# Infrared Spectroscopic Studies of the Adsorption and Reaction of 3-Methyl-2-butenal over Alkali-Promoted Ru/SiO<sub>2</sub> Catalysts

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Flow reaction studies of the hydrogenation of 3-methyl-2-butenal over  $Ru/SiO_2$  and potassium-promoted  $Ru/SiO_2$  were combined with *in situ* infrared spectroscopic monitoring of its adsorption and reaction as well as the adsorption of its reaction products. The presence of the alkali promoter significantly inhibited this hydrogenation to form the saturated aldehyde, a reaction which was followed by decarbonylation of the saturated aldehyde in a reverse migratory insertion process. The initial formation of adsorbed CO and hydrocarbon products from the saturated aldehyde may ultimately be responsible for the product distribution observed under steady-state reaction conditions.

# Introduction

There is currently an increased interest in the use of heterogenous catalysts for the syntheses of the fine chemicals,<sup>1,2</sup> of which the selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes to produce unsaturated alcohols is an example. Selectivity, a key issue in these reactions, may be improved by addition of promoters and/or an appropriate choice of support for the metal being used.<sup>3-10</sup>

We recently reported that the presence of alkali promoters has a dramatic influence on selectivity in the hydrogenation of 3-methyl-2-butenal (I) over supported ruthenium catalysts.<sup>3,6</sup> The possible reactions form a consecutive-parallel network as shown in Scheme I. The partial hydrogenation product II is thermodynamically favored over the desired product III and this indeed accounts for over 85% of the product formed over unpromoted  $Ru/SiO_2$  in the gas-phase flow reactions. With a potassiumpromoted catalyst, however, selectivities of over 70% to the desired product III, the unsaturated alcohol, could be achieved. While selectivities achieved at steady state were reported in that paper, the current work focuses on changes observed during the initial period leading up to steady-state operation. We report on the examination by *in situ* infrared spectroscopy of the nature of the surface species present during the initial stages of the reaction.

# **Experimental Section**

Catalyst Preparation and Characterization. The details of preparation and characterization have been reported elsewhere.<sup>3</sup> Briefly, the silica supported Ru (3 wt % nominal loading) catalyst was prepared from Ru(NO)(NO<sub>3</sub>)<sub>3</sub> (Alfa) and SiO<sub>2</sub> (Cabot Corp., Cabot M-5, 200 m<sup>2</sup>/g) by wet impregnation followed by drying overnight at 353 K. The catalyst was then reduced in flowing hydrogen at 673 K for 4 h following a 0.5 K min<sup>-1</sup> temperature ramp. The potassium promoted catalyst was prepared by wet impregnation of the reduced base catalyst with an aqueous solution of KNO<sub>3</sub>, corresponding to a nominal K/Ru atom ratio of 0.1. This was followed by a second treatment in hydrogen as described above.

In situ Infrared Spectroscopy. Infrared spectroscopic measurements were performed with a Mattson Polaris FTIR spectrometer equipped with a liquid nitrogen cooled MCT detector using 4 cm<sup>-1</sup> resolution and coaddition of 200 scans. Adsorption and reaction studies were carried out using a glass gas handling system equipped with bulbs containing the liquid adsorbates from SCHEME I



which vapor could be introduced into the cell at a known pressure. Self-supporting wafers of the catalysts were prepared by pressing at 100 MPa and were placed in a stainless steel *in situ* cell capable of evacuation of  $10^{-6}$  Torr and heating to 673 K. Samples were pretreated by heating under 700 Torr H<sub>2</sub> at 673 K for 2 h after ramping to the reduction temperature at 2 K min<sup>-1</sup>. The samples were then evacuated at 673 K for 1 h and cooled to 313 K where the various static adsorption experiments were performed. Typical partial pressures of the adsorbates were less than 2 Torr for I and II, up to 5 Torr for carbon monoxide, and about 700 Torr for H<sub>2</sub>.

**Reaction Studies.** Continuous-flow, gas-phase hydrogenation of 3-methyl-2-butenal (I) was carried out at atmospheric pressure in a heat-treated stainless steel system with a Pyrex reactor. The reactant I was admitted to the reactor in a stream of He gas bubbled through the liquid in a glass saturator kept at 298 K in a water bath. About 0.1 g of the catalyst was placed in the reactor and pretreated at 673 K in flowing hydrogen for 2 h after ramping at 0.5 K min<sup>-1</sup>, followed by a He flush at 673 K for 10 min. Flow of the reactants commenced after cooling the catalyst to the reaction temperature in flowing He. The flow rate of the reactant was 30  $\mu$ mol min<sup>-1</sup> and that of H<sub>2</sub> was 100 mL min<sup>-1</sup> at a constant total gas flow rate of 200 mL min<sup>-1</sup> and a reaction temperature of 313 K. Products formed were monitored over reaction times up to 4 h by GC analysis.

#### Results

Flow Reaction Studies. Figures 1 and 2 show the results of the flow reaction of 3-methyl-2-butenal (I) as a function of time over the unpromoted  $Ru/SiO_2$  and the potassium-promoted  $Ru/SiO_2$  catalysts, respectively. In our earlier report,<sup>3</sup> reaction results were reported only after steady-state operation had been achieved.

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Figure 1. (a) Reaction rates and (b) selectivities for products II, III, and IV as a function of time during the gas phase flow reaction of I and  $H_2$  over  $Ru/SiO_2$ .



Figure 2. (a) Reaction rates and (b) selectivities for products II, III, and IV as a function of time during the gas phase flow reaction of I and  $H_2$  over  $Ru-K/SiO_2$ .

It is clear from these figures that both the overall reaction rate and the product distribution changed dramatically during the initial 40 min of reaction leading up to steady-state. For the Ru-K/SiO<sub>2</sub> catalyst, the rate of production of the desired product III increased during this induction period (Figure 2a), resulting in the significant increase in selectivity to III that was observed at steady-state (Figure 2b). This is in contrast to the unpromoted catalyst where the rates of all products fell over time (Figure 1a).



**Figure 3.** IR spectra of (a) the SiO<sub>2</sub> support after pretreatment, (b) the vapor phase of I, and (c) the adsorption of I on pretreated SiO<sub>2</sub>.



Figure 4. IR spectra of the coadsorption of I with  $H_2$  on  $Ru/SiO_2$  over time (0-30 min) subtracted from the spectrum of the pretreated catalyst.

In situ Infrared Spectroscopy. (a) Adsorption of 3-Methyl-2-butenal (I). Figure 3 shows the IR spectra of the blank  $SiO_2$ support and the unsaturated aldehyde I adsorbed on the support compared to its vapor phase. Upon adsorption of I, the characteristic hydroxyl group stretching band for the silanol OH disappeared concomitant with the appearance of the broad band in the hydrogen bonded hydroxyl stretching frequency. In addition, the C=O stretching frequency of the unsaturated aldehyde was downshifted by about 40 wavenumbers from about 1700 cm<sup>-1</sup> in the vapor phase to about 1660 cm<sup>-1</sup> in the adsorbed state.

A comparison of the adsorption of I on the two catalysts  $Ru/SiO_2$  and  $Ru-K/SiO_2$  to that on the blank silica support showed that the frequency of the C=O stretching band was practically identical for the three samples.

(b) Coadsorption of I and H<sub>2</sub>. Figure 4 shows difference spectra of the coadsorption of I with H<sub>2</sub> on the Ru/SiO<sub>2</sub> catalyst taken over a period of 30 min. These are difference spectra subtracted from the pretreated catalyst prior to the adsorption of I, giving a negative silanol peak in each case. Changes in the spectrum over time suggest that surface reactions have occurred. After about 10 min two new bands appeared in the carbonyl stretching frequency region. One was centered at 1712 cm<sup>-1</sup>, in the range for organic carbonyl groups. A second band appeared at 1950 cm<sup>-1</sup> and shifted upward to 1985 cm<sup>-1</sup> as it grew over time. This band is in the region for CO bound to transition metals (the M-C



Figure 5. Integrated absorbances of IR peaks over time during coadsorption of I with  $H_2$  on  $Ru/SiO_2$ : (a) 1660 cm<sup>-1</sup>; (b) 1712 cm<sup>-1</sup>; (c) 1950–1985 cm<sup>-1</sup>; (d) 2965 cm<sup>-1</sup>.



Figure 6. IR spectra of the coadsorption of I with  $H_2$  on  $Ru-K/SiO_2$  over time (0-30 min) subtracted from the spectrum of the pretreated catalyst.

stretch for metal-bound CO which would be found between 400 and 500 cm<sup>-1 11</sup> is masked by the intense absorption bands of the support below 1200 cm<sup>-1</sup>). In addition, an increase in total intensity as well as a change in relative intensities of peaks in the C-H stretching region was observed, dominated by a strong peak at 2965 cm<sup>-1</sup>. Over a 30-min period a marked decrease in intensity of the carbonyl stretch of adsorbed I was observed with continued increase in intensity of the C-H stretching bands. The increase in intensity of the new band at 1712 cm<sup>-1</sup> on Ru/SiO<sub>2</sub> leveled off after about 10 min after the adsorption of hydrogen. Figure 5 illustrates these changes upon coadsorption of I with H<sub>2</sub> by plotting the integrated absorbances of these C=O and C-H stretching vibrations over time. Although a quantitative measure of the surface concentrations of these species should be made only after extensive calibration, this figure provides a qualitative, comparative picture of the growth of these species over time.

Figure 6 shows spectra of the time evolution of the coadsorption of I with  $H_2$  on the  $Ru-K/SiO_2$  catalyst over a period of 30 min. Comparison with Figure 4 reveals similar changes in the spectra as observed for  $Ru/SiO_2$  but of a much smaller magnitude. The C==O stretch of I did not decrease to the extent observed for  $I/H_2$  adsorption on  $Ru/SiO_2$  over the same period. The metalbound CO band was much weaker for the promoted catalyst, and it ranged from 1927 to 1943 cm<sup>-1</sup> as it increased very slowly over time. The new organic CO band at 1712 cm<sup>-1</sup> and the C=-H stretching region also increased at a much slower rate, never reaching the intensity of these bands during  $I/H_2$  coadsorption on unpromoted  $Ru/SiO_2$ .



Figure 7. IR spectra of the adsorption of II on (a)  $SiO_2$ , (b)  $Ru/SiO_2$ , and (c)  $Ru-K/SiO_2$  subtracted from the respective spectra of the pretreated samples.

(c) Adsorption of 3-Methylbutanal (II). In order to confirm the identity of the new peaks formed from the coadsorption of I with hydrogen, the intermediate product II was adsorbed on  $Ru/SiO_2$ ,  $Ru-K/SiO_2$ , and the silica support. The IR spectra of II on the two Ru catalysts shown in Figure 7 closely resemble the spectra of coadsorbed I and H<sub>2</sub> shown in Figures 4 and 6. Two bands similar to those which developed in the carbonyl stretching region during coadsorption of  $I/H_2$  appeared during adsorption of II, one centered at about 1715 cm<sup>-1</sup> and the other in the metalbound CO region of about 1960-1970 cm<sup>-1</sup>. The C-H stretching region more closely resembled that of the coadsorbed  $I/H_2$  than that of I alone, in both the overall and relative intensities of the peaks, dominated by the high frequency peak at 2965 cm<sup>-1</sup>. While the spectrum of I on the pure SiO<sub>2</sub> support (also shown in Figure 7) exhibited similar peaks in the C-H region and at 1715  $cm^{-1}$ , the peak in the metal-bound CO region was absent for II absorbed on the support.

(d) Coadsorption of I, CO and H<sub>2</sub>. In order to establish that it was indeed metal-bound CO that was observed in the 1950-1985 cm<sup>-1</sup> region, coadsorption of I and carbon monoxide was carried out. This was followed by the coadsorption of  $H_2$  to observe the effect of adsorbed CO on the interaction of I with H<sub>2</sub>. Figure 8 compares the spectra of coadsorption of I, CO, and  $H_2$  on the two catalysts over extended times after the addition of  $H_2$  (ca. 12 h). The adsorbed CO band appeared at slightly higher frequencies compared to metal-bound CO formed after coadsorption of  $I/H_2$ , giving peaks at 1999 and 1988 cm<sup>-1</sup> for I/CO coadsorption on Ru/SiO<sub>2</sub> and Ru-K/SiO<sub>2</sub>, respectively. No changes in either the carbonyl C=O stretching band or the C—H stretching region were observed for coadsorption of  $I/H_2/$ CO even after 12 h, contrary to the case of I/H<sub>2</sub> coadsorption in the absence of CO, where significant changes occurred in less than 1 h.

# Discussion

Flow Reaction Studies. The significant changes in reaction rate and product selectivities that were observed during the initial period of reaction before steady-state operation was reached suggest that the composition of species on the catalyst surface underwent changes during this period. This was especially important in the case of the Ru-K/SiO<sub>2</sub> catalyst where the selectivity to the desired product III rose from 10% at the outset to its steady-state value of close to 80%. This observation implies that it is not the clean catalyst surface which is responsible for



Figure 8. IR spectra after 12 h of coadsorption of I with CO and  $H_2$  on (a)  $Ru/SiO_2$  and (b)  $Ru-K/SiO_2$  subtracted from the respective spectra of the pretreated catalysts.

the high selectivity to III but rather a surface covered with a mixture of adsorbed reactants, products, and organic fragments that develops over time, altering the reactivity of surface sites. Such self-poisoning and self-promoting effects are common in catalytic reactions, and achievement of a fundamental understanding of the reaction relies on gaining an understanding of the nature of the *working* catalyst surface. In situ infrared spectroscopy provides a means of examining the evolution of surface species over time, and our results using this technique are discussed below.

In situ Infrared Spectroscopy. (a) Adsorption of I. The disappearance of the characteristic silanol stretching frequency and the appearance of the broad hydrogen bonded hydroxyl band upon adsorption of I suggest the occurrence of hydrogen bonding of I with the hydroxyl groups of the support. It has been observed that the carbonyl stretching absorption is displaced to lower frequencies when the carbonyl group of an aldehyde is hydrogenbonded with a hydroxylic substance.<sup>12</sup> The association of a hydrogen with a carbonyl group tends to decrease the double bond character of the carbonyl, thereby shifting the absorption of the organic C=O group of I to lower frequency. This is consistent with the downshift we observed upon adsorption of I, suggesting that the hydrogen bonding between I and support hydroxyl groups occurred through the carbonyl group.

The similarities in the IR spectra for adsorbed I on SiO<sub>2</sub>, Ru/SiO<sub>2</sub>, and Ru-K/SiO<sub>2</sub> imply that a significant fraction of the molecules were adsorbed in this manner on the support. This agrees with our observation in previous work<sup>3</sup> that the catalysts took up significant amounts of I during early stages of the flow reaction experiments, considerably larger quantities than could be accounted for by adsorption on the metal surface alone. Any differences in the nature of the adsorption of I on the metal sites of the two catalysts may therefore have been masked by the large uptake on the SiO<sub>2</sub> support.

(b) Coadsorption of I and  $H_2$  and the Adsorption of II. In situ IR monitoring of the coadsorption of I and hydrogen revealed evidence of chemistry occurring on ruthenium rather than on the support. One such sign was the appearance of a band in the metal-bound CO region, much more intense for  $Ru/SiO_2$  than for  $Ru-K/SiO_2$ , suggesting partial decarbonylation of the adsorbed organic molecule. The accompaniment of this decarbonylation with several other features helps us to interpret the reactions taking place on the surface.

The growth of peaks in the C-H stretching region and changes in their relative intensities compared to I may be attributed to hydrogenation of the C=C function of I to produce II. The C—H stretching region of adsorbed I (Figure 4, time = 0 min) and II (Figure 7) may be compared to spectra for the hydrocarbons isobutene and isobutane, respectively. A C—H region dominated by the high frequency peak at 2965 cm<sup>-1</sup> due to asymmetric CH<sub>3</sub> stretching is characteristic of molecules with methyl groups on a saturated tertiary carbon such as isobutane or II, while the C—H region of I resembles that of the unsaturated isobutene.

Consistent with the appearance of a C-H region characteristic of a molecule such as II is the appearance of the organic C=O peak at 1712 cm<sup>-1</sup>, just as was found for adsorbed II. It is likely that most of the hydrogenation of I to give the saturated aldehyde II preceded the decarbonylation reaction since metal-bound CO formed only very slowly upon adsorption of I in the absence of hydrogen. Carbonyl compounds are known to undergo decarbonylation on a number of transition-metal complexes in solution, the most efficient being (Ph<sub>3</sub>P)<sub>3</sub>RhCl, the Wilkinson hydrogenation catalyst.<sup>13,14</sup> This occurs via a "migratory de-insertion" reaction, in which an alkyl group migrates from the carbonyl group to the metal followed by the reductive elimination of the alkane. This last step is irreversible since alkanes do not oxidatively add to the metal carbonyl. We propose that the coadsorption of I and  $H_2$  on Ru catalysts produced adsorbed II, some of which underwent such a decarbonylation reaction forming isobutane and adsorbed CO on the Ru metal.

Figure 5 showed that the growth of the metal-bound CO peak and the butane-like hydrocarbon band were linked, both growing continuously concomitant with a steady decrease in I. The concentration of the saturated aldehyde species, however, seemed to reach a plateau after 5 min of reaction. This is consistent with the formation of II as an intermediate product, followed by decarbonylation to produce adsorbed CO and isobutane.

These C=C bond hydrogenation and aldehyde decarbonylation reactions occurred to a lesser extent on the potassium promoted catalyst than on the unpromoted catalyst. The significantly stronger intensity of the peaks for the saturated aldehyde and its decarbonylation products on the unpromoted catalyst is consistent with II being the predominant product on  $Ru/SiO_2$  in the steady state flow experiments reported earlier,<sup>3</sup> while II was formed in much smaller amounts on  $Ru-K/SiO_2$ . The potassium promoter may act to inhibit the C=C hydrogenation to form II as well as the subsequent decarbonylation reaction. The role of potassium in enhancing the parallel hydrogenation reaction of I to form III, however, is more difficult to discern from these IR studies. Lacking a strongly adsorbing C=O stretch, III exhibits as its characteristic IR fingerprint a weaker C=C stretch at 1675 cm<sup>-1</sup> when adsorbed on these catalysts. The presence of this peak may be masked by its proximity to the intense C=O stretch of I at 1660 cm<sup>-1</sup>. Thus, while the IR spectroscopic results help show how potassium suppresses production of II, they are unable to provide direct insight into how the promoter enhances the rate of formation of III.

The metal-bound CO appeared at a lower frequency for the promoted  $Ru/SiO_2$  than was observed for the unpromoted catalyst. While it may be tempting to attribute this difference to an electronic effect of the alkali species, it seems more likely to be due to differences in CO coverage. It is evident from Figures 4 and 6 that the frequency of the metal-bound CO is strongly coverage-dependent, with dipole-dipole interactions between neighboring CO molecules becoming more important as more CO molecules are adsorbed on the surface.<sup>15,16</sup> The concentration of metal-bound CO remained very low for the potassium-promoted catalyst even after extensive  $I/H_2$  coadsorption. When larger amounts of CO were added to both catalysts, as is discussed in the next section, the CO frequency for the promoted catalyst approached that of the unpromoted catalyst.

(d) Coadsorption of I, CO, and H<sub>2</sub>. The coadsorption of CO with I gave a high concentration of adsorbed CO at a slightly higher frequency than the CO peak formed from decarbonylation

during I/H<sub>2</sub> coadsorption, and there was only a slight difference in frequency between the promoted and unpromoted catalysts. This supports the suggestion that the frequency shifts observed in Figures 4 and 6 were indeed due largely to coverage-dependent dipole-dipole interactions. However, it is interesting to note that adsorbed CO is much more sensitive to the presence of the alkali species when coadsorbates are absent. Our previous work showed that adsorbed CO appears at about 2040 cm<sup>-1</sup> on clean  $Ru/SiO_{2}$ , and on the potassium-promoted catalyst this peak is slightly downshifted and a second peak is observed near 1940 cm<sup>-1</sup>.<sup>3</sup> The effect of coadsorbates on CO adsorption has been discussed in terms of possible geometric and electronic effects.<sup>17-20</sup> The coadsorbed organic molecule may help to screen the effects on the alkali species on adsorbed CO either by blocking a direct interaction between CO and potassium or by altering electronic effects of potassium on Ru.

The addition of H<sub>2</sub> to I and CO coadsorbed on the surface shows that adsorbed CO inhibited the hydrogenation of I on both catalysts. This inhibition suggests a mechanism for the deactivation of the catalyst observed in the early stages of the flow reaction experiments. As II formed and decarbonylated, the adsorbed CO partially "self-poisoned" the surface for further II formation. The attenuation of the initially high rates of reaction which we observed may have occurred as part of the active surface became covered with adsorbed CO and hydrocarbon fragments. This self-poisoning mechanism must be limited however, because the catalysts established steady-state reaction rates and a constant product distribution after the initial induction period, indicating that some sites remained available for reaction.

Changes in selectivity that accompanied the decrease in rate for Ru-K/SiO<sub>2</sub> may also be related to this CO deactivation mechanism. Adsorbed CO suppressed the formation of II, perhaps helping to divert the reaction pathway toward the desired product III. The presence of potassium is critical to promote formation of III, however, because self-poisoning alone failed to bring about a significant increase in the production of III over unpromoted  $Ru/SiO_2$ . Thus for potassium-promoted  $Ru-K/SiO_2$  the appropriate mix of surface species established in the initial minutes of the reaction may dictate the final steady-state product selectivities.

## Conclusions

The effects of alkali promotion on the adsorption and reaction of 3-methyl-2-butenal (I) over Ru/SiO<sub>2</sub> were investigated using in situ IR spectroscopy. A significant fraction of the adsorption of the unsaturated aldehyde occurred through hydrogen bonding between the carbonyl group and the hydroxyl groups on the support. Hydrogenation of the C=C bond of the unsaturated aldehyde (I) to produce the saturated aldehyde (II) was followed by partial decarbonylation of the product aldehyde on metal sites in a "reverse migratory insertion" process. The presence of the alkali promoter inhibited the C=C hydrogenation of I to form II, but the role of potassium in enhancing production of III was more difficult to assess by IR spectroscopy.

The adsorbed CO produced from the decarbonylation reaction of II caused a partial poisoning of the catalyst. The transient initial buildup of adsorbed CO and hydrocarbon products may ultimately be responsible for the product distribution observed at steady-state. These studies have provided information about how the composition of species adsorbed on the catalyst surface change over time and how these changes may dramatically influence the reaction rates and product selectivities observed under steady-state operation.

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