$ in the feed stream showed considerably longer surface residence time for ethane and ethylene in comparison to carbon dioxide and methane. These results combined with TPD and Raman spectroscopy studies that showed the existence of species containing carbonyl groups on the surface allowed us to explain the major changes observed in C_2 selectivity when alkali promoters are used in terms of relative reactivity of the surface oxygen species and the surface life of carbon species that were prevalent under the reaction conditions. On catalysts where the alkali ions were able to stay at the surface without forming additional phases, it was concluded that the alkali ion could be incorporated into the oxide lattice, creating defects that affect oxygen diffusion.

One of the difficulties associated with understanding the mechanism of alkane oxidation and its relationship to metal oxide structure is the fact that the abstraction of the first hydrogen is often the rate determining step with high activation energy. The relatively high temperatures used to overcome this barrier, on the other hand, result in rapid further oxidation of alkyl and alkoxy species, making it very difficult to assign individual steps to different structural sites. To overcome this problem, one approach we have employed is the use of alkyl halides in place of the alkane molecule. Since the abstraction of the halide is much easier than the abstraction of the hydrogen, this method provides alkyl radicals at much milder conditions, allowing the observation of subsequent steps more easily. However, the modification of the catalyst surface by the halide is a phenomenon that must be considered when using this technique. Alkyl iodides have been used to test proposed reaction mechanisms [77], verify importance of intermediates with short lives at reaction temperatures [78,79], as well as study the interaction of alkyl intermediates with the catalyst surface [80–83].

One of the questions often discussed in the literature is the role of the catalyst in the coupling step once the methyl species are formed. One possibility proposed is that the role of the catalyst is limited to the first hydrogen abstractions step and once the methyl species are formed, the coupling takes place primarily in the gas phase. In our work, methyl iodide was used as a probe molecule to further investigate the oxidative coupling of methane reaction over $MnMoO_4$ and the additional improvement provided by potassium promoted $MnMoO_4$ [84]. Methyl iodide readily decomposes to form methyl radicals, thereby eliminating the rate determining step of hydrogen abstraction.

Temperature programmed desorption profiles after methyl iodine adsorption were obtained for the $MnMoO_4$ and $K/MnMoO_4$ catalysts, respectively. No iodine desorbed from the catalyst surface within the temperature range studied (room temperature to 850 °C). To verify that the iodine did indeed remain on the catalyst surface, XPS was performed on the $MnMoO_4$ catalyst sample after CH_3I TPD. These results were used to prove that the iodine would remain on the catalyst surface under reaction conditions, eliminating the possibility of iodine ions or radicals in the gas phase contributing to the reaction network. Reaction studies were conducted by analysis of products obtained from pulses of methyl iodide over the catalyst bed. Since the pulses contained very low concentrations of the CH_3I feed, the modification of the surface during the first few pulses could be neglected. The products were monitored by TCD and FID. The thermal reaction (blank) produced mainly methane. Both $MnMoO_4$ and 1% $K/MnMoO_4$, catalysts showed a greater tendency toward C_2 formation than the thermal reaction. This effect, however, was much greater for the K promoted catalyst. The absolute amounts of C_2 hydrocarbons produced were much greater over the K promoted catalyst and became higher with successive pulses. This study provided significant evidence in showing the role of the catalyst in the coupling reaction. Although contributions from the gas phase reaction cannot be completely ruled out, it is clear that the role of the heterogeneous mechanism in the coupling reaction after the methyl species are formed is significant. Also, the K promoted catalyst suppressed CO_x formation. In agreement with our previous work [75,82], the K promoted $MnMoO_4$ provided a greater selectivity toward C_2 formation. This effect was much more pronounced when methyl iodide was used, eliminating the first hydrogen abstraction.

More recently, we have characterized the way in which alkali promotion can alter the surface redox properties, surface residence times of intermediates, as well as surface acidity over supported MoO_x species. Furthermore, we have characterized the mechanisms by which the alkali modifies supported metal oxide species to change these observable properties. The structural characteristics of supported MoO_x species inherent over a high TiO_2 content silica-titania mixed oxide support (1:1 molar ratio), combined with the structural effects that are induced by an alkali promoter, were the primary focus of these investigations. The observed effects of low-level alkali promotion were studied in order to obtain a better understanding of the way the observed MoO_x activity, altered by the presence of potassium, relates to the adsorption and reactivity of propane and the product propylene under various ODH conditions [85]. These studies were performed on a series of molybdate catalysts with increasing K/Mo molar ratio from 0 to 2 at constant (10 wt.%) loading of Mo and a Si:Ti molar ratio of 1 [86]. Our previous work has shown that the Mo/Si:Ti 1:1 catalysts are effective for the oxidative dehydrogenation of propane. The catalysts have shown a broad maximum in activity and selectivity with the amount of alkali (K) promoter added, i.e., an initial increase in activity at the low alkali content followed by a sharper decline. The reactions were run using equal surface area loading (65 m^2) in the reactor and at a temperature of 550 °C. The feed percentages for these experiments were N_2/C_3 or C_3^{2-}/O_2: 92.5/5/2.5. The results of the propane ODH and the propylene oxidation reactions are shown in Fig. 7. These are observed rates for propylene formation in that they are the summation of both formation from propane and its successive depletion that are observed during the reaction. The rates are seen to increase through a maximum between K/Mo = 0.07 and 0.14 and fall as K/Mo

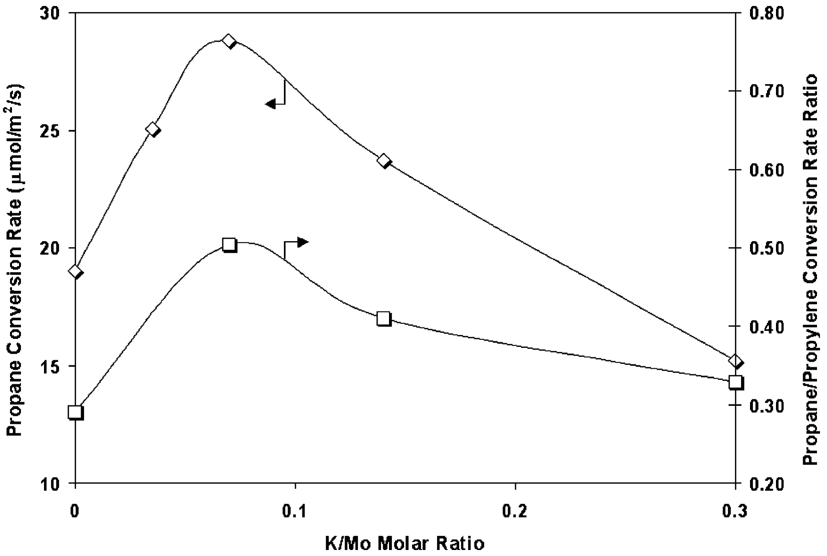


Fig. 7. Propylene formation rates (□) of Mo/Si:Ti 1:1 catalysts with different K/Mo molar ratios. Reaction conditions: equal surface area reactions (65 m^2), % $N_2/C_3/O_2$: 92.5%/5%/2.5%, 25 cc/min. Propane/propylene conversion ratio (◇) obtained under identical conditions. Reaction conditions: equal surface area reactions (65 m^2), % $N_2/C_3^{2-}/O_2$: 92.5%/5%/2.5%, 25 cc/min.

is increased to 0.3. Propylene oxidation experiments run under the same conditions revealed a propylene conversion rate that steadily decreased with K/Mo molar ratio. When propane and propylene oxidation experiments are compared under these identical conditions, a maximum exists in the ratio of propane to propylene conversion rates. This suggests that the increase in propylene formation at the low K/Mo molar ratios (0.07 and 0.14) during ODH experiments is due to a decreased reactivity of propylene caused by the addition of alkali. We have related this tendency to the "secondary" effect induced by alkali promotion. The surface oxygen species are affected "primarily" by the presence of potassium and this, in turn, affects the rates of both propane activation and propylene combustion. The reactivity trends are related to a combination of the decrease in Lewis acidity as observed from the IR band of adsorbed ammonia and the slight suppression of the reducibility at these low K/Mo molar ratios as observed from temperature programmed desorption experiments. Similarly, non-steady-state and steady-state isotopic transient kinetic analyses (SSITKA) have shown significant changes in lattice-oxygen mobility caused by the presence of potassium. Differential Scanning Calorimetry was used to determine the heat effects associated with propylene adsorption over the catalysts. The heat associated with the reversible and irreversible adsorption of propylene decreases with the addition of potassium. This information further corroborates the relationship between potassium addition and the decreased reactivity for propylene as elucidated in reaction experiments. Together with in situ-DRIFTS experiments, it was found that potassium can not only affect the transformation of propylene over MoO_x catalysts, but also change the interaction of the catalyst with propane, altering propane activation steps.

Structural characterization has shown that the Si:Ti 1:1 mixed oxide support is in a state of nano-dispersed titania (anatase) over silica [87]. With the introduction of molybdenum and successive levels of alkali promoter, the dispersion of titania decreases as does the interaction of TiO_x species with silica. Concurrent with this change is the observation of an enhanced interaction of the MoO_x species with silica. Solid state NMR data and DRIFT spectra taken in the hydroxyl-stretching region (3000–3900 cm^{-1}) support this observation, by showing that with the addition of alkali, the three-dimensionality of the silica support is changing to accommodate the change in MoO_x surface structure. A correlation was found between the propane ODH reactivity, surface coverage of oxidic molybdenum species, and the nature of the Si:Ti support. The presence of potassium significantly alters the electronic structure of the surface MoO_x domains, even before the formation of K-molybdate species is observed at higher K/Mo molar ratios. This electronic interaction was observed readily in the ESR spectrum of Mo(V) present in the dehydrated samples. The $g_\perp$ values are seen to go through a maximum at K/Mo = 0.07 and this trend is depicted as in Fig. 8. The variation of integral intensity calculated from the spectra in Fig. 8 is included as insert 2. The g-values for different coordination environments of Mo(V) are reported in literature as follows: 6-coordinate Mo(V), $g_\perp = 1.944$, $g_{||} = 1.892$; five-coordinate Mo(V), $g_\perp = 1.957$, $g_{||} = 1.866$; and four-coordinate Mo(V), $g_\perp = 1.926$, $g_{||} = 1.755$ [88–90] Since the perpendicular component is expected to be the most sensitive to the coordination of the isolated MoO_x species, the data indicate that with the addition of potassium, there is a change in the coordination sphere (six-coordinate distorted toward five-coordinate) of the Mo(V) species that reaches a maximum at K/Mo = 0.07. Furthermore, the integral signal intensity

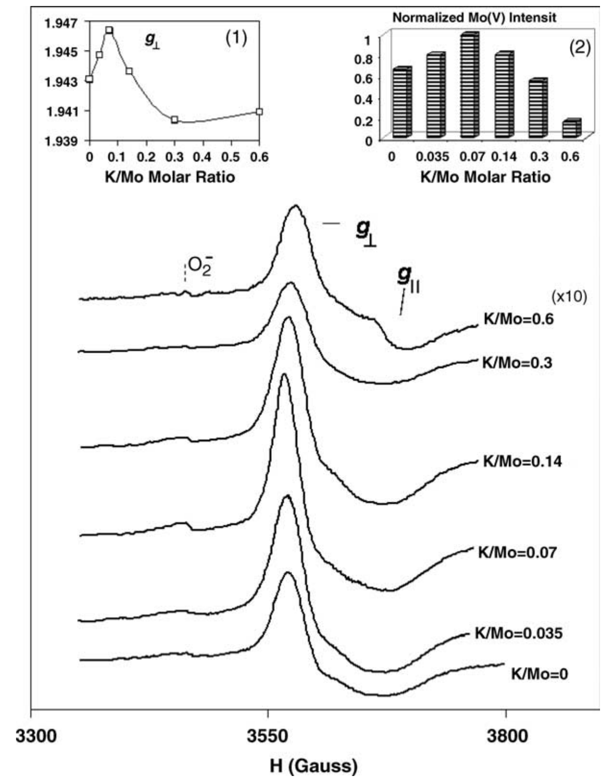


Fig. 8. ESR spectra of 10% Mo/Si:Ti 1:1 catalysts with differing K/Mo molar ratios under dehydrated conditions: (1) variation of *g* (perpendicular) with K/Mo molar ratio and (2) variation of normalized signal intensity with K/Mo molar ratio.

follows the same trend. The *g*-values of the K/Mo = 0.3 and 0.6 samples indicate a distortion in the opposite direction toward that of a four-coordinate Mo(V) species that can arise from the formation of K-molybdates.

Data suggest that surface supported species, present as distorted octahedral MoO_x, become the most distorted at low levels of alkali (K/Mo = 0.07) where they can alter the coordination environment without necessarily forming additional phases/species. The MoO_x species can be altered to generate a decrease in Lewis acidity, which causes them to be more reactive toward electronegative Si–O-support ligands than in the absence of potassium. Thus, the observed increase in propane ODH reactivity at the low K/Mo molar ratios may be ascribed to a highly distorted structure sharing both titania and silica ligands. Thus, the positive effects of alkali promotion arise from not only the effect of decreasing surface acidity, but to the alteration of metal oxide domains.

7. The use of "novel" oxidants

In an attempt to find methods to deconvolute the structural effects of metal oxides on surface acidity, redox properties, oxygen mobility, and the activation of gas phase molecules, we have begun to look into alternative oxidants as a means to examine the role of gas phase oxidation and surface oxidation–reduction processes occurring during ODH reactions.

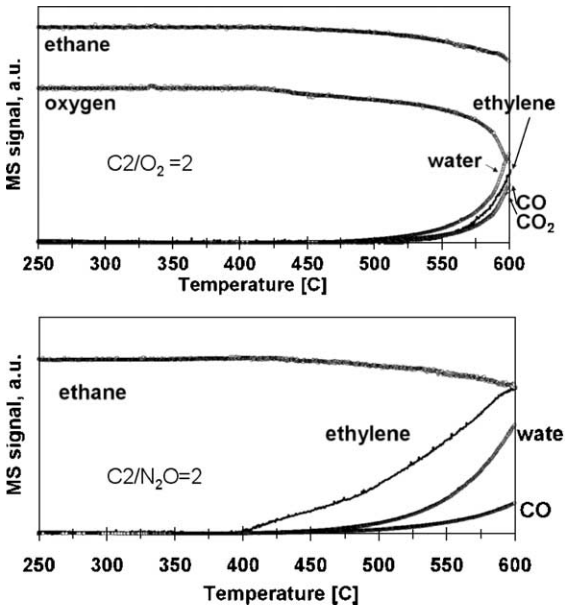


Fig. 9. Products arising from ethane/oxygen and ethane/nitrous oxide temperature programmed reaction over 10% Mo/Si:Ti = 1 catalysts.

In testing different catalytic oxidation systems, the use of different oxidizing agents has also been investigated by using nitrous oxide instead of molecular oxygen [91–96]. While the enhancement effect of a milder oxidizing agent like N_2O on the partial oxidation selectivity is not totally clear, the inhibitive cost of nitrous oxide as an oxidizing agent makes this option rather impractical for commercial applications unless a nearby waste stream of N_2O is available, such as in adipdic acid production [2]. However, using N_2O as a matter of study, rather than a development effort for an industrial process does allow the investigation of surface oxygen reaction pathways that may eliminate some of the charged di-oxygen species involved in surface reactions or re-oxidation steps occurring during the selective oxidation process.

Using a temperature programmed reaction technique; we have evaluated the performance of molecular oxygen versus N_2O in ethane oxidation. The reaction experiments were performed using 100 mg of 10% Mo/Si:Ti 1:1 catalyst described previously. The temperature program was run from room temperature to 600 °C using a ramp rate of 10 °C/min. The feed composition was 7.5% hydrocarbon/2.5% oxidant/90% helium. The data were collected with an on-line quadrupole mass spectrometer. The results for ethane/oxygen and ethane/N_2O are shown in Fig. 9. The common ion ($m/z = 44$) shared by N_2O and CO_2 prevented accurate tracking of these species for the ethane/N_2O reaction. As can be seen, a significant improvement in ethylene formation is observed with the use of N_2O. This trend was also observed from steady-state reaction data taken in our laboratory over the same catalyst. The data shown in Fig. 9, combined with steady-state reaction results suggest that N_2O can provide enhanced selectivity to olefins when used during ODH reactions. We believe that a possible reason for this enhanced selectivity obtained using N_2O is the lack of adsorbed di-atomic oxygen species that may be more selective toward complete oxidation. However, ongoing work in our laboratory is attempting to deconvolute the other possible effects of the oxidation state the molybdenum species, the role of structure in the adsorption and dissociation of N_2O, and the gas phase source of oxygen and its role in re-oxidation of the surface.

There is additional information in the literature pointing the use of CO_2 as an oxidant. The oxidative dehydrogenation of ethane into ethylene by carbon dioxide over Cr_2O_3-based catalysts has been reported [97,98]. Development in this area would have major impact in the utilization of carbon dioxide, a greenhouse gas whose regulation is likely to become stricter in the upcoming years. However, the use of CO_2 as a mild oxidant in hydrocarbon oxidation may provide insight similar to that obtained by using N_2O. As summarized in a recent review, carbon dioxide can be used as a mild oxidant for methane coupling to ethylene, C_2–C_4 alkanes dehydrogenation to their corresponding olefins, dehydroaromerization of lower hydrocarbons to benzene, and dehydrogenation of ethylbenzene to styrene [99]. In the catalytic systems reported, CO_2 can play different roles depending upon the catalyst used. Carbon dioxide may dissociate and produce surface oxygen species, liberating CO. It may also participate in the redox cycle of a metal oxide, actively participating in surface exchange. Carbon dioxide exchange has been observed in several systems in our laboratory during oxidation reactions; however, we have yet to address its role in the formation of oxygen species that participate in the oxidation. The utilization of CO_2 in oxidation reactions is an emerging area in which much work is needed to characterize reaction mechanisms for a variety of oxidation reactions over a variety of metal oxide catalysts. Future research combining what is known of molecular oxygen participation in selective oxidation with the knowledge of how surface structure influences the participation of oxygen would benefit from the use of such ‘‘novel’’ oxidants as a means to generate single oxygen species on the surface. Studies such as this have the possibility to unravel the nature of electrophillic and nucleophillic oxidations that occur during oxidative dehydrogenation and other oxidation reactions. More importantly, the function that surface structure plays on these oxidation routes may be revealed.

8. Future directions

Although the last several decades have brought significant improvements to existing oxidation processes and opened up new possibilities for developing novel selective oxidation processes, there is still need for catalytic and reaction engineering research to achieve higher selectivity, to minimize waste, to reduce or eliminate the use of toxic or hazardous chemicals, to use environmentally benign and renewable feedstocks while decreasing energy requirements and minimizing the cost at the same time. While many structure–function relationships in the field of selective oxidation are better understood today, there are many questions left unanswered. The surface of a metal oxide catalyst under reaction conditions is a dynamic one, with multiple adsorption/desorption, reduction/oxidation steps taking place. A fundamental understanding of the molecular processes that take place on the surface of the metal oxide catalysts during an oxidation reaction continues to pose challenges. The nature of metal oxide species on the surface, support effects, the role of promoters continue to be important factors in determining the activity and selectivity of these catalysts and need to be addressed for a better understanding of function-structure relationships. Especially important are the questions related to the nature of surface oxygen species, their roles in selective versus complete oxidation steps, and the molecular interactions that lead to the formation of different oxygen species. Only the continued use of in situ techniques to analyze the bulk and surface characteristics of the catalysts under both steady-state and transient conditions would bring us closer to designing highly selective and active oxidation catalysts based on a fundamental understanding of the catalytic phenomena involved in oxidation reactions.

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