# Influence of Alkali Promoters in the Selective Hydrogenation of 3-Methyl-2-butenal over Ru/SiO<sub>2</sub> Catalysts

#### Akshay Waghray, Jian Wang, Rachid Oukaci, and Donna G. Blackmond\*

Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania 15261 (Received: December 20, 1991; In Final Form: April 7, 1992)

The addition of potassium as a promoter to a  $Ru/SiO_2$  catalyst resulted in a striking shift in product selectivity in the hydrogenation of 3-methyl-2-butenal. The rate of hydrogenation at the C=O bond to produce the unsaturated alcohol increased concomitant with a decrease in the rate of C=C hydrogenation. IR spectroscopy showed a strong perturbation of the C=O bond for the alkali-promoted catalyst, and volumetric chemisorption and TPD results suggested that the alkali species blocked adsorption at low-coordination Ru sites. These adsorption and reaction studies suggest that polarization of the adsorbed substrate at the C=O bond is responsible for the significant shift in product selectivity upon alkali promotion. This work combines spectroscopic tools with the use of the catalytic reaction itself as a probe of catalyst surface chemistry.

## Introduction

The selective hydrogenation of carbonyl groups in the presence of olefin groups in  $\alpha,\beta$ -unsaturated aldehydes is an important reaction in the synthesis of fine chemicals used in perfumes, flavorings, and pharmaceuticals. Much recent research has been devoted to improving the selectivity of heterogeneous supported metal catalysts in these reactions,<sup>1-12</sup> and in most cases the active component of the catalyst is a group VIII metal whose behavior has been optimized by the addition of promoters or by appropriate choice of the support. Both electronic and geometric effects have been invoked to explain observed changes in product selectivity. Although recent studies have examined a number of supported metal,<sup>3-9</sup> oxide,<sup>10,11</sup> and even single-crystal<sup>12</sup> systems, much is still lacking in our fundamental understanding of how catalyst modifications may alter the intrinsic hydrogenation ability of the metal.

The purpose of the present study was to examine how selectivity in the hydrogenation of the unsaturated aldehyde (UAL) 3methyl-2-butenal was affected when an alkali promoter was added to a  $Ru/SiO_2$  catalyst. Because selectivity is sensitive to the nature of the catalyst, these reactions can serve as a probe of how the surface chemistry of Ru is affected by the presence of alkali.

The reactions of UAL form a consecutive-parallel network in which selectivity to the two half-hydrogenated products, the saturated aldehyde (SAL) 3-methylbutanal and the unsaturated alcohol (UOL) 3-methyl-2-buten-1-ol, may be controlled by the catalyst. The total hydrogenation product, the saturated alcohol (SOL) 3-methylbutanol, is formed in secondary reactions of the intermediate products. At higher temperatures, isomerization from UOL to SAL has also been observed as shown in eq 1.



Alkali promoters have been found to inhibit the hydrogenation of olefins which are formed as primary products during  $CO/H_2$ reactions,<sup>13,14</sup> and this fact suggests that they might also influence selectivity in the hydrogenation of 3-methyl-2-butenal, where Ru itself exhibits high intrinsic selectivity to the saturated aldehyde (SAL), by suppressing C=C bond hydrogenation. Indeed, just such an effect was invoked as the cause of a marked shift in selectivity to the unsaturated alcohol (UOL) in recent studies over Ru/NaY and Ru/KY zeolites.<sup>3</sup> The effects of alkali promoters on the surface chemistry of metals have been studied extensively,<sup>15–20</sup> in particular using CO adsorption and IR spectroscopy as a probe. The hydrogenation reactions in the present studies were complemented by studies of the temperature programmed desorption of  $H_2$  as well as IR spectroscopic studies of CO chemisorption on the promoted and unpromoted Ru catalysts. This work helps to demonstrate that combining spectroscopic tools with the use of the catalytic reaction itself as a probe can provide additional insights into the surface chemistry of these catalysts.

#### **Experimental Section**

Materials. Ultrahigh purity  $H_2$ , He, and Ar (Linde, 99.995%) and commercial purity CO (Linde, 99.5%) gases were used in all pretreatments, characterization experiments, and reactions studies, and all gases were further purified by molecular sieve traps. An oxygen-removing unit (Deoxo) was also placed in the hydrogen line before the molecular sieve trap. 3-Methyl-2-butenal was used as received (Alpha Products, 97% purity) and was stored under refrigeration.

Catalyst Preparation. Supported Ru catalysts were prepared by wet impregnation of a nonporous SiO<sub>2</sub> support (Cab-O-Sil M5, Cabot Corporation, 200  $m^2 g^{-1}$ ) with ruthenium(III) nitrosyl nitrate,  $Ru(NO)(NO_3)_3$  (Alpha Products), to a nominal weight loading of 3% Ru. Catalysts were dried in air overnight at 353 K and reduced by heating in flowing  $H_2$  at 0.5 K min<sup>-1</sup> to 673 K, holding there for 4 h. After cooling in inert gas, the catalyst was then treated with boiling distilled water to remove any chlorine-containing impurity followed by a second identical reduction procedure. Samples were dried in air at 373 K and either stored for use as Ru/SiO<sub>2</sub> or promoted with potassium in a second impregnation with aqueous KNO<sub>3</sub> to give a molar ratio of Ru:K<sup>+</sup> of 10:1, followed by reduction and drying steps identical to the procedure already described. Previous studies<sup>15</sup> with supported Rh indicated that this sequential impregnation procedure produced promoted catalysts with metal particle sizes similar to those of the unpromoted catalysts. Both Ru and K<sup>+</sup> concentrations were measured by atomic absorption analysis (Galbraith Laboratories). Volumetric chemisorption, TPD, and reaction experiments were carried out on the dried catalyst samples without pelleting, crushing, or meshing of the free-flowing powder. Only for IR experiments, where the catalyst was pressed into self-supporting wafers as described below, did the catalyst samples receive any physical treatment after preparation. Table I gives characteristics of the catalysts.

**Catalyst Characterization.** Volumetric hydrogen chemisorption measurements were made on both unpromoted and promoted catalysts in a standard glass high vacuum system. Samples were pretreated by heating under 400 Torr of  $H_2$  at 673 K for 2 h after ramping to the reduction temperature at 0.5 K min<sup>-1</sup>. The samples were then outgassed at 673 K for 1 h and cooled to ambient temperature where  $H_2$  chemisorption isotherms were performed

TABLE I: Characterization of Ru Catalysts

	Ru	Ru-K	
catalyst characteristics			
wt % Ru <sup>e</sup>	2.48	2.48	
K/Ru mole ratio <sup>a</sup>	0	0.14	
$H_2$ chemisorption ( $\mu$ mol $H_2$ /g cat)			
volumetric <sup>b</sup>	55	25	
TPD <sup>c</sup>	31	22	
particle size $(nm)^d$			
volumetric	2.4	5.3	
TPD	4.3	6.0	

<sup>a</sup> Determined by atomic absorption spectroscopy. <sup>b</sup> Chemisorption isotherms at 298 K and 100-400 Torr of H<sub>2</sub>; uptake determined from difference between total and reversible isotherms extrapolated to zero pressure. <sup>c</sup> Uptake determined from area under H<sub>2</sub> desorption curve. <sup>d</sup> Diameter of spherical particles.

by measuring equilibrium uptakes at four points between 100 and 400 Torr of  $H_2$ . Reversible adsorption was measured by performing a second isotherm after evacuation for 10 min at ambient temperature. Metal particle sizes were calculated using the irreversible uptake and assuming the particle shape to be a cube with five sides exposed to the gas phase.

X-ray diffraction measurements were made using a General Electric XRD 700 X-ray diffraction spectrometer with a Cu K $\alpha$  X-ray source. Metal particle sizes greater that about 4 nm may be measured from X-ray line broadening using this source.

Temperature-programmed desorption of  $H_2$  was measured in an Altamira Instruments AMI-1 computer-controlled temperature programmed apparatus. Samples of 250 mg were pretreated in flowing  $H_2$  at 673 K for 2 h after ramping to the reduction temperature at 10 K min<sup>-1</sup>. This treatment was followed by cooling in  $H_2$  to ambient temperature where the flow was switched to Ar to flush gas-phase hydrogen from the cell before beginning the desorption temperature ramp. The cell was heated at 30 K min<sup>-1</sup> in flowing Ar while the  $H_2$  desorbing from the surface was monitored by a thermal conductivity detector. The use of small sample size and a nonporous SiO<sub>2</sub> support help to minimize effects that readsorption of hydrogen might have on the TPD spectra.<sup>21</sup>

Infrared spectroscopic measurements of CO adsorption were performed in a Mattson Polaris FTIR spectrometer (250 scans, 4-cm<sup>-1</sup> resolution). Self-supporting wafers of the catalyst were prepared by pressing at 150 MPa and placed in a stainless-steel in situ cell capable of evacuation at  $10^{-6}$  Torr and heating to 673 K. Pretreatment of the samples in this cell was similar to that for volumetric hydrogen chemisorption measurements described above. IR spectra were recorded at ambient temperature under 10 Torr of CO and after brief evacuation.

**Reaction Studies.** Continuous-flow, gas-phase hydrogenation of 3-methyl-2-butenal (UAL) was carried out in a stainless steel system with a Pyrex reactor. UAL was admitted to the reactor in a stream of He gas bubbled through the liquid in a gas 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 for 4 h after ramping at 0.5 K min<sup>-1</sup>. Flow of the substrate in He and H<sub>2</sub> was started after cooling the catalyst to reaction temperature in flowing  $H_2$ . The flow rate of the substrate and of  $H_2$  ranged from 7 to 35 mol min<sup>-1</sup> and from 20 to 180 mL min<sup>-1</sup>, respectively, at a constant total gas flow rate of 200 mL min<sup>-1</sup>. Reaction rates and product selectivities were measured at temperatures between 313 and 393 K in separate reaction runs with freshly reduced catalyst samples for each reaction temperature. Products formed under steady-state reaction conditions were analyzed by manual as well as on-line GC analysis. Reaction rates are reported as turnover frequencies based on hydrogen chemisorption data.

#### Results

**Reaction Studies.** The most striking effect of the alkali promoter on  $Ru/SiO_2$  was its influence on selectivity toward UOL in hydrogenation of 3-methyl-2-butenal. At 313 K, the  $Ru/SiO_2$ catalyst produced nearly 100% SAL, while over the potassiumpromoted catalyst the selectivity to UOL increased dramatically



Figure 1. Selectivity of 3-methyl-2-butenal hydrogenation over (A) unpromoted and (B) K-promoted  $Ru/SiO_2$  as a function of reaction temperature. UOL = unsaturated alcohol; SAL = saturated aldehyde; SOL = saturated alcohol.

TABLE II: Hydrogenation of 3-Methyl-2-butenal over Ru/SiO<sub>2</sub> and Ru-K/SiO<sub>2</sub><sup>a</sup>

	Ru		Ru-K	
	313 K	373 K	313 K	373 K
conversion (%) <sup>b</sup>	2.1	41	2.6	13
overall rate <sup>b</sup>	62	1175	200	928
TOF $(10^3/(\text{site}/\text{min}))^c$				
product formation rates				
TOF $(10^3/(\text{site}/\text{min}))^c$				
unsaturated aldehyde (SAL)	61	1045	56	594
unsaturated alcohol (UOL)	0	12	140	297
saturated alcohol (SOL)	1	118	4	37
activation energy (kcal/mol) <sup>c</sup>				
consumption of (UAL)	11.7		7.2	
formation of (SAL)	11.2		10.1	
formation of (UOL)	d		3.5	

<sup>a</sup> Reaction at 0.1 MPa total pressure; 200  $\mu$ m<sup>3</sup>/min total flow rate, 50/50 H<sub>2</sub>/He, 35  $\mu$ mol/min substrate. <sup>b</sup> Conversion and rate measurements made after steady-state operation was attained; turnover frequencies based on metal surface area determined by volumetric H<sub>2</sub> chemisorption. <sup>c</sup> Reaction conditions as specified in *a*, except reaction temperature between 313 and 393 K. <sup>d</sup> Rates over temperature range too low for measurement of E<sub>a</sub>.

to 70% at the expense of SAL. The reactivities of the two catalysts are compared in Table II. Figure 1 shows that although this high selectivity toward UOL diminished somewhat as reaction temperature increased, the alkali-promoted catalyst continued to produce more unsaturated alcohol than the unpromoted catalyst even at the highest reaction temperature. At the low conversions employed in these studies, neither catalyst produced a significant amount of the totally hydrogenated product, SOL, at any temperature.

Apparent activation energies reported in Table II were obtained from the Arrhenius plots of Figure 2. The apparent activation energy for overall UAL conversion over the alkali promoted catalyst was nearly 40% lower than that for the unpromoted catalyst. Figure 2B shows Arrhenius plots based on the rates of formation of SAL and UOL. The apparent activation energy for UOL formation was significantly less than that for formation of



Figure 2. Arrhenius plots for reaction of 3-methyl-2-butenal (UAL) over unpromoted and K-promoted Ru/SiO<sub>2</sub>. (A) Overall reaction of UAL; (B) formation of products SAL and UOL.



Figure 3. Rate of hydrogenation of 3-methyl-2-butenal over K-promoted  $Ru/SiO_2$  as a function of the concentration of the substrate.

SAL over the promoted catalyst. For the unpromoted catalyst, SAL was the only significant product at any temperature, and its apparent activation energy was similar to that found for the formation of SAL over the promoted catalyst.

As seen in Table II, the turnover frequency for the overall reaction of UAL at 313 K was nearly 3 times higher for the promoted catalyst. This difference in rates of UAL reaction was reversed at higher temperatures, where the unpromoted catalyst exhibited the higher rate. In considering the rates of reaction for the individual products, it can be noted that while the activation energy for formation of SAL was similar for the two catalysts, the rate for this reaction was significantly suppressed for the promoted catalyst.

The overall reaction rate at 313 K was found to be nearly independent of the partial pressures of the reactants UAL and  $H_2$  over the range employed in these studies, as shown in Figure 3 for Ru-K<sup>+</sup>/SiO<sub>2</sub>. Product selectivities were also unchanged by this change in UAL concentration. All of the activity and selectivity data reported are given for the catalysts during steadystate operation which was attained 20-40 min after flow of the reactants over the catalysts commenced. Both the promoted and unpromoted catalysts displayed high activity during this initial period, stabilizing at lower conversions as steady-state operation was reached. For the promoted catalyst, product selectivity also

TABLE III: Adsorption of UAL on Ru/SiO<sub>2</sub> and Ru-K/SiO<sub>2</sub><sup>a</sup> Estimates of UAL Surface Coverage

	$Ru/SiO_2$	Ru-K/SiO <sub>2</sub>
$\mu$ mol/g cat. <sup>b</sup>	2480	720
molecules UAL/Rus <sup>c</sup>	22	14
molecules UAL/surface OH group <sup>d</sup> no. of monolayers UAL	1.6	0.5
(based on BET surface area) <sup>e</sup>	3.8	1.1

<sup>*a*</sup>Adsorption of UAL from gas-phase flow of UAL-saturated stream of He at 200 mL min<sup>-1</sup> (35  $\mu$ mol min<sup>-1</sup> UAL). <sup>*b*</sup>Uptake of UAL estimated from the integrating the concentration of UAL remaining in the effluent stream during the initial adsorption period before mass balance was established, i.e., before [UAL]<sub>in</sub> = [UAL]<sub>out</sub>. <sup>*c*</sup>Assuming adsorption of UAL on metal sites only; Ru<sub>s</sub> = number of surface Ru atoms estimated from hydrogen chemisorption (see Table I and the Experimental Section). <sup>*d*</sup>Concentration of surface OH groups for SiO<sub>2</sub> treated at 673 K estimated to be approximately 8  $\mu$ mol/m<sup>2</sup> (from ref 22). <sup>*c*</sup>Assuming flat adsorption of the UAL molecule covering an area of 50 Å<sup>2</sup>/UAL molecule.

changed from primarily SAL production to the high UOL selectivity observed at steady state. During this initial period, a mass balance between the reactant UAL and the products was not achieved due to significant uptake of UAL by the catalyst.

Experiments with UAL/He streams showed that the catalyst exhibited no catalytic activity in the absence of H<sub>2</sub> in the gas phase but revealed that significant adsorption of UAL occurred before the flow of UAL at its initial feed concentration was re-established in the reactor effluent stream. The amount of UAL taken up by the catalyst was estimated by integrating the area under curves of the effluent UAL concentration vs time. Adsorption increased under higher partial pressures of UAL, and the uptake was about 3 times greater for the unpromoted catalyst than for the promoted catalyst. Table III reports these uptakes for the highest UAL partial pressure employed, relating these amounts to several different measures of catalyst surface area, both metal and support. The number of UAL molecules adsorbed exceeded the number of exposed Ru atoms by 1 order of magnitude. The adsorbed UAL was comparable to the number of hydroxyl groups estimated to be present on the nonporous SiO<sub>2</sub> after pretreatment at 673  $K^{22}$ or between one and four monolayers of the BET surface area of the supported metal catalyst, assuming flat adsorption of the molecule.

Catalyst Characterization Studies. Table I reports hydrogen chemisorption uptakes from volumetric and TPD measurements as well as metal particle sizes calculated from these uptakes. The uptake of hydrogen was smaller for the promoted catalyst, and metal particle sizes calculated from these data are accordingly larger for the alkali-promoted catalyst. In X-ray diffraction line broadening studies, however, no signal was detected for either catalyst, which would be the case if both samples exhibited particle sizes smaller than the 4-nm detection limit of the Cu K $\alpha$  X-ray source.

Temperature-programmed desorption data revealed this same trend in hydrogen uptake for the two samples, although, as is often observed, the amount of chemisorbed hydrogen was lower for both samples than that calculated from volumetric chemisorption isotherms due to the failure of the flow technique to measure weakly held hydrogen. H<sub>2</sub> TPD spectra for the two catalysts shown in Figure 4 show a common peak near 330 K. A broader higher temperature desorption feature centered near 400 K found on the unpromoted catalyst was absent on the alkali-promoted sample, suggesting that the lower uptake on the alkali-promoted sample was due to suppression of the more strongly-held hydrogen.

Figure 5 shows IR spectra of CO adsorbed on the two catalysts. The CO spectrum for the unpromoted Ru is in close agreement with published spectra<sup>16,23-26</sup> which assign a peak in the range 2020–2090 cm<sup>-1</sup> to linear CO and features at 2140 and 2080 cm<sup>-1</sup> to a Ru tricarbonyl species. The linear CO peak at 2044 cm<sup>-1</sup> (Figure 5A) appeared at the slightly lower frequency of 2037 cm<sup>-1</sup> after evacuation of the cell for at least 20 min (Figure 6A), while the tricarbonyl frequencies were similar under 10 Torr of CO pressure and under vacuum.



Figure 4.  $H_2$  TPD spectra for (A) unpromoted and (B) K-promoted  $Ru/SiO_2$  catalysts.



Figure 5. IR spectrum of CO adsorbed on (A) unpromoted and (B) K-promoted  $Ru/SiO_2$  catalysts at 298 K under 10 Torr of CO.

The IR spectrum was significantly different for CO adsorbed on the alkali-promoted Ru (Figures 5B and 6B). Features due to the tricarbonyl species were suppressed and the linear CO peak decreased in intensity. Under 10 Torr of CO, the linear CO peak appeared at 2033 cm<sup>-1</sup>, 11 wavenumbers lower than the unpromoted catalyst, and as for the unpromoted catalyst it also shifted slightly to lower wavenumbers upon evacuation. A new broad feature developed near 1940 cm<sup>-1</sup> which showed no CO coverage dependence in its frequency.

### Discussion

The addition of alkali species had a striking effect on the selectivity of Ru in hydrogenation of 3-methyl-2-butenal toward production of UOL. This shift from hydrogenation at the C=C bond (to produce SAL) to hydrogenation at the C=O bond (to produce UOL) suggests that the promoter had a dual effect of suppressing hydrogenation at one location in the molecule and enhancing it in another. Kinetic analyses of the reaction network<sup>8</sup> have suggested that adsorption of the conjugated system gives a common intermediate for either the saturated aldehyde or the unsaturated alcohol product. Modification of this intermediate species by the presence of alkali species may be an important factor in increasing the relative rate of hydrogenation at the C=O bond.

Poltarzewski et al.<sup>5</sup> observed an increase in overall reaction rate and enhanced selectivity to UOL in the hydrogenation of cinnamaldehyde when small amounts of tin were added to Pt catalysts. They attributed this to two effects: the suppression of olefin hydrogenation through an electronic interaction which poisoned activation of hydrogen was less severe than the activation of the C==O bond by increased polarization in the presence of Sn which increased the electron density on Pt. Vannice and Sen<sup>4</sup> found large increases in turnover frequencies and higher selectivities to UOL for the reaction of 2-butenal over  $Pt/TiO_2$  catalysts reduced at high temperatures. They also attributed these changes to increased



Figure 6. IR spectrum of CO adsorbed on (A) unpromoted and (B) K-promoted  $Ru/SiO_2$  catalysts at 298 K after evacuation for at least 20 min following the adsorption measurement shown in Figure 5.

polarization of the C—O bond, but they suggested that this came about due to an interaction between the C—O function and unique sites at the metal-support interface of the catalyst.

We propose that the alkali species added to  $Ru/SiO_2$  altered adsorption of the UAL molecule to polarize the C=O bond and promote hydrogenation there rather than at the C=C bond. The question of whether these effects can be explained by invoking electronic effects on Ru or by the direct influence of the alkali on adsorbed species cannot be addressed by reaction data alone, although both suggestions have been put forward to explain how the surface chemistry of adsorbates on metals is affected by alkali promotion.<sup>15-20</sup>

Both the TPD and volumetric chemisorption experiments showed a decrease in hydrogen uptake on alkali-promoted Ru, leading to the calculation of a larger particle size (ca. 5-6 nm) for the promoted catalyst. However, since XRD measurements implied that the Ru particles were smaller than 4 nm in both cases, the decreased H<sub>2</sub> uptake for the alkali-promoted catalyst may represent a suppression of H<sub>2</sub> chemisorption on some sites rather than a true particle size difference between the two samples. This suggestion was made in previous studies of alkali-promoted Rh.<sup>15</sup> The TPD experiments showed that this suppression affected the most strongly held hydrogen. It has been suggested that stronger adsorption occurs on corner, edge, or defect sites where metal atoms have fewer metal-metal bonds than atoms on a flat crystallite face,<sup>27</sup> which implies that the alkali species preferentially blocked these low coordination sites. Our IR studies support this suggestion. The tricarbonyl species observed upon adsorption of CO on Ru was absent in the IR spectrum of CO adsorbed on the alkali-promoted catalyst. In analogy to formation of the gem-dicarbonyl species on supported  $Rh^{28-31}$  this species is thought to form through the corrosive and oxidative chemisorption of CO by reaction with surface hydroxyl groups. These carbonyl species break away from Ru particles as partially oxidized monometallic Ru tricarbonyl entities. The fact that the frequency of the tricarbonyl species was unperturbed by changes in CO coverage also supports the idea that it is an isolated species.

Corrosive chemisorption occurs more readily on small, defective particles through the detachment of Ru atoms with fewer than average Ru–Ru bonds. The formation of these tricarbonyl species from low-coordination Ru would be prevented if the alkali species blocked adsorption at these sites. The alkali species might also suppress Ru tricarbonyl formation by interacting with SiO<sub>2</sub> hydroxyl groups near the support-metal interface to block their reaction with Rh–CO species. A recent study of CO adsorption on Rh/Al<sub>2</sub>O<sub>3</sub> by Yates and co-workers<sup>31</sup> found that impregnation of Al<sub>2</sub>O<sub>3</sub> with K<sub>2</sub>CO<sub>3</sub> led to the functionalization of isolated hydroxyl groups as Al–O–K, which helped to stabilize Rh particles from corrosive CO chemisorption to form Rh<sup>+</sup>(CO)<sub>2</sub>.

Other studies of alkali-promoted metals have correlated suppression of hydrogen chemisorption with a decreased capacity to hydrogenate olefins,<sup>14,15</sup> and indeed the rate for SAL formation decreased with the addition of the alkali promoter. It could be suggested, then, that the defect sites which were blocked by alkali promotion exhibited higher activity for C—C hydrogenation than high-coordination Ru sites. Structure sensitivity in these selective hydrogenation reactions has been discussed previously in a study showing that smaller Co particles exhibited higher selectivity to SAL than did large ones.<sup>9</sup> It may be assumed that the smaller Co particles in that study contained a higher percentage of low coordination metal sites than did the larger particles,<sup>27</sup> supporting our suggestion that these sites are active for C—C hydrogenation.

Alkali promotion affected the surface chemistry of Ru in other ways in addition to blocking low-coordination sites. The appearance of a new peak at still lower frequency, a common observance from IR spectra of CO adsorbed on alkali-promoted metals,<sup>15-17</sup> indicated that a strong interaction occurred which destabilized the C=O bond. While the frequency of the linear CO peak was sensitive to the CO coverage, the peak for this strongly perturbed CO did not appear to shift upon evacuation of CO. Shifts in CO frequency with coverage are often attributed to dipole-dipole interactions between neighboring adsorbed CO molecules.<sup>32,33</sup> Such dipole-dipole interactions might be expected to be less significant for adsorbed CO involved in a strong interaction with an alkali species, as has been suggested for strongly perturbed CO adsorbed on K-promoted Ni(111).<sup>17</sup>

Studies of metals with interacting supports or additive species have suggested that interaction between CO and electropositive centers may weaken the CO bond and make it more reactive. The IR spectra for CO adsorbed on metals with such additives often show new features due to CO-additive interactions at frequencies lower than CO adsorbed on the unpromoted metal, similar to the peak we observed at 1940 cm<sup>-1</sup> for Ru-K<sup>+</sup>/SiO<sub>2</sub>. In CO/H<sub>2</sub> reactions to form alcohols, it has been suggested that alkali species promote C=O hydrogenation by stabilizing enolate or aldolate surface species.<sup>34</sup> In addition, examples of Lewis acid-assisted hydrogenation of carbonyl ligands in metal complexes<sup>35</sup> support the idea that a cationic alkali species on the catalyst surface might promote reaction at the C=O function in unsaturated aldehydes. This argument was discussed earlier for 2-butenal hydrogenation over Pt/TiO<sub>2</sub>.<sup>4</sup> Thus the suggestion that K<sup>+</sup> helps to polarize the UAL molecule at the C=O function to promote UOL formation is supported by the IR spectrum of CO adsorbed on the promoted catalyst.

The significant shift in product selectivity observed with alkali promotion was accompanied by a decrease in the apparent activation energy for UAL reaction. Similar observations have been made for alkali promotion in other reactions including ethane hydrogenolysis and CO hydrogenation,<sup>15,36,37</sup> leading in some cases to speculation about an electronic influence of the alkali species on the metal. In our case, however, a simpler interpretation for the decreased apparent activation energy for the promoted catalyst derives from examination of the consecutive reaction network in eq 1. For the unpromoted catalyst, the overall reaction rate of UAL was essentially that for the formation of SAL, which accounted for 98% of the product at 313 K. In the case of the promoted catalyst, however, two competing parallel reactions account for the consumption of UAL, and the lower apparent activation energy for this catalyst reflects the fact that these two rate processes have very different individual apparent activation energies, as can be seen in Figure 2B. The apparent activation energy  $(E_s)$  for the formation of SAL over Ru was unchanged by addition of the alkali promoter, but the much smaller  $E_a$  for UOL formation led to a lower value for the overall apparent activation energy for UAL reaction over the promoted catalyst.

Competition between various adsorbed species has been suggested to play a role in determining selectivity. Weaker adsorption of the unsaturated alcohol led to higher selectivity to UOL as a product over Co catalysts.<sup>9</sup> Similarly, the other half-hydrogenated product, SAL, has also been implicated in rate inhibition over Pt catalysts because of poisoning due to strong adsorption.<sup>38</sup> The changes we observed in product selectivity over the alkali-promoted Ru catalyst during the initial period of reaction over the promoted catalyst in these studies suggest that the surface composition changed as the catalyst approached steady state, perhaps due to self-poisoning by products or intermediates formed in the early stages before steady-state conditions were established. The surface coverages of different adsorbed products and intermediate species as well as their relative strengths of adsorption may be different for the two catalysts, leading ultimately to different product selectivity under steady-state conditions.

The overall rate of hydrogenation as well as the individual product rates appeared to be zero-order in aldehyde concentration over the range studied. The insensitivity of the reaction rate to the partial pressure of UAL suggests that UAL was in excess under all conditions. This was confirmed by the significant uptake of UAL observed at the beginning of the reaction and in UAL adsorption studies. The uptakes reported in Table III along with several example calculations of how they might relate to catalyst surface area indicate that the aldehyde was adsorbed in large quantities on the support as well as on the metal and that the alkali-promoted catalyst partially suppressed this adsorption. This suppression could be related to interaction of the SiO<sub>2</sub> hydroxyl groups with the potassium promoter as was suggested earlier to explain the absence of the Ru tricarbonyl species after CO adsorption on the alkali-promoted catalyst. Whatever the manner of adsorption of UAL, it is clear that for both promoted and unpromoted catalysts a large pool of reactant was available for reaction on the metal, perhaps by inverse spillover from the support. Further adsorption studies were currently underway to elucidate the role of the support and the access of the reactants to the surface sites.

Several observations help to confirm that diffusion processes were not limiting the rate of reaction over these nonporous supported metals. Contrary to the anomalously low apparent activation energies of 1–2 kcal/mol we found for similar reactions over zeolite-supported  $Ru^{39}$  where strong diffusional constraints existed in the micropores, the activation energies of 7–11 kcal/mol measured for the SiO<sub>2</sub>-supported Ru and Ru-K were in the range observed for reactions of these types.<sup>4</sup> In addition, the total hydrogenation product, SOL, was never significant under any of the conditions reported here, as one might expect to find in a diffusion-limited system where secondary reactions could take place.<sup>39</sup> Indeed, we have observed the selectivity to SOL increase over these catalysts in the limit of very low reactant flow rates.<sup>40</sup>

The combination of selective hydrogenation reactions with chemisorption, TPD, and IR studies provides a picture of how the surface chemistry of Ru was influenced by the presence of alkali to alter the adsorption and reaction of 3-methyl-2-butenal. C—C hydrogenation activity was suppressed when defect sites were blocked by alkali species. Increased polarization of the C—O function of the adsorbed reactant also enhanced selectivity to the unsaturated alcohol.

#### Conclusions

The addition of alkali promoter to a Ru/SiO<sub>2</sub> catalyst resulted in a significant change in the selectivity of hydrogenation of 3methyl-2-butenal. Hydrogenation activity shifted from the C=C bond to the C=O bond, and this effect was attributed to an increased polarization of the C=O group of the adsorbed aldehyde due to the presence of the alkali species, leading to increased reactivity at this center. This suggestion was supported by IR evidence of perturbation of the C=O bond for CO adsorption on the promoted catalyst. Suppression of hydrogen chemisorption on the alkali-promoted catalyst also contributed to a decrease in reactivity at the C=C bond. The decrease in apparent activation energy of the overall reaction in the presence of the alkali species was attributed to a shift in the relative contributions to the overall rate of the formation of the two half-hydrogenated products which exhibit very different individual activation energies. When the formation of UOL contributed more significantly to the overall rate, the apparent activation energy for UAL consumption shifted from one which reflected SAL formation to one more representative of an average between SAL and UOL formation. These data demonstrate how product selectivity considerations in a complex parallel-consecutive reaction network may provide useful clues about catalyst surface chemistry when combined with spectroscopic probes in the study of alkali-promoted supported metals.

Acknowledgment. Support from the National Science Foundation through the Presidential Young Investigator Program (CBT-8552656) is gratefully acknowledged.

Registry No. (CH<sub>3</sub>)<sub>2</sub>C=CHCHO, 107-86-8; Ru, 7440-18-8; K, 7440-09-7

#### **References and Notes**

(1) (a) Heterogeneous Catalysis and Fine Chemicals. Proceedings from the 1st International Symposium, 1987; Guisnet, M., et al. Eds.; Elsevier: Amsterdam, 1988. (b) Heterogeneous Catalysis and Fine Chemicals II. Proceedings from the 2nd International Symposium, 1990; Guisnet, M., et al., Eds.; (Elsevier, Amsterdam, 1991).

(2) See, for example, the following patents: Cordier, G.; Fouilleux, P.; Grosselin, J. M. French Patent App. No. 882919, 1988. Horner, M.; Irgang, M. German Patent No. 81-313805, 1981. Ichikawa, Y.; Suzuki, M.; Sawaki,

T. Japanese Patent No. 52084193, 1977. (3) Blackmond, D. G.; Oukaci, R.; Blanc, B.; Gallezot, P. J. Catal. 1991,

131, 401.

(4) Vannice, M. A.; Sen, B. J. Catal. 1989, 115, 65. (5) Poltarzewski, A.; Galvagno, S.; Pietropaolo, R.; Staiti, P. J. Catal.

1986, 102, 190.

(6) Giroir-Fendler, A.; Richard, D.; Gallezot, P. In Heterogeneous Catalysis and Fine Chemicals; Guisnet, M., et al., Eds.; Elsevier: Amsterdam, 1988, p 171.

(7) Campelo, J. M.; Garcia, A.; Luna, D.; Marinas, J. M. J. Catal. 1988, 113, 172.

- (a) (a) Simonik, J.; Beranek, P. J. Catal. 1972, 24, 348. (b) Simonik, J.;
  Beranek, P. Collect. Czech. Chem. Commun. 1972, 37, 353.
  (9) (a) Nitta, Y.; Ueno, K.; Imanaka, T. Appl. Catal. 1989, 56, 9. (b)
  Nitta, Y.; Hiramatsu, Y.; Imanaka, T. J. Catal. 1990, 126.
  (10) Lenck L: Germain L. F. J. Catal. 1990, 65, 14.

(10) Jenck, J.; Germain, J. E. J. Catal. 1980, 65, 14.

(11) Hubaut, R.; Daage, M.; Bonnelle, J. P. Appl. Catal. 1986, 22, 231.

- (12) Beccat, P.; Bertolini, J. C.; Gauthier, Y.; Massardier, J.; Ruiz, R. J. Catal. 1990, 126, 451.
- (13) Cavalcanti, F. A. P.; Blackmond, D. G.; Oukaci, R.; Sayari, A.; Erdem-Senatalar, A.; Wender, I. J. Catal. 1988, 113, 1.
- (14) Oukaci, R.; Sayari, A.; Goodwin, J. G. J. Catal. 1986, 102, 126. (15) Kesraoui, S.; Oukaci, R.; Blackmond, D. G. J. Catal. 1987, 105, 432.
- (16) McClory, M. M.; Gonzalez, R. D. J. Catal. 1984, 89, 392.
  (17) Uram, K. J.; Ng, L.; Yates, J. T., Jr. Surf. Sci. 1986, 177, 253.
  (18) DePaola, R. D.; Hrbek, J.; Hoffmann, F. M. J. Chem. Phys. 1985, 82, 2484
- (19) Ertl, G.; Weiss, M.; Lee, S. B. Chem. Phys. Lett. 1979, 60, 391.
   (20) Lang, N. D.; Holloway, S.; Norskov, J. K. Surf. Sci. 1985, 150, 24. (21) Falconer, J. L.; Schwarz, J. A. Catal. Rev.-Sci. Eng. 1983, 25, 141.
- (22) Little, L. H. Infrared Spectra of Adsorbed Species; Academic Press: London, 1966; Chapter 10.
- (23) Dalla Betta, R. A. J. Phys. Chem. 1975, 79, 2519.
- (24) Robbins, J. L. J. Catal. 1989, 115, 120.
  (25) Yokomizo, G. H.; Louis, C.; Bell, A. T. J. Catal. 1989, 120, 1.
  (26) Solymosi, F.; Rasko, J. J. Catal. 1989, 115, 107.

- (27) van Hardeveld, R.; Hartog, F. Adv. Catal. 1975, 22, 75.
   (28) Van't Blik, H. F. J.; van Zon, J. B. A. D.; Huizinga, T.; Vis, J. C.; Konigsberger, D. C.; Prins, R. J. Am. Chem. Soc. 1985, 107, 3139.
- (29) Bergeret, G.; Gallezot, P.; Gelin, P.; Ben Taarit, Y.; Lefebvure, F.;
- Naccache, C.; Shannon, R. D. J. Catal. 1987, 104, 279. (30) Basu, P.; Panayotov, D.; Yates, J. T., Jr. J. Am. Chem. Soc. 1988,
- 110. 2074 (31) Zaki, M. J.; Ballinger, T. H.; Yates, J. T., Jr. J. Phys. Chem. 1991,
- 95, 4028 (32) Hammaker, R. M.; Francis, S. A.; Eischens, R. P. Spectrochim. Acta
- 1965, 21, 1295.
  - (33) Crossley, A.; King, D. A. Surf. Sci. 1977, 68, 528

(34) Nunan, J. G.; Bogdan, C. E.; Klier, K.; Smith, K. J.; Young, C. W.;
Herman, R. G. J. Catal. 1989, 116, 195.
(35) Horvitz, C. P.; Shriver, D. F. Adv. Organomet. Chem. 1984, 23, 219.
(36) Okuhara, T.; Tamaru, H.; Misono, M. J. Catal. 1985, 95, 41.
(37) Hoost, T. E.; Goodwin, J. G., Jr. J. Catal. 1991, 130, 283.

- (38) Goupil, D. Ph.D. dissertation, University of Lyon, France, 1986.
   (39) Waghray, A.; Oukaci, R.; Blackmond, D. G. Catal. Lett. 1992, 14, 115
- (40) Waghray, A.; Blackmond, D. G., unpublished results.

# Study of Photoreduction of PtCl<sub>6</sub><sup>2-</sup> on CdS

Qinglin Li,\* Zhengshi Chen, Xinhua Zheng, and Zhensheng Jin\*

Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, P. R. China (Received: December 23, 1991; In Final Form: March 18, 1992)

The photoinduced reduction of PtCl<sub>6</sub><sup>2-</sup> on CdS was investigated by means of XPS, DTA, and TEM. The experimental results indicate that the photoreduced product of  $PtCl_6^{2-}$  on CdS is PtS in acidic solution and  $Pt(OH)_2$  in basic solution. PtS can be converted to  $Pt^0$  by further treatment in air at high temperature. But the photoreduced product of  $PtCl_6^{2-}$  on high-temperature air-treated CdS is  $Pt(OH)_2$  in both acidic and basic solution.  $Pt(OH)_2$  can be dehydrated to PtO at high temperature under ultra-high-vacuum conditions.

#### 1. Introduction

Some new findings have led to the recent surge of interest in the photoinduced reduction of  $PtCl_6^{2-}$ . Bocarsly observed that the formation of platinum metal ( $Pt^0$ ) occurs only when ca. 90% of  $PtCl_4^{2-}$  is formed on photoreduction of  $PtCl_6^{2-}$  in aqueous *i*-PrOH solution and suggested that  $PtCl_6^{2-}$  acts as an inhibitor in Pt<sup>0</sup> formation.<sup>1</sup> Shagisultanova found the presence of Pt(III) species in cryogenic ESR studies of the photolysis of PtCl<sub>5</sub><sup>2-</sup> ions in organic glasses.<sup>2</sup> Using ESR and spin trapping technique, Kemp confirmed that the photoreduction of  $PtCl_6^{2-}$  by alcohols involves a photoredox process yielding Pt(III) and a hydroxyalkyl radical.<sup>3</sup> The photodeposition of Pt<sup>0</sup> on some semiconductor oxide powders in acidic  $PtCl_6^{2-}$  solution is now a method for the preparation of photocatalysts, such as  $Pt/TiO_2$  and  $Pt/WO_3^{4.5}$  The photoreduction product Pt<sup>0</sup> is mainly determined by XPS. But there are arguments on the photoreduced product of PtCl<sub>6</sub><sup>2-</sup> over powder CdS. Some researchers considered it as Pt<sup>0;6,7</sup>

$$PtCl_{6}^{2-} + 4e^{-}_{cb} \xrightarrow{h\nu} Pt^{0} + 6Cl^{-}$$
$$PtCl_{6}^{2-} + 2H_{2}O \xrightarrow{h\nu} Cds Pt^{0} + O_{2} + 4H^{+} + 6Cl^{-}$$

Reber inferred that the photodeposit is a mixture of Pt<sup>0</sup>/Pt<sup>+</sup>/Pt<sup>2+,8</sup> By means of XPS and DTA, Jin and Li discovered that the photoreduced product of  $PtCl_6^{2-}$  in acidic solution is PtS which can be converted to Pt<sup>0</sup> in high-temperature air<sup>9</sup>

$$PtS + O_2 \rightarrow Pt^0 + SO_2$$

In this paper, the effects of the surface property of CdS and the pH of solution on the forms of photoreduced product are reported and the mechanism discussed.

#### 2. Experimental Section

1. Preparation of Specimen. Two grams of CdS powder was added into 20 mL of deionized water containing 0.66 mL of 7.72