intensities for this molecule and the $\partial \bar{p}/\partial Q_i$ directions obtained theoretically. For the derivative corresponding to the CH stretch two sets of APT's were calculated, one corresponding to an angle of 128° determined by transference of the cis APT's and the other by using 67° as indicated by the ab initio calculation using the 9s5p/3s2p basis set. Since the two sets have very similar values only one set (67° set) is presented in Table II.

The largest discrepancy between cis and trans polar tensor elements occurs for $\partial p_x/\partial y_c$ where 0.57 and 0.46 e values are encountered. In general, the differences between corresponding polar tensor elements for the *cis*- and *trans*-difluoroethylenes is of the same magnitude as the expected experimental errors in these values. Very similar polar tensors for these molecules are certainly not surprising in view of the fact that the only structural differences for these isomers occurs in the cis-atom interactions; two H···F cis interactions in the cis isomer are replaced by the H···H and F···F cis interactions in the trans isomer.

Now that the experimental APT's of *cis*- and *trans*-difluoroethylene have been shown to be almost identical it is natural to investigate whether quantum chemical calculations also predict practically equivalent APT's. Tables III and IV contain values of the APT's for both molecules calculated with the 9s5p/3s2p basis set and MNDO wave functions. In addition, the values for the three principle contributions to the APT's as defined by the CCFO model are presented. Independent of the level of calculation the APT elements for the trans molecule are almost equivalent to their corresponding cis isomer values. Furthermore this equivalence between polar tensor elements is preserved even if the APT's are decomposed into their different CCFO contributions. The largest difference observable in these tables, 0.05*e*, occurs for the ab initio estimates of the overlap contribution to the $\partial p_x/\partial x_H$ value and the total $\partial p_z/\partial z_F$ value.

The above theoretical and experimental results show that the electronic structures and their variations for small vibrations are essentially equivalent for *cis*- and *trans*-difluoroethylene if differences in symmetry are taken into account. This result may hold in general for cis–trans isomers. For example, the infrared fundamental intensities of *trans*-$C_2H_2Cl_2$ have also been successfully calculated by transference of the APT's of its cis isomer.[17] These results also suggest the intriguing possibility that quantum chemical results, even at the semiempirical level, may serve as a criterion for choosing experimental reference APT's to be used in the polar tensor transference procedure. Studies are currently being carried out in our laboratories to determine the usefulness of this criterion for other molecules.

Registry No. *cis*-$C_2H_2F_2$, 1630-77-9; *trans*-$C_2H_2F_2$, 1630-78-0.

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An ESCA Study of Alkali Promoter Effects on Silica-Supported Ruthenium Catalysts

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An ESCA study has been carried out to characterize the effect of alkali promotion on ruthenium–silica catalysts. Alkali promotion of Ru was found to result in a significant increase in the atomic relaxation energy in addition to a presumed reduction in the work function. While it was not possible to determine the amount, if any, of electron charge transfer from the promoter to the Ru, it was also not possible to rule out such a transfer. The anions associated with the alkali ions, however, appeared to have little effect on the electronic structure of the Ru. The study reported in this paper is one of the most complete investigations to date of the *modification by alkali promotion* of the electronic structure of a *supported* transition-metal catalyst.

Introduction

Alkali metals are known to be promoters in many catalyst systems. For example, potassium is used as a promoter for ammonia synthesis on Fe catalysts,[1] for the synthesis of higher alcohols on Cu/ZnO-based catalysts,[2] and in the Fischer–Tropsch synthesis on Fe[3] and Ru[4] catalysts. It has been reported that, in the case of potassium ion promoted Fe catalysts, K$^+$ became more electropositive when interacting with the Fe.[5,6] Also, significant reduction of the work function (ϕ) of Fe was observed by doping with K$^+$.[5,6] However, correlation between promoter effects on NH_3 synthesis activity and the decreased work function of Fe catalysts as a result of K$^+$ promotion indicated that the observed promoter effect was not simply related to modifications in the work function of Fe.[6] This suggests that other factors such as the electron density in the valence band and the chemical environment of Fe may also be important in alkali promotion. Dry et al.[7] proposed charge transfer from alkali promoters to Fe to explain the promotion effect, based on a strengthened carbon–iron bond during the Fischer–Tropsch synthesis. It has been suggested by Broden et al.[5] that the major function of alkali promoters is to modify the electronic structure of iron by electron donation. Ozaki proposed a similar mechanism for alkali promotion of Ru catalysts.[8] Recently, Somorjai et al.[9] have observed a strong enhancement of electron back-donation of Pt to chemisorbed carbon monoxide caused by potassium promotion. They attributed this phenomenon to increased Pt electron density as a result of potassium promotion. Although the evidence derived from chemisorption and catalytic reaction studies favors the idea of electron donation by alkali promoters, little direct measurement of changes in the electron density of a catalyst induced by alkali promoters has yet been reported.

Charge transfer between *alkali-metal* atoms and transition-metal catalysts requires that the first ionization potential (IP) of

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the alkali-metal atom be lower than the work function of the transition metal; alkali-metal atoms are assumed to give up their electrons to transition metals.[10,11] Such charge transfer has been demonstrated by measuring the dipole moments of alkali coated nickel,[11,12] tantalum,[13] iron,[5] and tungsten.[13] These results are in good agreement with the theory developed by Gadzuk et al.[14,15] Nevertheless, for supported transition-metal catalysts promoted by *alkali-metal salts*, such as K_2CO_3 or K_2O, direct electron transfer from alkali-metal ions to transition metals would seem unlikely because of the inert gas electronic configurations (ns^0) and high ionization potentials of the alkali-metal ions. Efforts to probe changes in the electronic structure of Fe in Fe/Al_2O_3 catalysts promoted by K_2O using Mossbauer spectroscopy have not been successful.[16] However, results for a number of different catalyst systems indicate that the presence of an electronegative element, such as oxygen, in conjunction with the alkali element reduces the effect of promotion.[17-19] Such a promoted surface is less active than when the alkali promoter exists alone in the "metallic" state.

Thus, while the effects of promoters on catalytic properties have been extensively studied in the past, very little firm understanding of the mechanism(s) of promotion of supported metal catalysts has resulted. This has been primarily due to the fact that most studies have been based on only indirect measurements, such as reaction activities and selectivities or the strength of the C–O bond in adsorbed CO as determined by IR. McClory and Gonzalez[20] have even suggested based on reaction results that site blockage by the promoter may be the primary effect of the promoter rather than an electronic modification of the metal. Recent theoretical treatments of the effect of alkali adatoms on coadsorbing molecules suggest a role for the outer surface electrostatic potential in promotion.[21-23] However, an increase in electron density in the metal cannot be ruled out as an important factor.

X-ray photoelectron spectroscopy (XPS or ESCA) has proved to be a promising tool for studying the electronic structure of transition metals. In the present paper, the electronic states of Ru were characterized by core-electron binding energies (BE's) for Ru $3p_{3/2}$, Ru $3d_{5/2}$, Ru 4s, and Ru 4p photoelectrons. Changes in the electronic states of Ru caused by alkali ion promotion were reflected by the BE shifts of Ru in the above regions. Anion effects of the Ru salts used to prepare the Ru/SiO_2 catalysts were also investigated. Limited results for Ni[24] and Fe[25] suggest that these shifts in BE occur for alkali-promoted transition metals in general.

Experimental Section

Apparatus and ESCA Measurements. ESCA spectra were recorded on an AEI ES200 electron spectrometer with a DS100 data system. This spectrometer was equipped with an aluminum anode (Al Kα = 1486.6 eV) and was operated routinely at 12 kV and 22 mA. The base pressure of the ESCA chamber was below 5×10^{-8} torr.

TABLE I: Hydrogen and CO Adsorption on Ru and RuK Catalysts[a]

catalysts	H_2 uptake,[b] µmol/g	CO uptake,[b] µmol/g	av particle diameter, nm: H_2 chem.	XRD
6.2% Ru/SiO_2	98	50	34	35
$K/Ru/SiO_2$ (K/Ru = 0.6)	14	51.5	226	41

[a] Reference 4. [b] Irreversible chemisorption at 298 K on the freshly reduced catalysts.

BE's in the ESCA spectra were referenced to internal standards which were directly referenced to Au $4F_{7/2}$ (= 83.8 eV).[26] For silica-supported Ru catalysts, BE's were referenced to Si 2p (= 103.0 eV) while BE's for unsupported Ru metal were referenced to Ru $3d_{5/2}$ (= 280.0 eV).[27-29]

Reduction of Ru catalysts was accomplished by using a sealable probe on which a pellet sample was mounted. This sealable probe allowed one to reduce the catalyst in the pretreatment chamber and then to transfer it to the ESCA chamber without exposure to air.[30]

ESCA spectra were smoothed by a linear smoothing method.[31] The corrected intensity ratios, Ru/Si, were calculated by taking the ratio of the integrated areas of Ru $3p_{3/2}$ to Si 2p, corrected for photoelectron cross sections. Overlapping Ru $3d_{5/2}$ and C 1s peaks were resolved with a DuPont 310 analog curve resolver.

Materials. Ru Powder, $RuCl_3$, and the SiO_2 support (BET area = 300 m^2/g) were obtained from Strem Chemical Co. $Ru(NO)(NO_3)_3$ was obtained from Johnson Mathey. Impregnated Ru/SiO_2 catalysts were prepared by the standard incipient wetness method with an aqueous solution of $RuCl_3$ (designated as Ru/SiO_2-Cl) or $Ru(NO)(NO_3)_3$ (designated as Ru/SiO_2-N). For Na- or K-promoted Ru/SiO_2 catalysts, sequential impregnation was used in which first aqueous solutions of Ru salts ($RuCl_3$ or $Ru(NO)(NO_3)_3$) were added followed by drying at 40 °C and then impregnation with an aqueous solution of $NaNO_3$ or K_2CO_3. The Ru content of the Ru/SiO_2 catalysts was determined by atomic absorption spectroscopy to be 6.2 wt %; the atomic ratios of Na/Ru and K/Ru for the promoted catalysts were in the range 0.6–0.7.

All of the freshly prepared catalysts, after being dried at 40 °C overnight, were pressed into pellets for ESCA measurements. In order to minimize Ru sintering, reduction of the Ru catalysts was conducted in a stream of H_2 (40 mL/min). The temperature was increased from room temperature to 200 °C in steps of 50 °C, the holding time at each temperature being 30 min; the temperature was then raised to 400 °C and held for 2 h. All the ESCA spectra of catalyst samples were obtained after reduction.

The ESCA BE's obtained for Ru metal (Ru^0) (from Ru metal powder reduced at 400 °C for 4 h) were 461.2, 280.0, 74.0, and 43.3 eV for Ru $3p_{3/2}$, Ru $3d_{5/2}$, Ru 4s, and Ru 4p, respectively; relative standard deviations were ±0.15 eV. The BE's for Ru^0, which correspond to reported BE's,[27-29] were used to characterize bulk Ru metal.

A relatively high level of promotion was used in order to ensure adequate promotion of the metal. Such a high level is required in supported metal systems due to the fact that a significant fraction of the promoter may sit on the high surface area support. Determination of the exact location of the promoter species and the fraction of it in contact with the metal in a supported catalyst is still difficult. That this level of promotion was adequate can be seen in the results for chemisorption and reaction given in Tables I and II for the unpromoted and the potassium-promoted Ru/SiO_2 following reduction. Hydrogen chemisorption and

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TABLE II: Catalytic Properties of Unpromoted and K-Promoted Ru/SiO_2 for CO Hydrogenation[a]

catalyst	activity,[b] µmol/(g s)	production distribution, wt %							
		CH_4	$C_{2=}$	C_{2-}	$C_{3=}$	C_{3-}	$C_{4=}$	C_{4-}	C_5^+
6.2% Ru/SiO_2	1.50	64.5	3.8	8.1	10.8	2.7	2.4	3.2	4.5
K/Ru/SiO_2 (K/Ru = 0.6)	0.64	56.7	6.2	5.6	14.5	1.6	4.5	3.1	7.8

[a] Reaction at 553 K, H_2/CO = 1, GHSV = 1800 h^{-1}, and 1 atm. Reference 4. [b] Catalyst activity based on rate of CO conversion.

TABLE III: ESCA Data for SiO_2-Supported Ru Catalysts[a]

sample	BE, eV: C 1s	Ru $3p_{3/2}$	Ru $3d_{5/2}$	Ru 4s	Ru 4p	K $2p_{3/2}$	corr surface intens ratio[b]: Ru/Si	Cl/Si
Ru/SiO_2-Cl[c]	284.7	461.1	279.9	73.7	43.0		0.014	
(Ru+K)/SiO_2-Cl	284.4	460.4	278.8	72.4	41.3	293.4[e]	0.024	0.08
(Ru+Na)/SiO_2-Cl	284.5	460.3	278.8				0.027	0.09
Ru/SiO_2-N[d]	284.6	461.1	279.9	73.5	43.2		0.021	
(Ru+K)/SiO_2-N	284.5	460.3	278.8	71.9	41.3	292.7[f]	0.029	

[a] All catalysts were reduced under the conditions described in the text. [b] Calculated based on the corrected surface intensity ratio Ru/Si = $(I_{Ru}/I_{Si})(\sigma_{Si}/\sigma_{Ru})$, where Ru $3p_{3/2}$ and Si 2p signals were used and σ_{Si} and σ_{Ru} denote photoelectron cross sections of Si 2p and Ru $3p_{3/2}$, respectively. [c] Prepared by impregnation of $RuCl_3$ solution. [d] Prepared by impregnation of $Ru(NO)(NO_3)_3$ solution. [e] XRD data show KCl crystallites. [f] No diffraction lines from K were observed by XRD.

specific activity were greatly suppressed while there was a concomitant increase in the olefin fraction and hydrocarbon chain growth probability—typical results for alkali promotion of Ru. The greater decrease in hydrogen chemisorption than specific activity—given the similarity in average Ru particle size based on X-ray diffraction line broadening—as well as the lack of decrease in CO chemisorption further confirms the chemial nature of the promotion as opposed to only a physical blockage effect. That some blockage of the surface by the promoter occurs, however, cannot be ruled out.

Results

The ESCA spectra of Ru^0, reduced Ru/SiO_2-Cl, and (Ru+Na)/SiO_2-Cl in the Ru $3d_{3/2}$ and Ru $3d_{5/2}$ regions are shown in Figure 1. The Ru 3d lines, which are the most prominent and commonly used regions for Ru, suffer from overlap with the C 1s line from carbon contamination. Therefore, in the present study, only the BE of the Ru $3d_{5/2}$ line was used to determine the chemical state of Ru.

An ESCA spectrum of the reduced Ru/SiO_2-Cl catalysts is shown in Figure 1b. The peak position of the Ru $3d_{5/2}$ line of Ru/SiO_2-Cl is very close to that of Ru metal, suggesting at most weak interaction between Ru and SiO_2. This result is consistent with the work of others.[32] However, after addition of Na^+ to the Ru/SiO_2-Cl catalyst, the BE of Ru $3d_{5/2}$ (Figure 1c) shifts negative by 1.2 eV relative to Ru metal, as shown in Table III. No chlorine signals could be detected in the ESCA spectra of the undoped Ru/SiO_2-Cl catalysts. However, after addition of Na ions, XRD data indicated that significant amounts of sodium was present as NaCl and the corrected ESCA [Cl $2p_{3/2}$]/[Si 2p] intensity ratio was 0.029.

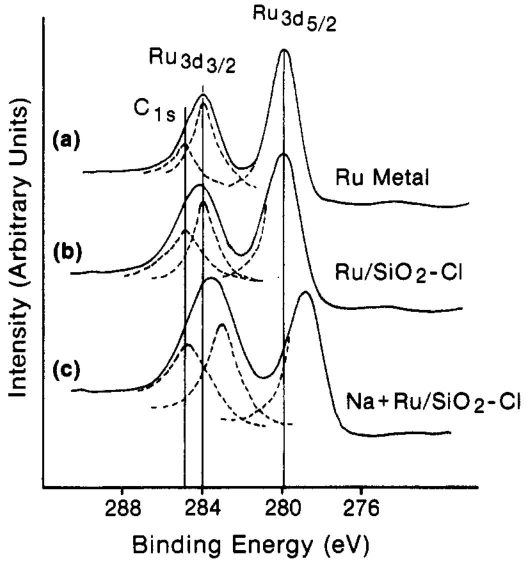

Figure 1. Ru $3d_{5/2}$ ESCA spectra of reduced Ru catalysts: (a) bulk Ru^0; (b) Ru/SiO_2-Cl; (c) (Ru+Na)/SiO_2-Cl.

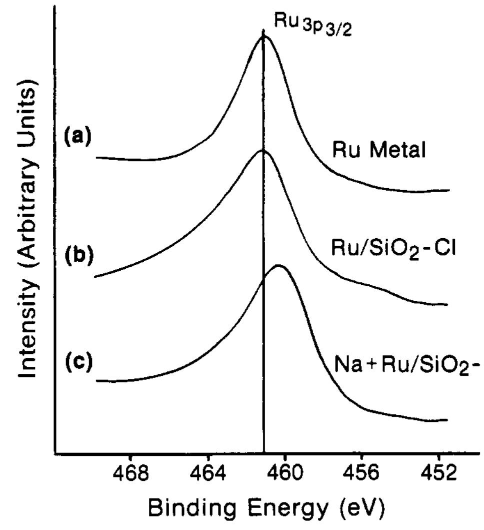

Figure 2. Ru $3p_{3/2}$ ESCA spectra of reduced Ru catalysts: (a) bulk Ru^0; (b) Ru/SiO_2-Cl; (c) (Ru+Na)/SiO_2-Cl.

There are two major factors which can cause BE shifts in the ESCA spectra of insulating materials, namely, chemical interactions (chemical shift) and charging effects. The latter is a complex competitive effect relating the rate of positive charge build-up, as a result of photoemission, and the rate of charge neutralization, through the probe itself or by stray electrons from the vacuum. Resultant inhomogeneous charge distribution will inevitably lead to peak broadening (diffuse charging), peak shift (discrete or equilibrium charging), and possibly multiple peak formation (differential charging). In the present study, the BE's of Ru were internally referenced to the Si 2p line of SiO_2, which is an insulator. Charging effect differences could arise if the Ru particles in the unpromoted and promoted catalysts had different average sizes, since larger Ru particles have increased electronic conductivity. As a result of suppression of H_2 chemisorption upon promotion, average Ru metal particle sizes had to be determined by XRD line broadening (using a Mo Kα source). These XRD results indicate that the average Ru particle size remained un-

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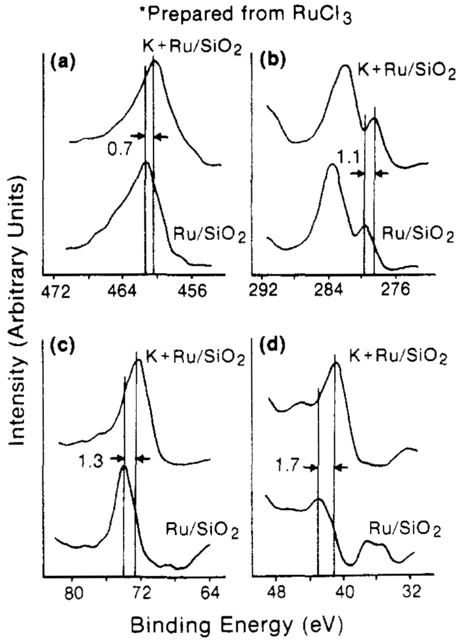

Figure 3. ESCA spectra of reduced Ru/SiO_2-Cl and (Ru+K)/SiO_2-Cl catalysts: (a) Ru $3p_{3/2}$; (b) Ru 3d; (c) Ru 4s; (d) Ru 4p.

changed before and after sodium addition (ca. 3.5 nm). Finally, if a charging effect were to be present, it can be argued that it should result in a BE for the Ru higher than that of the bulk metal[41]—the opposite of what is seen. Therefore, it is concluded that the BE shift of the Ru $3d_{5/2}$ line caused by doping with Na^+ is essentially chemical in nature and not due to charging effects.

To examine the electronic state of Ru more closely, ESCA spectra of Ru catalysts in the Ru $3p_{3/2}$ region were obtained; these are shown in Figure 2. The BE shifts for reduced Ru/SiO_2-Cl and (Ru+Na)/SiO_2-Cl catalysts relative to Ru metal are –0.1 and –0.8 eV, respectively. The former BE shift is within experimental error (±0.15 eV),[26] while the latter is outside these limits. The BE shifts of Ru in different regions and the unchanged C 1s lines indicate that the changes in Ru BE's are due mainly to the modification of the electronic structure of Ru as a result of promotion.

In general, a lower BE of an atom indicates electron-rich character, assuming factors such as relaxation energy and work function remain constant. To elucidate the chemical nature of alkali promotion effects on Ru/SiO_2 catalysts, a systematic study of the BE shifts was undertaken for a (Ru+K)/SiO_2-Cl catalyst to evaluate the importance of such effects. ESCA spectra of Ru/SiO_2-Cl and (Ru+K)/SiO_2-Cl in the various Ru regions are shown in Figure 3. It should be noted that, in Figure 3, the absolute values of the differences in BE's between the potassium promoted and unpromoted catalysts increase in the order of Ru $3p_{3/2}$ < Ru $3d_{5/2}$ < Ru 4s < Ru 4p, the actual values being –0.7, –1.1, –1.3, and –1.7 eV, respectively. It is evident that the order of decreasing BE's in Figure 3 is opposite to the trend of increasing atomic radius of Ru orbitals. This result implies that the Ru BE shift is a function of the average atomic radius of a specific Ru orbital. Exactly the same order of decrease in Ru BE's is observed for sodium-promoted catalysts. XRD results indicated that potassium was predominantly present as KCl. The corrected ESCA [Cl 2p]/[Si 2p] intensity ratio after potassium addition was 0.073.

To determine whether chlorine played an important role in the variation of Ru BE's in (Ru+K)/SiO_2-Cl catalysts, we prepared Ru/SiO_2 catalysts by impregnation with an aqueous solution of $Ru(NO)(NO_3)_3$ (designated as Ru/SiO_2-N). After reduction of Ru/SiO_2-N and (Ru+K)/SiO_2-N in H_2, complete decomposition of the Ru salt was indicated by the absence of nitrogen signals in the ESCA spectra. For the (Ru+K)/SiO_2-N catalyst after reduction, potassium is believed to be present as K_2O.[33] However, XRD was not able to detect any K species in the catalyst, suggesting that K was present in a dispersed or amorphous phase which could not be observed by XRD.

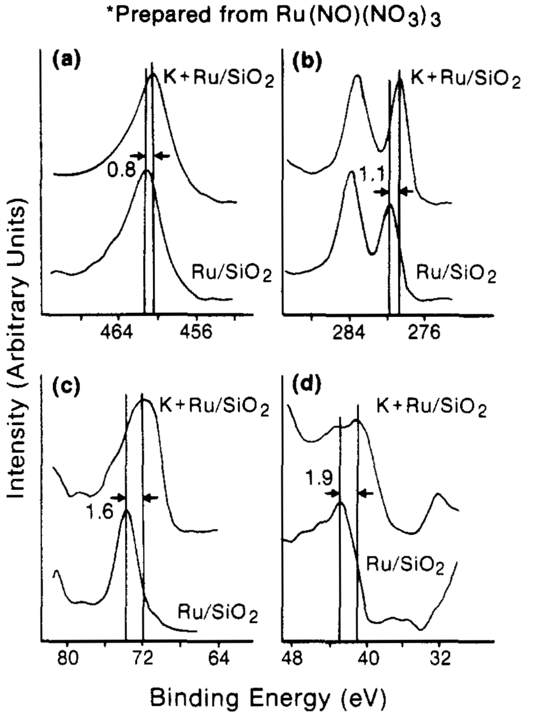

Figure 4. ESCA spectra of reduced Ru/SiO_2-N and (Ru+K)/SiO_2-N catalysts: (a) Ru $3p_{3/2}$; (b) Ru 3d; (c) Ru 4s; (d) Ru 4p.

ESCA spectra of Ru/SiO_2-N and (Ru+K)/SiO_2-N are shown in Figure 4. The BE shifts of Ru caused by potassium promotion, as indicated in Figure 4, are –0.8, –1.1, –1.6, and –1.9 eV in the regions of Ru $3p_{3/2}$, Ru $3d_{5/2}$, Ru 4s, and Ru 4p, respectively. Thus it is clear that potassium produces similar effects on the BE shifts for (Ru+K)/SiO_2-N as for (Ru+K)/SiO_2-Cl catalysts. Consequently, it can be concluded that the lowering of the BE of Ru in both N and Cl series of (Ru+K)SiO_2 catalysts results primarily from interaction between potassium and ruthenium, and the anion associated with potassium has very little influence on the Ru BE's.

Discussion

Metal–Support Interaction. Lytle et al.[34] have indicated that, for Ru/SiO_2 catalysts, the coordination number of Ru in small Ru crystallites is 8 ± 1. This coordination number is substantially lower than the value of 12 for Ru bulk metal, suggesting that some of the Ru atoms are bound to the SiO_2 surface. Based on the ESCA data in the present study, we conclude that the Ru–SiO_2 interaction is weak regardless of the Ru precursor. As indicated by the ESCA data, chlorine was not detectable after reduction of the unpromoted catalyst. This indicates that very little chlorine was present as an impurity, a result in accordance with the results of Koopman et al.[35] Even though chlorine is considered to be an electronegative element which may be a poison for Ru,[6] the quantity of chlorine present was almost negligible and did not produce any effects on the ESCA spectra of Ru in the Ru/SiO_2-Cl catalysts. Therefore, no matter what Ru precursors were used, they produced essentially a similar final product. As evidenced by ESCA data, the interaction between Ru and SiO_2 for both Ru/SiO_2 catalysts (-Cl and -N) was very weak. The weakness of this interaction was probably due to the extremely stable structure of the tetrahedrally coordinated SiO_2 support and the low ion exchangability of the surface hydroxyl groups on the SiO_2 surface.[26]

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Interpretation of the BE Shifts of Ru Due to Alkali Promotion. The ESCA data demonstrates that, for both the Cl and N series of Ru/SiO_2 catalysts, Ru showed the characteristic BE's of reduced Ru metal. However, after doping with Na^+ or K^+, decreases in the BE's of Ru were observed for all Ru/SiO_2 catalysts. Lowering of the Ru BE's can be attributed to a strong interaction between Ru and the alkali promoters. Direct electron transfer from alkali metal ions to Ru would seem unlikely because of the high ionization potentials and inert gas configurations (ns^0) of alkali ions.

So that the nature of the alkali promotion effect can be understood, it is useful to review details of core level BE shifts in ESCA. Kim and Winograd[36] have shown that a particular core level BE shift (ΔBE) can be represented by

$$\Delta \mathrm{BE} = \Delta q/r - \Delta V - \Delta E_\mathrm{R} - \Delta\phi \qquad (1)$$

where Δq is the difference in valence electron density, r is the average radius of the valence shell, ΔV is the difference in the Madelung crystal field potential energy, ΔE_R is the change in atomic relaxation energy due to polarization of photoionized holes, and $\Delta\phi$ is the change in spectrometer work function. $\Delta\phi$ can be dropped out of the equation for our purposes since the same ESCA apparatus was used for all the samples. In eq 1, the only term that depends upon the atomic orbital radius of the particular core level being observed is ΔE_R.[37] Since the magnitude of the BE shift following alkali promotion depended upon the particular core electrons being observed (Figures 3 and 4), it may be concluded that at least a part of the BE shift was caused by a change in atomic relaxation energy. ΔV, the change in crystal field potential energy on Ru, arises from changes in dipole–dipole interaction between Ru and its environment. By modification of the preparation procedure it was possible to produce catalysts having potassium predominantly in the KCl or, presumably, K_2O form. If ΔV were important in the shifts in BE upon promotion, the different preparation procedures should have affected ΔBE's because of the different dipole moments for KCl and K_2O.[33] No such effect was seen. Thus, it may be concluded that ΔV did not contribute significantly to the changes in BE upon promotion and may be neglected.

Shirley[37] has pointed out that relaxation energy in ESCA can be classified into intra- and extraatomic relaxation energies. The former is an intrinsic property of an atom and depends little on the chemical environment; the latter is important when the chemical environment of an atom is changed significantly. Therefore, in the present study, only extraatomic relaxation needs to be considered.

Extraatomic relaxation can be thought of as a polarization of the photoionized holes by the chemical environment of surface atoms. The magnitude of a change in extraatomic relaxation energy (ΔE_R) can be as large as several electronvolts. Gadzuk[38] has shown that extraatomic relaxation arises from two contributions, volume and surface relaxation. The total change in extraatomic relaxation energy for a metal can be considered to be a weighted average of the changes in volume and surface relaxation energies

$$(\Delta E_\mathrm{R})_\mathrm{TOT} = (\Delta E_\mathrm{R})_\mathrm{v} P_\mathrm{v} + (\Delta E_\mathrm{R})_\mathrm{s} P_\mathrm{s} \qquad (2)$$

where P_v and P_s are the fractions of atoms in the bulk and on the surface, respectively. This averaging effect on ΔE_R comes about because of the presence of conduction band electrons and their ability to move about to screen positive holes.[38] Thus, particle size can be an important factor in determining the amount of extraatomic relaxation in systems containing small, supported metal clusters.[42] However, in the present case, there was no apparent difference in Ru particle sizes in the unpromoted and promoted catalysts. In addition, any particle size effect would cause positive Ru BE shifts relative to the bulk metal rather than the negative ones actually seen for the promoted catalyst. Thus, a Ru particle size effect can be ruled out as a cause of the BE shifts seen.

TABLE IV[a]

	Ru $3p_{3/2}$	Ru $3d_{5/2}$	Ru 4s	Ru 4p
$\Delta \mathrm{BE} \simeq (\Delta q/r) - \Delta E_\mathrm{R}$	−0.75	−1.10	−1.45	−1.80
$\Delta E_{\mathrm{R_i}} - \Delta E_{\mathrm{R},3p_{3/2}}$	0	0.35	0.70	1.05
$\Delta q/r >$	−0.75	−0.75	−0.75	−0.75

[a] Units: electronvolts.

Values of P_v and P_s can be estimated from the particle size, ESCA sampling depth, and thickness of the outermost Ru layer. The average particle diameter of the Ru/SiO_2 catalyst was estimated by XRD to be ca. 3.5 nm,[4] and the inelastic mean free path of ESCA for Ru reported by Penn is approximately 1.59 nm.[39] The thickness of the outermost layer can be estimated from the average atomic distance between adjacent Ru atoms on SiO_2. Lytle et al.,[34] using EXAFS, found that the average atomic distance between two adjacent Ru atoms on a Ru/SiO_2 catalyst was 0.268 nm. The thickness of the surface layer should be approximately the atomic distance between Ru atoms. Ru particles with diameters of 3.5 nm have dispersions of approximately 30%, i.e., 30% of the atoms exist on the surfaces of the particles. This can be easily verified by simple calculations assuming cubic particle geometires. Thus, $P_\mathrm{v} = 0.7$ and $P_\mathrm{s} = 0.3$. These fractions hold since ESCA can sample as deep as ca. 4.8 nm into a Ru surface (3λ). Substitution of these values for P_v and P_s into eq 2 leads to

$$(\Delta E_\mathrm{R})_\mathrm{TOT} = 0.7(\Delta E_\mathrm{R})_\mathrm{v} + 0.3(\Delta E_\mathrm{R})_\mathrm{s} \qquad (3)$$

While it is not possible to determine the values for ΔE_R for the various Ru core electrons following alkali promotion, it is possible to determine differences in the ΔE_R's since only ΔE_R is a function of the particular core electron observed (Table IV).

$$\Delta \mathrm{BE_i} = \frac{\Delta q}{r} - \Delta V - \Delta E_{\mathrm{R_i}} = \frac{\Delta q}{r} - \Delta E_{\mathrm{R_i}}$$

$$\Delta \mathrm{BE}_{3p_{3/2}} - \Delta \mathrm{BE_i} = \left(\frac{\Delta q}{r} - \Delta E_{\mathrm{R},3p_{3/2}}\right) - \left(\frac{\Delta q}{r} - \Delta E_{\mathrm{R_i}}\right)$$

$$\Delta E_{\mathrm{R_i}} - \Delta E_{\mathrm{R},3p_{3/2}} = \Delta \mathrm{BE}_{3p_{3/2}} - \Delta \mathrm{BE_i}$$

In the absence of electron charge transfer to the Ru, the presence of the promoter would increase the extraatomic relaxation for the core holes being created in the surface Ru atoms. This would result in an increase in kinetic energy of the ejected electrons and a decrease in the BE measured relative to the unpromoted Ru. Therefore, since ΔBE would be less than zero, $\Delta E_{\mathrm{R_i}}$ would be greater than zero, again relative to unpromoted Ru. The total extraatomic relaxation effect for the Ru surface atoms would thus be due to (a) the conduction band electrons of the Ru particle (also operative in the unpromoted case) and (b) relaxation by electrons of the alkali species in a next-neighbor position to the surface Ru atoms. On the other hand, if there were electron charge transfer to the Ru from the promoter this would also increase the relaxation effect and $\Delta E_{\mathrm{R_i}}$ would again be greater than zero. Since it is highly unlikely that the alkali promoter acts as an electron withdrawer we can conclude that $\Delta E_{\mathrm{R_i}} > 0$. Since

$$\Delta \mathrm{BE_i} = (\Delta q/r) - \Delta E_{\mathrm{R_i}}$$

$$\Delta q/r = \Delta \mathrm{BE_i} + \Delta E_{\mathrm{R_i}}$$

$$\Delta q/r > \Delta \mathrm{BE_i} + \Delta E_{\mathrm{R_i}} - \Delta E_{\mathrm{R},3p_{3/2}}$$

it can be seen from Table IV that

$$\Delta q/r > -0.75$$

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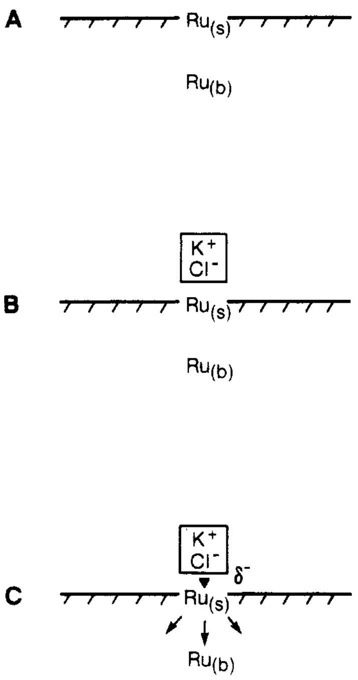

Figure 5. Models of Ru–K$^+$ interactions: (A) clean surface; (B) without electronic interaction; (C) with electronic interaction.

Now, if no charge transfer occurs, $\Delta q = 0$; if charge transfer occurs to the Ru, $\Delta q < 0$. Thus, the range of possible values for $\Delta q/r$ is

$$0 \geqslant \Delta q/r > -0.75$$

As already mentioned, the extraatomic relaxation energy of a metal is a weighted average of the volume and the surface relaxation energies because of the conduction band electrons. Thus, as a result, a clean Ru surface, as illustrated by Figure 5A, would exhibit unique BE's for the core electrons of all the Ru atoms sampled by ESCA. Let us take Figure 5B as a model of alkali promotion of a metal surface and let us consider than no charge transfer occurs from the promoter to the metal. A positive hole created in the surface Ru atom during photoemission should be screened by not only the electrons in the conduction band of Ru but also by a short-range relaxation toward the core hole of the outer electrons of a component of the alkali species. A positive hole created in the bulk Ru atom shown should be screened by the electrons in the conduction band. However, because of this band, these bulk atoms would also experience a relaxation effect due to interaction of the alkali promoter species with the surface Ru atoms. The overall effect would be to produce a change in BE identical, or at least nearly, for both surface and bulk Ru atoms.

Obviously, Na$^+$ or K$^+$ cannot donate electrons. However, the alkali promoter species is actually a charge neutral molecule which is highly polar. If there were a displacement of electron density toward the surface Ru atom resulting in a net increase of charge on that atom, as illustrated by Figure 5C, all of the Ru atoms would experience an increase in extraatomic relaxation because of the conduction band of the metal. All of the Ru atoms would then exhibit a similar decrease in BE of the core electrons upon promotion.

ESCA results have demonstrated decreases in BE's for Ru upon promotion by Na$^+$ or K$^+$ which can be shown to reflect in large part a modification of extraatomic relaxation. Decreases in BE relative to the bulk metal have also been found for Ni[24] and Fe[25] catalysts; however, only single BE's were measured. In addition, a negative shift in BE of Pd relative to Pd foil has recently been reported for a Pd/La$_2$O$_3$ catalyst following calcination in air at 350 °C and reduction at 300 °C.[40] This result has been explained by a movement of partially reduced support material up onto the Pd surface where it interacts electronically with Pd atoms. Since only one core BE of Pd was measured (Pd 3d$_{5/2}$), no firm conclusion about this negative shift in BE can be made. However, its value, −0.7 eV, is in line with the results for alkali-supported Ru. The comparison of these two sets of results is very interesting since it suggests a possible link between at least some forms of SMSI and standard catalyst promotion. Thus, the electronic structure of a transition metal would appear to be affected by a number of types of additive species.

Conclusion

While alkali promotion of Ru definitely increases the amount of electronic relaxation, it is as yet not possible to identify by ESCA the presence of electron charge transfer. However, the ESCA results do suggest the possibility that such a transfer may occur. The range of possible values for $\Delta q/r$ is broad enough to accommodate significant charge transfer.

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Registry No. Ru, 7440-18-8; K, 7440-09-7; Na, 7440-23-5; CO, 630-08-0; hydrogen, 1333-74-0.

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