



Chlorine modification of Mo/silica-titania mixed-oxide catalysts for the oxidative dehydrogenation of ethane

Rick B. Watson, Shannon L. Lashbrook, Umit S. Ozkan*

Department of Chemical Engineering, The Ohio State University, 140 West 19th Avenue, Columbus, OH 43210, USA

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Abstract

A series of molybdenum-based catalysts have been prepared and studied in regard to their performance in the oxidative dehydrogenation (ODH) of ethane. The effect of alkali (K and Li) and halide (Cl^-) modifiers on catalyst performance has been evaluated by doping at a low level (dopant/Mo molar ratio = 0.1). The changes in reaction performance are related to the nature of the supported MoO_x surface species that are significantly affected by the introduction of chlorine. While the addition of halide modifiers is known to positively affect the gas-phase mechanisms of ethane ODH at higher temperatures ($>650^\circ\text{C}$), current work indicates that the effect for surface redox mechanisms over MoO_x -based catalysts may be somewhat less-pronounced, but still beneficial, at lower temperatures of operation.

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1. Introduction

Because alkanes are relatively inexpensive and are abundant due to side products of refineries and natural gas, one of their potential uses is in the conversion to alkenes [1]. Specifically, ethane is the second major component in natural gas, which makes it an abundant source of chemicals such as light olefins, oxygenates, and aromatic hydrocarbons [2]. A method that has been widely used to utilize ethane is steam cracking to form alkenes. This method is constrained in many ways, namely thermodynamic limitations, endothermic reactions that require a large input of heat, and formation of coke on the catalyst [3]. Because of these limitations, recent studies have focused on the oxidative dehydrogenation (ODH) of ethane. ODH is a desirable alternative because, when a proper catalyst is selected, the reaction occurs at lower temperatures and is exothermic, preventing heat input requirements.

According to Cavani and Trifiro [3], catalysts that are active in the ODH of ethane can be grouped into two main categories. Catalysts based on ions and oxides of Group IA and IIA metals are active at a temperature above 600°C . The

reaction occurs through the formation of ethyl radicals that react in the gas phase to form ethylene. Thus, the catalyst chiefly participates in initiating the gas-phase reaction.

The activity of the catalysts based on Group IA and IIA metals can be significantly increased by the addition of small amounts of chlorine-containing materials in the feed or directly into the catalyst as part of the preparation method [4–8]. Operating at high temperatures, the increase in activity would seem to arise from chlorine radicals, present in the gas phase, favoring the gas-phase decomposition of ethyl radicals to ethylene. However, Burch et al. [9] have concluded that, during trichloromethane treatment, Cl^- mainly modifies surface sites and does not participate in gas-phase reactions. The same conclusion was reached after trichloromethane addition to $\text{Mg}_3(\text{PO})_4$ catalysts [6]. Thus, it also seems possible to improve catalyst performance by incorporation of chlorine during catalyst preparation or by a subsequent treatment after preparation. Au et al. have achieved a higher yield of ethylene by adding BaCl_2 to Ho_2O_3 catalysts [10]. Also, inclusion of Cl^- ions in La/Sr/Fe oxide catalysts increased ethylene selectivity and surface oxygen mobility in studies performed by Dai et al. [11]. While many studies have shown the positive effects of modifying catalysts with halides in order to enhance the homogeneous radical reaction in the ODH of ethane, there are significant environmental implications associated with the use

* Corresponding author. Tel.: +1-614-292-6623; fax: +1-614-292-3769.

E-mail address: ozkan.1@osu.edu (U.S. Ozkan).

of chlorinated compounds as feed materials. Furthermore, the stability of chlorine phases on the catalyst surface at high temperature can also contribute to the release of chlorine. It has been stated [12] in a recent review on ethane conversion that the role of these additives on supported metal oxides is still poorly understood in regard to structural, redox, and acid–base modifications. Therefore, further research is needed to develop halide-modified catalysts that operate at lower temperatures and exhibit stable and active structures.

The second class of ethane ODH catalysts includes those based on transition metal oxides and, in the absence of gas-phase contributions, are typically less active than those operating at the higher temperatures. One such catalyst, Mo/V/Nb, is active in ethane ODH at much lower temperatures, $\sim 350^\circ\text{C}$ [13]. The reaction is heterogeneous and follows a redox cycle, with homogeneous reactions occurring only at high temperatures. Examples from literature indicate that most supported transition metal oxide-based catalysts (Mo and V, in particular) operating by a redox mechanism achieve ethylene yields in the range 15–30% [3,14].

Our previous work [15–18] has shown that the addition of alkali, in small amounts, to Mo/Si:Ti catalysts can beneficially alter the electronic structure of the surface MoO_x domains for the ODH of propane. It was found that with addition of low levels of potassium, distorted MoO_x units, experiencing a decreased Lewis acidity, could be more reactive toward electronegative Si-O^- support ligands on the Si:Ti (1:1) support and a highly distorted structure sharing both titania and silica ligands may be ascribed to an observed increase in propane ODH reactivity at low K/Mo molar ratios. In the current investigation, these results are extended to the ODH of ethane in order to compare their effectiveness. In addition, several catalysts are modified with chlorine to determine if the addition of halide over transition metal oxide-based catalysts, operated at lower temperatures ($<650^\circ\text{C}$), are able to modify the nature of MoO_x domains and thus the redox mechanism of ethane ODH.

A series of chlorine-modified molybdena catalysts (Cl/Mo molar ratio = 0.1) have been tested in ethane ODH and characterized by several methods. These catalysts have been prepared by a “one-pot” sol–gel/co-precipitation technique with the exception of one chlorine-containing catalyst prepared by wet impregnation for comparison purposes. Surface areas were measured using the BET N_2 adsorp-

tion method. Characterization has been performed using temperature-programmed reduction (TPR), laser Raman spectroscopy, X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) to elucidate surface structure, the nature of MoO_x species, and their interaction with Si and Ti domains of the support.

2. Experimental

2.1. Catalyst preparation

Catalysts were prepared using a modified sol–gel/co-precipitation technique described previously [19]. For the molybdenum precursor, ammonium heptamolybdate (AHM; Mallinkrodt) was used. Tetraethylorthosilicate (TEOS; Aldrich) and titanium(IV) isopropoxide (TIPO; Aldrich) were used for the mixed-oxide supports. Isopropyl alcohol was used for the solvent. The modified sol–gel technique uses calculated amounts of silica and titania alkoxide precursors placed in solvent to yield SiO_2 - TiO_2 mixed-oxides with a 1:1 ratio after calcination. The solution was stirred while adding an aqueous solution with the desired amount of AHM (10% Mo loading) using a syringe pump. The stoichiometric amount of water needed to hydrolyze all of the alkoxide precursors was contained in the aqueous solution with one exception explained later. The gels formed from this preparation were stirred for an additional 15 min following the complete addition of the aqueous solution and then dried overnight in an oven at 110°C . Following drying, the catalysts were ground to a powder and calcined under oxygen at 550°C for 5 h. For catalysts modified with chlorine, a calculated amount of HCl (Fisher) or NH_4Cl (Mallinkrodt) was included in the aqueous solution to give the desired Cl/Mo ratio. For catalysts containing alkali, KOH or LiOH was added to the aqueous solution to give the desired alkali/Mo molar ratio.

A list of the prepared catalysts is given in Table 1. Catalyst (a) is a 10 wt.% molybdate catalyst on a mixed-oxide support of Si:Ti in a molar ratio of 1. Catalyst (b) is a molybdate catalyst with a Cl/Mo ratio of 0.1 prepared by sol–gel/co-precipitation using NH_4Cl . Catalyst (c) has the same composition, but was prepared using wet impregnation of a molybdate catalyst (catalyst (a)) in powder

Table 1
Sol–gel catalysts for the ODH of ethane

Catalyst	Composition	Preparation	Surface area (m^2/g)
(a)	10% Mo/Si:Ti (1:1)	Sol–gel/co-precipitation	133
(b)	10% (Cl/Mo = 0.1)/Si:Ti (1:1)	Sol–gel/co-precipitation using NH_4Cl	223
(c)	10% (Cl/Mo = 0.1)/Si:Ti (1:1)	Wet impregnation using HCl	139
(d)	10% (Cl/Mo = 0.1)/Si:Ti (1:1)	Sol–gel/co-precipitation using HCl	190
(e)	10% (Cl/Mo = 0.1)/Si:Ti (1:1)	Sol–gel/co-precipitation using HCl	246
(f)	10% (K/Mo = 0.1)/Si:Ti (1:1)	Sol–gel/co-precipitation using KOH	188
(g)	10% (Li/Mo = 0.1)/Si:Ti (1:1)	Sol–gel/co-precipitation using LiOH	170

For catalyst (e), the amount of hydrolyzing water was doubled from the amount used for catalyst (d).

form by dropwise addition of HCl. Catalyst (d) is a molybdate catalyst with a Cl/Mo ratio of 0.1 prepared by sol–gel/co-precipitation using HCl. For catalyst (e), the amount of hydrolyzing water was doubled from the amount used for catalyst (d). Catalysts (f) and (g) are alkali-modified catalysts, prepared by sol–gel/co-precipitation using KOH and LiOH, respectively, to give an alkali/Mo molar ratio of 0.1.

2.2. Physical and spectroscopic characterization

In this study, the surface areas of the catalysts were determined by BET surface area measurement and nitrogen adsorption/desorption isotherms were recorded using a Micrometrics AccuSorb 2100E instrument. X-ray diffraction patterns were obtained with a Scintag PAD-V diffractometer using Cu K α radiation. X-ray photoelectron spectroscopy was performed using a ESCALAB MKII ESCA/Auger spectrometer operated at 12.5 kV, 20 mA, and using Mg K α radiation. Spectra were corrected using the C 1s signal, located at 284.6 eV. Surface concentrations were determined using instrumental atomic sensitivity factors.

Laser Raman spectroscopy was used to investigate the vibrational modes of the surface-supported MoO $_x$ species in the catalyst samples. In this study, Raman spectra were recorded with a Dilor spectrometer using the 514.5 nm line of an Innova 300 Ar laser. Spectra were taken in the range 200–1800 cm $^{-1}$ in 180° back-scattering mode with a Spectrum One CCD detector. Raman spectroscopy under dehydrated conditions was performed using a quartz in situ flow-cell that contacted the catalysts with gas flows at high temperature. A portion of prepared samples were re-calcined at 550 °C for 30 min under pure O $_2$ and transferred into the Raman cell. Additional dehydration occurred at 350 °C for 30 min under a flow of dry 10% O $_2$ /He after which the cell was sealed. Spectra were taken under 10% O $_2$ /He atmosphere at room temperature.

2.3. Temperature-programmed reduction

TPR is one of several characterization techniques used to relate catalyst performance to redox properties. TPR of catalysts was performed using a laboratory-made gas flow system described in detail elsewhere [20]. Catalyst samples (100 mg) were placed in a 1/4 in. i.d. U-tube quartz reactor and pre-treated under oxygen flow at 550 °C for 30 min followed by cooling to room temperature under nitrogen. The reduction was performed with 10% hydrogen in nitrogen (25 cm 3 /min). The thermal conductivity detector (TCD) was operated in differential mode and the signal transferred to a data acquisition computer. The outlet of the reactor was passed through a column of silica gel to remove moisture formed during the reduction. The temperature program was as follows: 10 min at room temperature, 10 °C/min ramp rate to 850 °C, and holding at 850 °C for 10 min.

2.4. Oxidative dehydrogenation of ethane

Each catalyst was tested in a fixed-bed, quartz reactor operating at ambient pressure. Reaction products were separated and analyzed online using a HP 5890 series II gas chromatograph containing FID and TCD detectors. Separations were performed using three columns: (1) Hayesep D (8 ft \times 1/8 in.) for hydrocarbons and partially oxygenated hydrocarbons, (2) Porapak Q (6 ft \times 1/8 in.), and (3) molecular sieve 5 Å (6 ft \times 1/8 in.) for N $_2$, O $_2$, CO, CO $_2$, and H $_2$ O. Reactions were carried out at steady state using 200 m 2 of catalyst surface area in the reactor. Catalyst samples, ranging from 0.1 to 1.5 g, were held in place by a quartz frit. The feed consisted of ethane/oxygen/nitrogen at a flow of 25 cm 3 /min. The concentration of the feed stream was maintained outside the flammability limits of ethane/oxygen/nitrogen mixtures for all runs. The main products of the dehydrogenation reaction were ethylene, methane, carbon dioxide, carbon monoxide, and water.

For the ODH of ethane, the contribution of homogeneous reaction due to ethyl radicals formed at the surface and desorbed into the gas phase can be significant. Thus, it is necessary to distinguish catalytic activity from gas-phase activity in order to study the effectiveness of the catalysts. Burch and Crabb have studied homogenous contributions to the catalytic ODH of ethane and have confirmed that filling the dead space of the reactor with quartz inhibits gas-phase radical reactions [21]. To assure that the homogenous reaction is indeed eliminated by this technique, reaction tests were run using an empty-volume quartz reactor. The results of this experiment showed no conversion of ethane up to 650 °C under the feed conditions studied. During catalytic reaction experiments, the dead volume of the quartz reactor was packed with quartz wool and ceramic beads to minimize any gas-phase effects that may occur in the presence of a catalyst. Reaction with 200 m 2 reactor loading of the Si:Ti (1:1) support (no Mo component) showed a level of 6% ethane conversion at 600 °C, in which ethylene and carbon dioxide were the only observed reaction products.

3. Results and discussion

3.1. Structural and physical characterization

Comparing the surface area of the prepared catalysts (Table 1), it is seen that all alkali- and chloride-modified catalysts exhibit higher surface area than the Mo-only catalysts. Furthermore, wet impregnation of the Cl $^-$ modifier results in the smallest increase in surface area. Comparing the chloride-containing catalysts prepared by sol–gel/co-precipitation, it is seen that preparation with twice the necessary hydrolyzing water (catalyst (e)) caused a significant increase in surface area (\sim 30%), which was the purpose of this preparation.

X-ray diffraction patterns were obtained on the Cl-modified catalysts. X-ray diffraction of the Si:Ti (1:1) support yielded a pattern characteristic of a silica-titania mixed-oxide containing surface segregated, or “extra-framework”, anatase [22]. One broad peak with center located at a d -spacing of 3.59 Å was observed, which is indicative of a finely dispersed, anatase nanostructure supported over amorphous silica. When the size of individual crystals is below 50 nm, a reasonably good measure of particle size can be determined from the broadening of diffraction lines measured at half of their maximum intensity [23]. Results of this measurement, together with the diffraction patterns, are shown in Fig. 1. With the addition of molybdenum, the anatase diffraction peak becomes narrower, indicating a change in the dispersion and segregation of titania in the Si:Ti matrix with the addition of Mo. With the introduction of molybdenum to the Si:Ti (1:1) support, the particulate size increases from approximately 2–9 nm. Introduction of chlorine by the “one-pot” sol-gel/co-precipitation technique does not appear to increase the segregation of crystalline anatase as indicated by similar XRD patterns. With the addition of chlorine, the average anatase particulate size remains roughly the same as that of the Mo-only catalyst with the exception of that prepared by wet impregnation using HCl (Fig. 1d), which shows an increase. Furthermore, the XRD patterns indicate that molybdena species are finely dispersed as no MoO₃ diffraction features were observed for any of the samples studied.

Raman spectra of 10% Mo catalysts, modified with chlorine, are presented in Fig. 2 (ambient conditions). Bands

associated with Mo=O terminal stretches and Mo–O–Mo structures are shown together with the ~640 cm⁻¹ band from TiO₂ (anatase). An important feature of these spectra is that there is little or no evidence of crystalline MoO₃ since the most intense band characteristic of Mo–O–Mo stretching vibrations in MoO₃ is not present as a sharp peak. In general, bands in the range of 750–950 cm⁻¹ are attributed to antisymmetric stretching of Mo–O–Mo bonds or the symmetric stretch of (–O–Mo–O–)_n bonds, while bands in the range 950–1050 cm⁻¹ can be attributed to the stretching mode of Mo=O bonds present in supported species [24]. The Raman spectra of the 10% Mo/Si:Ti (1:1) catalyst contains a broad Mo=O stretching band centered at 996 cm⁻¹. Compared to the Mo-only catalyst, the addition of chlorine by co-precipitation methods brings about a sharpening of the terminal Mo=O bands. The bands associated with isolated terminal Mo=O stretching vibrations are visible in the 970–1005 cm⁻¹ region and the contributions to this band can arise from MoO_x supported solely on silica or titania domains of the support, or from species sharing mixed support-O ligands. The catalysts modified with chlorine exhibit similar Raman spectra under ambient conditions with the exception of that prepared by wet impregnation using HCl (Fig. 2c). Additionally, the spectrum taken over the wet impregnated catalyst shows small features indicative of polymolybdate structures at 866 and 918 cm⁻¹ and is very similar to that of the Mo-only catalyst.

To elucidate the nature of the supported MoO_x species, a set of Raman spectra taken under dehydrated conditions and is presented in Fig. 3. Under dehydrated conditions, new

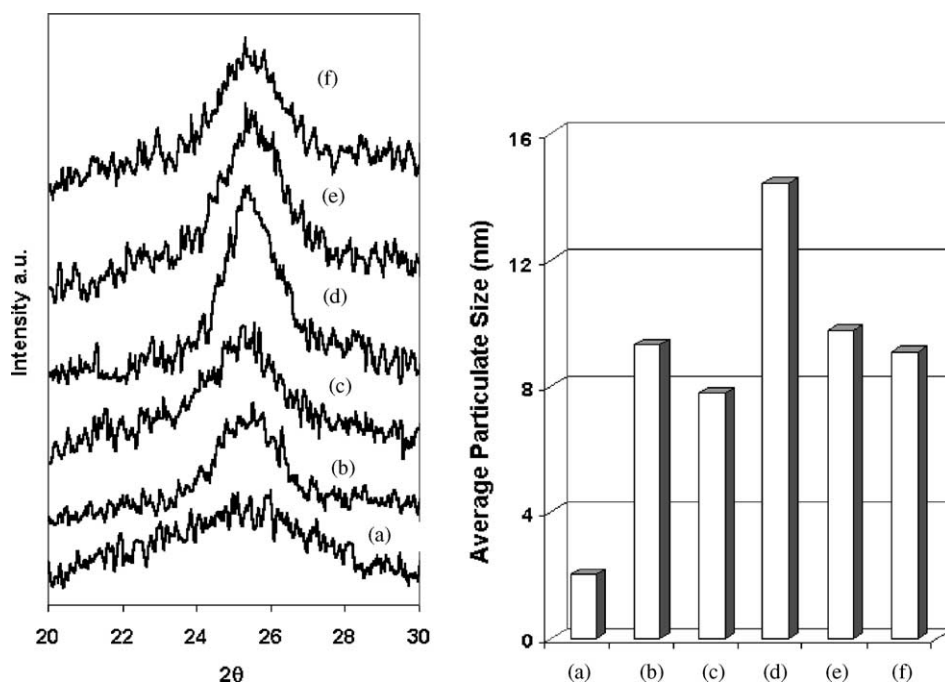


Fig. 1. X-ray diffraction patterns and average anatase particulate size for the Mo/Si:Ti (1:1) catalyst modified by chlorine: (a) Si:Ti (1:1); (b) Mo/Si:Ti (1:1); (c) co-precipitation using NH₄Cl; (d) wet impregnation using HCl; (e) co-precipitation using HCl; (f) same as (e), using double the stoichiometric hydrolyzing water.

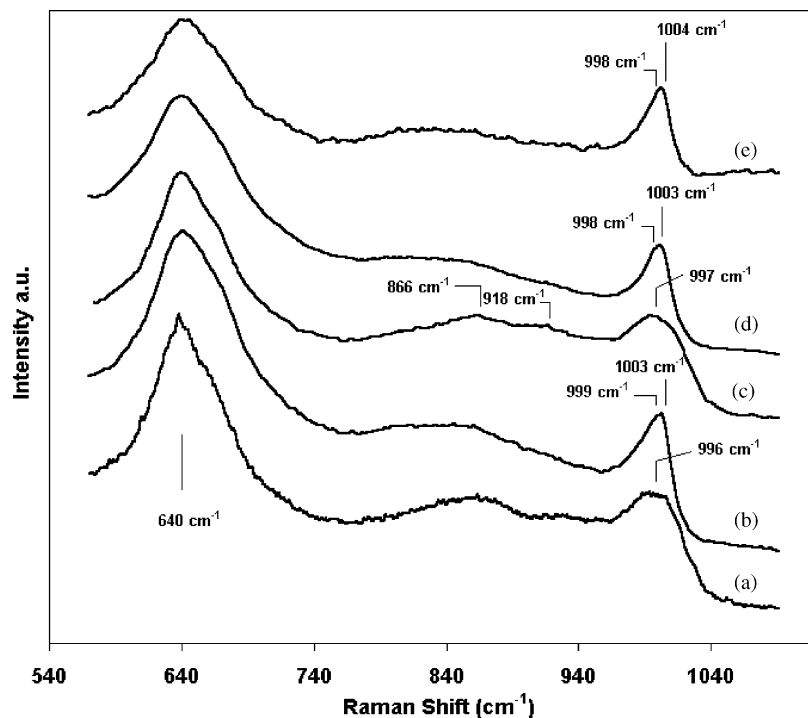


Fig. 2. Raman spectra (ambient conditions) of Mo/Si:Ti (1:1) catalyst modified with chlorine: (a) Mo/Si:Ti (1:1); (b) co-precipitation using NH_4Cl ; (c) wet impregnation using HCl; (d) co-precipitation using HCl; (e) same as (d), using double the stoichiometric hydrolyzing water.

Raman bands associated with the silica surface are resolved. In previous work, the dehydrated Si:Ti (1:1) support surface revealed broad Raman bands at 605, 800, and $\sim 1070\text{ cm}^{-1}$ [17]. The band at 605 cm^{-1} is assigned to a defect struc-

ture present in tri-cyclosiloxane rings produced via the condensation of surface hydroxyls upon dehydration while the band at 800 cm^{-1} is attributed to the symmetric mode of Si–O–Si stretching [25]. Pure silica possesses a Si–O–Si

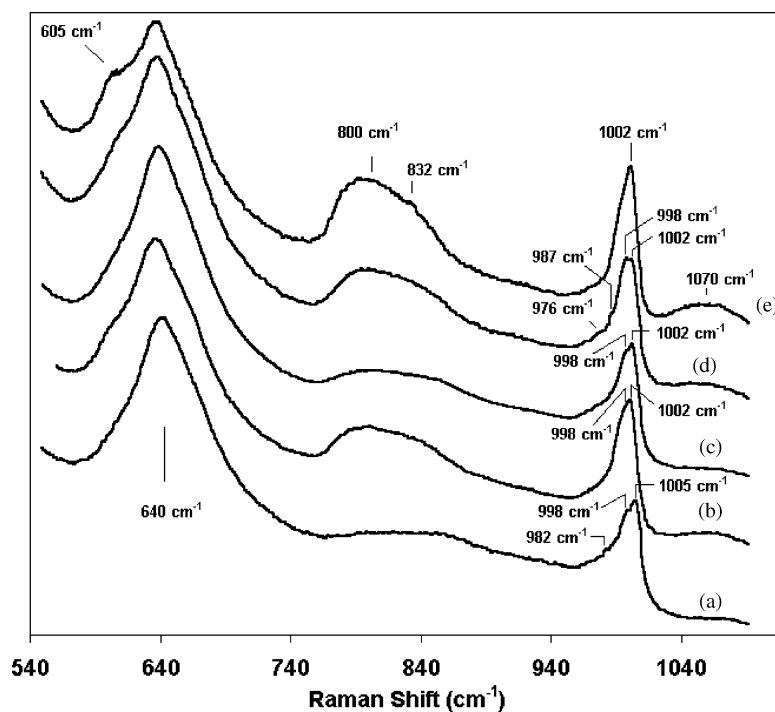


Fig. 3. Raman spectra (dehydrated conditions) of Mo/Si:Ti (1:1) catalysts modified with chlorine. Spectra taken under 10% O_2/He at room temperature: (a) Mo/Si:Ti (1:1); (b) co-precipitation using NH_4Cl ; (c) wet impregnation using HCl; (d) co-precipitation using HCl; (e) same as (d), using double the stoichiometric hydrolyzing water.

stretching vibration located at $\sim 1050\text{ cm}^{-1}$ [26]. In Fig. 3, this band is shifted to 1070 cm^{-1} , which shows a perturbed vibration that is indicative of Ti–O–Si bonds [25,27,28]. Chlorine-modified catalysts, prepared by the “one-pot” technique, show a significant increase in the broad band associated with Si–O–Si centered at 800 cm^{-1} (Fig. 3b, d and e) when compared to the Mo-only and wet impregnated catalyst. This could be an indication of a decreased coverage of the MoO_x species over silica and/or a significantly altered silica network due to the presence of Cl^- ions. Chlorine has been referred to as a “damaging precursor” when present on silica glasses and has been found to significantly distort silica glass networks [29,30]. Furthermore, the presence of halides (Cl and F), over low Mo-content silica has been found to decrease the interaction of molybdenum oxide domains with silica by the elimination of Mo–O–Si bonds [31]. The presence of chlorine can also bring about the appearance of defects in the silica network as indicated by the band at $\sim 605\text{ cm}^{-1}$ present in Fig. 3c.

Upon dehydration, the Raman bands associated with Mo=O stretching for the 10% Mo/Si:Ti (1:1) catalyst are seen to shift to higher frequencies and contain several contributions. However, for the chlorine-modified catalysts, the band locations do not exhibit a large shift indicating that the surface-supported species are stable through the dehydration process. A similar effect was found on $\text{MoO}_x/\text{SiO}_2$ catalysts, in which the interference of adsorbed water was inhibited with the introduction of chlorine [29]. Bands located at 982 and 998 cm^{-1} can be ascribed to MoO_x species experiencing a stronger interaction with silica while that located at 1005 cm^{-1} corresponds to a supported species interacting more strongly with titania [16,17]. With the addition of chlorine to the catalyst, the band at $\sim 982\text{ cm}^{-1}$ disappears on all catalysts except for one of the samples prepared by sol–gel/co-precipitation using HCl (Fig. 3d) while the two bands at higher frequency become sharper. A small shoulder present at 832 cm^{-1} provides some evidence for the presence of polymolybdate structures on the catalyst prepared by sol–gel/co-precipitation with HCl using excess hydrolyzing water.

Wachs [32] has summarized the Raman spectroscopy results, under dehydrated conditions, of Mo/SiO_2 and Mo/TiO_2 catalysts prepared by several methods and stated that Mo=O Raman bands of surface-supported MoO_x on titania appear in the range 998 – 1001 cm^{-1} . On silica under dehydrated conditions, these bands are reported to be a function of weight loading and appear in the range 975 – 990 cm^{-1} . However, in another study [33], bands arising from dehydrated surface-supported MoO_x species on silica were observed up to 998 cm^{-1} . The data present in literature suggest that it may be possible to interpret Raman spectrum of MoO_x supported over binary oxides to gain qualitative information about the interaction of MoO_x with the Si:Ti surface. Considering the spectra in Fig. 3, it appears that different preparation methods for the introduction of chlorine changes the relative contribution of the sup-

ported species that experience a stronger interaction with silica or titania. While chlorine has been reported to cause a decrease in the interaction of MoO_x with silica, there does not exist a significant decrease in the Mo=O bands for those species interacting with silica except for the Cl/Mo = 0.1 catalyst prepared with excess hydrolyzing water. For this catalyst, the broad band at 800 cm^{-1} and the defect band at 605 cm^{-1} are more prominent indicating that, perhaps only under certain preparation conditions, chlorine can significantly distort the silica network so that a diminished interaction of MoO_x with silica may exist.

3.2. X-ray photoelectron spectroscopy

To further study the nature of MoO_x species over the surface of the Si:Ti (1:1) support, XPS was performed over the various chlorine-modified catalysts. XPS (Mo 3d region) of Si:Ti (1:1) supported catalysts exhibited one linked doublet, indicative of molybdenum trioxide, corresponding to Mo $3d_{5/2}$ and $3d_{3/2}$ levels at 232.6 and 235.7 eV , respectively (Fig. 4). However, the Mo 3d spectra of the catalysts prepared by sol–gel/co-precipitation with HCl become slightly broader and a convoluted feature at lower binding energy is present near 231.6 eV for Mo $3d_{5/2}$ indicating an additional Mo component. This feature, which is likely related to chlorine introduction, is located at higher binding energy than what has been reported for molybdenum chlorides. The Mo $3d_{5/2}$ binding energy for molybdenum chlorides (MoCl_4 and MoCl_5) are reported to be located at 230.4 – 230.7 eV [34–36]. However, a reduced Mo(V) species has been reported to have a binding energy between 231 and 231.5 eV on alumina-supported catalysts [37–39]. It is therefore conceivable that this extra Mo $3d_{5/2}$ feature in Fig. 4 arises from the electronic interaction of Cl^- with MoO_x surface species without forming a new molybdenum chloride compound.

Additional XPS characterization (Si 2p, Ti 2p, and O 1s) was performed over the Cl-modified catalysts. The Si 2p spectra of all samples studied exhibited a peak located at 102.3 eV characteristic of SiO_2 . The Ti 2p spectra of 10% Mo/Si:Ti (1:1) exhibited one linked doublet corresponding to Ti $2p_{3/2}$ and $2p_{1/2}$ levels at 458.4 and 464.1 eV , respectively. The Ti 2p spectra remained unchanged in all Cl-modified catalysts. Since shifts in the Ti 2p binding energies are indicative of changes in the dispersion of TiO_x over silica [15,17,40], it is concluded that the introduction of chlorine, at the loading level that we studied, does not significantly alter the dispersed nature of TiO_x over the silica surface. This is in agreement with the XRD patterns obtained for the Cl-containing catalysts, which have shown a comparable anatase crystallite size. It is conceivable that higher Cl loading levels could cause an increase in the crystallinity of the anatase phase. In our earlier studies, the introduction of potassium to the 10% Mo/Si:Ti (1:1) catalyst caused a decrease in the dispersion of titania as well as the interaction of TiO_x species with silica [15,17]. But this effect was only noticeable a higher alkali loading levels. The O1s XPS

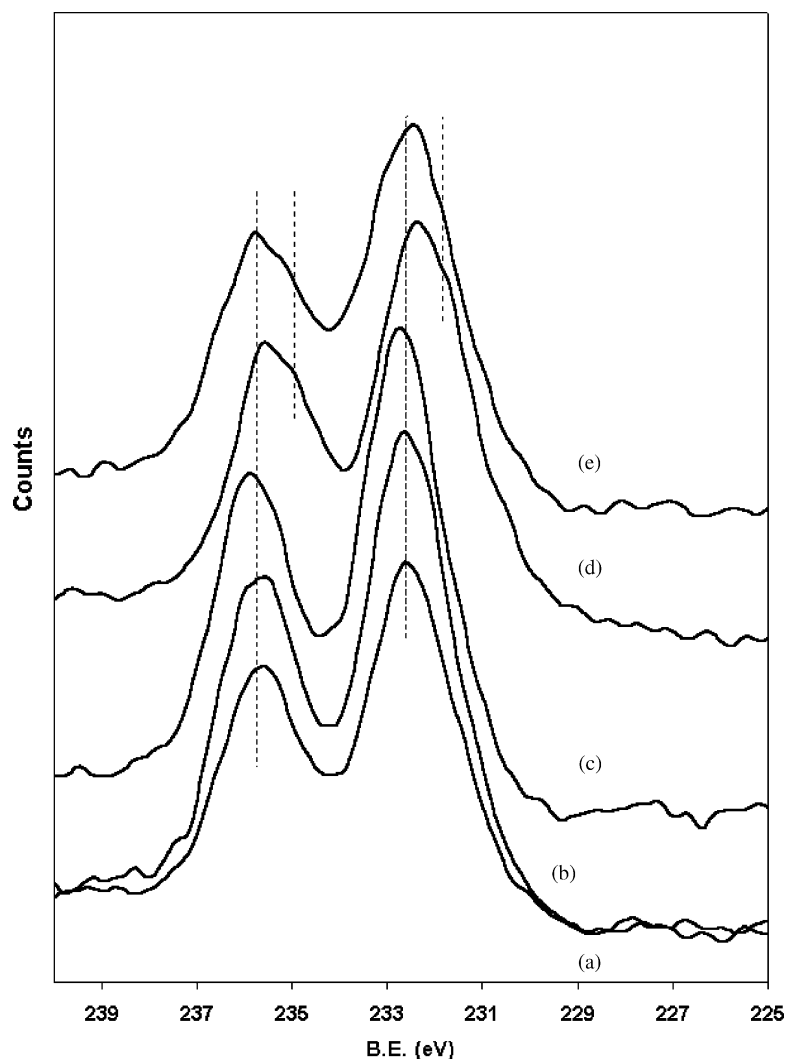


Fig. 4. Mo 3d XPS spectra of Mo/Si:Ti (1:1) catalysts modified with chlorine: (a) Mo/Si:Ti (1:1); (b) co-precipitation using NH_4Cl ; (c) wet impregnation using HCl; (d) co-precipitation using HCl; (e) same as (d), using double the stoichiometric hydrolyzing water.

spectra of the chlorine-containing catalysts did exhibit some differences, however, and are shown in Fig. 5. Each sample exhibits oxygen contributions from TiO_x , SiO_x , and MoO_x . O 1s from SiO_x is located at ~ 533.4 eV, while the signal from TiO_x and MoO_x coincide around 531.5 eV. A subtle difference is noted in the spectrum for the catalyst prepared by co-precipitation with HCl (Fig. 5d and e). These samples have a broader O 1s spectrum that tails out from the MoO_x - TiO_x region in the range 531–526 eV. These broad features could arise from the same Cl–Mo interaction species observed in the Mo 3d spectra. The broadness of this feature shows that the interaction comes not from one but a distribution of chemical environments. This suggests that the Cl–Mo interaction could be restricted to an electronic one and can affect the environment of MoO_x species, without forming Mo–Cl bonds.

The surface concentrations, as determined by XPS, are shown in Table 2. As expected, there is an increase in Si surface concentration when compared to the as-prepared val-

ues for catalysts studied. A decrease in Ti concentration observed by XPS measurements is common for Si:Ti binary oxides prepared by a variety of methods and is due to the difficulty of dispersing TiO_x over silica [41,42]. It has also been suggested that a majority of Ti atoms may reside on the surface of inside channels or pores of silica, which can be out of the XPS detection range [27]. Within the experimental limits of the technique, it is seen that the surface concentrations do not vary much with the introduction of chlorine by the various methods employed. There is only a slight decrease in the Ti concentration for the catalyst prepared by wet impregnation with HCl, which may be due to segregation of a crystalline anatase phase, as seen in the XRD patterns.

The data indicate that the introduction of chlorine at this loading level does not significantly alter the state of the Si:Ti support and that the chlorine predominantly acts upon MoO_x domains without significantly changing the surface concentrations (as determined by XPS). It may be possible that in

Table 2
Atomic concentrations as determined by XPS

Catalyst	Composition	Preparation	Si (%)	Ti (%)	Mo (%)
		As-prepared (bulk)	46.25	46.25	7.5
(a)	10% Mo/Si:Ti (1:1)	Sol-gel/co-precipitation	53	37	10
(b)	10% (Cl/Mo = 0.1)/Si:Ti (1:1)	Co-precipitation using NH ₄ Cl	50	41	9
(c)	10% (Cl/Mo = 0.1)/Si:Ti (1:1)	Wet impregnation using HCl	56	36	8
(d)	10% (Cl/Mo = 0.1)/Si:Ti (1:1)	Co-precipitation using HCl	53	37	10
(e)	10% (Cl/Mo = 0.1)/Si:Ti (1:1)	Co-precipitation using HCl	52	39	9

For catalyst (e), the amount of hydrolyzing water was doubled from the amount used for catalyst (d).

the “one-pot” preparation method, in which components are dispersed together during gelation, all the MoO_x and TiO_x species may not be preferentially located at the surface of silica readily accessible for detection. However, the present data indicate that there is not a large change in homogeneity of the catalyst with preparation method. While Raman data suggest that, with certain preparations, the presence of chlorine may decrease the interaction of MoO_x with silica, there were no Raman features from MoO₃ crystallites detected. It is likely that the presence of chlorine, by affecting the electronic structure of MoO_x domains, can alter the nature of the support-O ligands at the surface without causing significant changes in MoO_x dispersion or agglomeration. As the Raman data indicate, MoO_x species may be supported at the surface through different types of support ligands with differing electronegativity. Furthermore, this distribution of

oxygen environments can be affected by the presence of chlorine, as indicated by the XPS data. The electronic effect of chlorine can alter the nature of these ligands and thereby affect reactivity of the supported species as well as their interaction with the support surface, without a detectable change in dispersion.

3.3. Reaction experiments for the oxidative dehydrogenation of ethane

(Cl/Mo)/Si:Ti catalysts were compared in the ODH reaction using equal surface area loading (200 m²) in the reactor and at temperatures of 550 and 600 °C. For comparison to the effects of alkali promotion, the alkali-promoted (K and Li) catalysts were also tested. The feed percentages for these experiments were N₂/C₂/O₂ = 85/10/5. Oxygen conversion was nearly 100% in all runs. Reaction data were taken after steady state was reached. Ethane conversion and the yield of reaction products for these reaction tests is given in Table 3. Compared to the Mo-only catalyst, all promoted catalysts exhibited a decrease ethane conversion at 550 °C with the exception of the Li promoted catalyst, which showed a slight increase. At 600 °C, the highest conversion is achieved using the catalyst modified with lithium, followed by the potassium-modified catalyst with ethane conversions of 41 and 37%, respectively. While the alkali-modified catalysts increase ethane conversion at 600 °C compared to the molybdenum-only catalyst, all chlorine-modified catalysts decreased ethane conversion.

The data indicate that the highest yield of ethylene is obtained over the catalyst prepared by sol-gel/co-precipitation with HCl (using only the stoichiometric amount of hydrolyzing water necessary to form the support structure). Doubling the hydrolyzing water in the preparation of catalyst (e) in Table 3, was attempted to increase ethylene yield by increasing the dispersion of the MoO_x species. As Table 3 indicates, this attempt was unsuccessful, as the yield of this catalyst is lower than that of the Mo-only catalyst on an equal surface area basis. It is apparent that only certain preparation methods may be able to modify the catalyst for ethane ODH in a favorable way. Thus, co-precipitation with HCl was the only method that enhanced ethylene yield when compared to the Mo-only catalyst. The data indicate that this increase is accompanied by a decrease in the formation of CO₂. The Raman spectrum of this catalyst (Fig. 3d) shows a higher

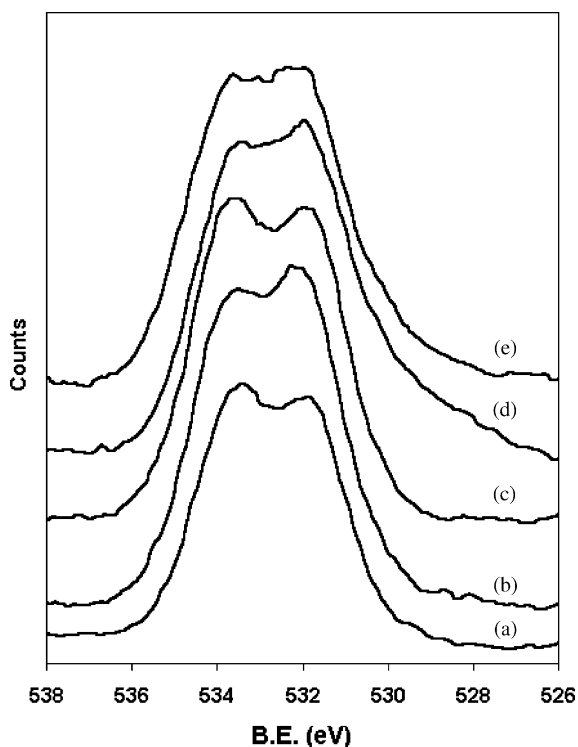


Fig. 5. O 1s XPS spectra of Mo/Si:Ti (1:1) catalysts modified with chlorine: (a) Mo/Si:Ti (1:1); (b) co-precipitation using NH₄Cl; (c) wet impregnation using HCl; (d) co-precipitation using HCl; (e) same as (d), using double the stoichiometric hydrolyzing water.

Table 3
Reaction results for the ODH of ethane (equal surface area experiments, 200 m²)

T (°C)	Conversion (%)	Yield			
		C ₂ H ₄	CO ₂	CO	CH ₄
10% Mo/Si:Ti (1:1) (a)					
550	30.5	11.9	6.1	11.2	1.1
600	34.8	16.3	6.6	9.5	2.2
10% (Cl/Mo = 0.1)/Si:Ti (1:1) (b)					
550	25.1	9.1	6.9	8.5	0.5
600	29.8	12.7	7.0	8.9	1.2
10% (Cl/Mo = 0.1)/Si:Ti (1:1) (c)					
550	25.8	9.6	6.6	9.0	0.4
600	29.3	13.2	8.1	5.5	2.2
10% (Cl/Mo = 0.1)/Si:Ti (1:1) (d)					
550	28.4	14.1	3.8	10.4	0.2
600	34.2	18.6	4.8	9.5	1.3
10% (Cl/Mo = 0.1)/Si:Ti (1:1) (e)					
550	27.0	12.4	4.9	9.2	0.5
600	33.5	16.0	6.4	8.8	2.3
10% (K/Mo = 0.1)/Si:Ti (1:1) (f)					
550	27.4	12.8	6.1	7.1	1.4
600	37.1	15.0	8.2	6.8	7.1
10% (Li/Mo = 0.1)/Si:Ti (1:1) (g)					
550	31.3	11.0	6.4	9.6	4.4
600	40.6	12.8	7.9	7.2	12.8

Method of preparation for catalysts: (a) sol–gel/co-precipitation; (b) co-precipitation using NH₄Cl; (c) wet impregnation using HCl; (d) co-precipitation using HCl; (e) same as (d), using double the stoichiometric hydrolyzing water; (f) co-precipitation using KOH; (g) co-precipitation using LiOH.

contribution from bands that could be associated with MoO_x species experiencing a stronger interaction with silica at 976, 987, and 998 cm⁻¹. Previous results [16,17] have also shown an increase in propylene formation in propane ODH experiments when the interaction of MoO_x with the silica of the Si:Ti support is increased in such manner. Furthermore, the electronic interaction of Cl with MoO_x species appears to be maximized over this Cl/Mo = 0.1 catalyst as indicated by the XPS data.

It is interesting to note that, in contrast to propane ODH results, low levels of alkali (K or Li) do not increase the yield of olefin and form a much larger amount of methane during the ethane ODH experiments when compared to the Mo-only catalyst. Alkali promotion has been shown to increase olefin yields in lower alkane ODH by affecting the nature of the transition metal–oxygen bond and thus affecting acid–base and redox characteristics of the surface ([12], and references therein). Concerning the Si:Ti (1:1) support, work from our laboratory has shown that the presence of potassium significantly alters the electronic structure of the surface MoO_x domains even before the onset of K-molybdate formation [17]. Surface-supported species, present as distorted octahedral MoO_x, become the most distorted at low levels of alkali (K/Mo = 0.07) and exhibit an increase in propylene yield

during propane ODH experiments. However, the positive effects of alkali doping for higher hydrocarbons has been reported to be reversed for ethane ODH [12,43]. This reversal is partially due to the fact that ethylene is more stable than the higher olefins. In attempts to decrease further oxidation of the formed olefin, a large benefit in ethane ODH would not be obtained by decreasing the Lewis acidity of the catalyst surface by introduction of alkali.

The reaction data presented in Table 3 can be normalized to molybdenum atoms in the form of turn over frequencies (TOFs). Calculation of MoO_x surface densities, assuming all Mo is located at the surface, while applicable for impregnated Si:Ti supports, may be inaccurate for the “one-pot” preparation method employed for these catalysts. As discussed previously, there may be a significant amount of molybdena species located inside larger titania aggregates or deeper inside the silica network. However, since the XPS data indicate that there are not large surface concentration changes present with the preparation method for the introduction of chlorine, the TOF calculation may give a fair comparison between the catalysts, although absolute numbers may be significantly smaller than the “true” TOFs. Such calculations showed that all three of the co-precipitation catalyst increased the TOF of ethylene compared to the Mo-only catalyst.

3.4. Temperature-programmed reduction

Temperature-programmed reduction experiments were performed on 10% Mo catalysts with the chlorine modifiers. TPR profiles were obtained over the three Cl-containing catalysts prepared by sol–gel/co-precipitation. The results are plotted in Fig. 6. The bare Si:Ti support showed no reduction under these conditions. The profiles for the Si:Ti (1:1) supported catalysts are similar, consisting of one major reduction feature in the temperature range 350–500 °C due to the reduction of supported MoO_x species. The center of each major reduction peak and shoulders present within this peak, are listed in Table 4. The major reduction peak for 10% Mo/Si:Ti (1:1) is centered at 431 °C. With the addition of chlorine to the catalysts the major reduction peaks become noticeably asymmetrical, representing two different reduction sites. The catalyst prepared using NH₄Cl shows the lowest temperature reduction peak, centered at 410 °C

Table 4
Temperature-programmed reduction of promoted Mo/Si:Ti (1:1) catalysts

Catalyst	First peak maxima (°C)
10% Mo/Si:Ti (1:1) (a)	431
10% (Cl/Mo = 0.1) (b)	410, 446 (sh)
10% (Cl/Mo = 0.1) (c)	403 (sh), 448
10% (Cl/Mo = 0.1) (d)	421 (sh), 455

Method of preparation for catalysts: (a) sol–gel/co-precipitation; (b) co-precipitation using NH₄Cl; (c) co-precipitation using HCl; (d) same as (c), using double the stoichiometric hydrolyzing water; sh: shoulder.

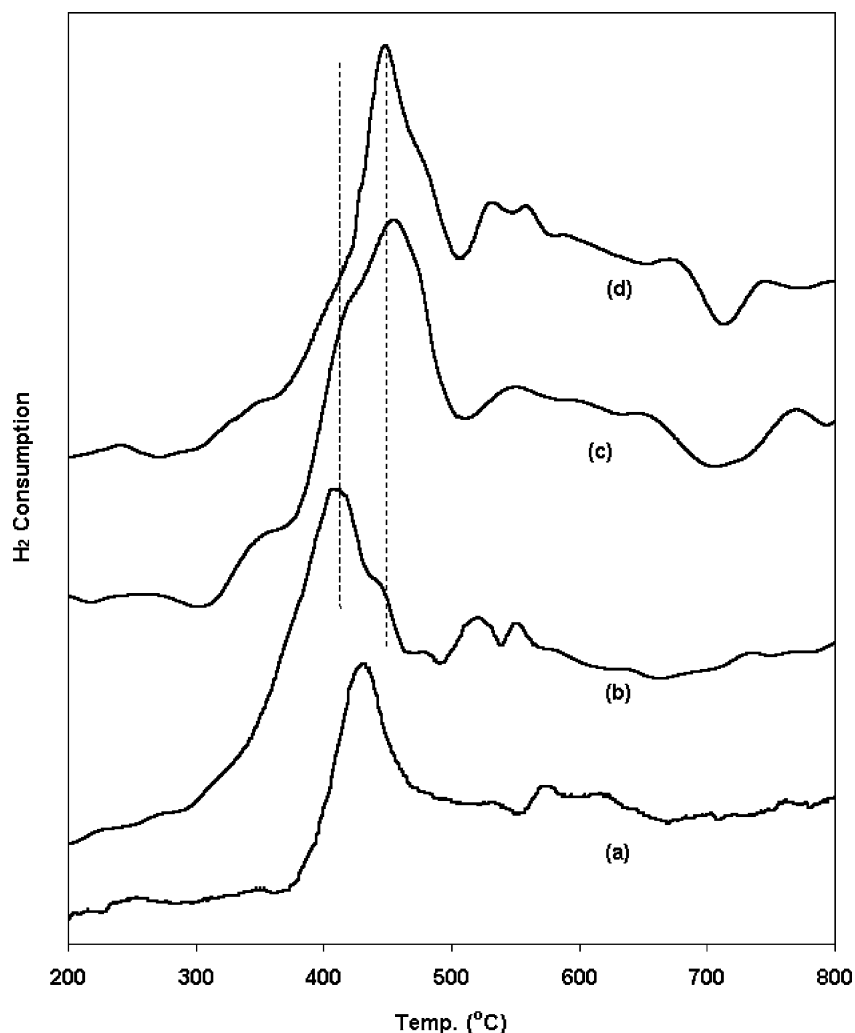


Fig. 6. Temperature-programmed reduction profiles obtained for Mo/Si:Ti (1:1) catalysts modified with chlorine by co-precipitation: (a) Mo/Si:Ti (1:1); (b) co-precipitation using NH_4Cl ; (c) co-precipitation using HCl ; (d) same as (c), using double the stoichiometric hydrolyzing water.

with a shoulder at 446°C . When this profile is compared to the other Cl/Mo catalysts, we can see that the shoulder in the TPR profile of the NH_4Cl catalyst is also present there, but as the main reduction feature. Furthermore, the main reduction peak in the NH_4Cl catalyst is present in the HCl -prepared 10% Cl/Mo catalysts (c) and (d) at 421 and 403°C , respectively. The major reduction feature for 10% Cl/Mo catalysts (c) and (d) occur at higher temperatures at 448 and 455°C , respectively. All chlorine-containing catalysts also show an increased hydrogen consumption in the temperature range 500 – 600°C when compared to the Mo-only catalyst.

It is apparent that the introduction of chlorine to the catalyst enhances the number of reducible sites present on the catalysts. All chlorine-containing catalysts have shown two main reduction features while the Mo-only sample shows only one. The best performing catalyst in this study (Fig. 6c), has close to equal contributions from both a lower temperature reduction feature (421°C) and a higher temperature reduction feature (455°C). This mix of reducible species may

provide an optimum balance of oxygen availability at differing strengths. As a result, the C–H bond activation step of ethane, which would require the reduction of a Mo^{6+} site, may proceed more readily on a more reducible surface. The origin of these reducible sites could be related to the interaction of MoO_x domains with the support. Wachs and co-workers [44] have reported a TPR spectrum that splits into two reduction peaks for the 1% $\text{V}_2\text{O}_5/30\%$ $\text{TiO}_2/\text{SiO}_2$ sample where both TiO_2 crystallites and the surface titanium oxide species coexist on silica. Furthermore, Arena and Parmaliana [45] have claimed that the several surface Mo(VI) species of silica-supported molybdena catalysts detected in TPR measurements arise from different interaction strengths with the underlying support. Thus, it can be argued that the two reduction sites, that are in somewhat equal proportion (10% Cl/Mo = 0.1, Fig. 6c), are due to MoO_x domains strongly interacting with titania and silica, respectively. Raman data presented in this study would be consistent with this argument, indicating that there is a more even distribution of MoO_x species interacting with the silica and titania

domains of the support over this catalyst. This may be, in part, the explanation for the higher ethylene yield obtained over this catalyst when compared to the Mo-only catalyst. However, when reaction data is normalized per Mo atom, all Cl-containing catalysts prepared by co-precipitation appear to perform better than the Mo-only catalyst. The differing performance amongst the preparations likely arises from the degree to which chlorine is able to modify the oxygen environment around MoO_x species, thereby affecting their reactivity and interaction with the support structure.

It is believed that activity in the oxidative dehydrogenation of ethane is a strong function of redox characteristics of the catalyst. This is especially true for transition metal oxides on which reaction proceeds via a redox mechanism at low temperatures. When we compare the chlorine-containing catalysts it seems apparent that through different preparations, we are altering the redox properties of the catalysts. All chlorine-containing catalysts have shown two distinct reduction features while the alkali-promoted sample shows only one. It has previously been observed [17], from XPS and ESR data, that the low-level addition of alkali to MoO_x-based catalysts is able to alter the electronic properties of supported MoO_x species while significantly affecting their interaction with the binary oxide support. This can naturally lead to positive effects in reducibility and acidity of those supported centers. Thus, it seems reasonable to conclude that, under the right preparation conditions, the addition of Cl to the MoO_x-based catalysts can alter the surface species in a similar manner. The fact that alkali addition has a strong promotional effect in propane ODH while ethane ODH seems to be better served by halide promotion could be due to the differences in the catalytic functionalities needed for alkane activation versus further reaction of the olefin molecule in these two reactions.

4. Conclusions

This study has examined the effects of chlorine modification on molybdenum catalysts supported on the mixed-oxide of SiO₂ and TiO₂. These catalysts were prepared using “one-pot” sol–gel/co-precipitation or wet impregnation techniques. Ethane ODH reaction experiments were performed with constant feed conditions at two different temperatures. The highest improvement in ethylene yield was achieved using a catalyst modified with chlorine by co-precipitation with HCl. However, reaction performance comparisons normalized per Mo atom, suggest that all Cl-modified catalysts prepared by co-precipitation were able to improve performance. Addition of alkali (Li, K) to the 10% Mo/Si:Ti (1:1) catalyst did not improve the ethane ODH performance compared to the unmodified catalyst, in contrast to previous results obtained for propane ODH.

The introduction of chlorine by the co-precipitation technique at the Cl/Mo ratio used in this study does not appear to increase the segregation of crystalline anatase in the Si:Ti

(1:1) support, as indicated by X-ray diffraction results. Similarly, XPS shows that the surface concentrations of Si, Ti, and Mo remain relatively constant with different preparation methods for the introduction of chlorine to the 10% Mo/Si:Ti (1:1) catalyst. The data suggest that, without forming a specific Mo–Cl phase or compound, and without causing detectable MoO_x aggregation, chlorine is able to significantly alter the reducibility of the supported species. Furthermore, Raman and XPS data suggest that, under certain preparation conditions, this can lead to an optimal interaction of the oxygen environment surrounding the Mo atoms and that of the Si:Ti binary support.

While the addition of halide modifiers is known to positively affect the gas-phase mechanisms of ethane ODH at higher temperatures (>650 °C), current work indicates that the effect for surface redox mechanisms over MoO_x-based catalysts may be somewhat less-pronounced, but still beneficial, at lower temperatures of operation. It may be possible that the addition of other halide modifiers may offer a more pronounced benefit in terms of ethylene yield. Additional work is being performed in our laboratory to evaluate catalyst performance at higher chlorine contents and to determine the halide’s effect on the oxygen environment of the catalyst.

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