Lawrence Berkeley National Laboratory

Recent Work

Title

Alkali Metals as Structure and Bonding Modifiers of Transition Metal Catalysts

Permalink

https://escholarship.org/uc/item/0tc5n86v

Authors

Somorjai, Gabor A.
Garfunkel, E.L.

Publication Date

1989

LBL-27307 c.2

Center for Advanced Materials

CAM

To be published as a chapter in **Alkali Adsorption on Metals and Semiconductors**, H.P. Bonzel, A.M. Bradshaw, and G. Ertl, Eds., Elsevier Science Publishers, BV, Amsterdam, The Netherlands, 1989
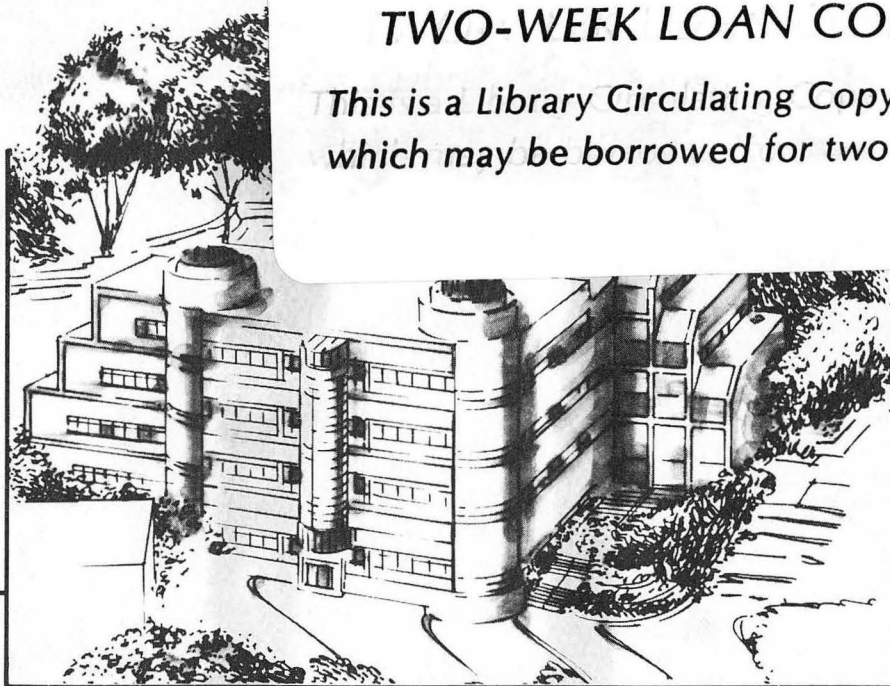
Alkali Metals as Structure and Bonding Modifiers of Transition Metal Catalysts

G.A. Somorjai and E.L. Garfunkel

June 1989

Materials and Chemical Sciences Division

Lawrence Berkeley Laboratory • University of California

ONE CYCLOTRON ROAD, BERKELEY, CA 94720 • (415) 486-4755

DISCLAIMER

ALKALI METALS AS STRUCTURE AND BONDING MODIFIERS OF TRANSITION
METAL CATALYSTS

G.A. Somorjai and E.L. Garfunkel*

Department of Chemistry, University of California, Berkeley, CA
94720 U.S.A.; and Center for Advanced Materials, Materials and
Chemical Sciences Division, Lawrence Berkeley Laboratory,
1 Cyclotron Road, Berkeley, CA 94720, U.S.A.*

Alkali metals can play the roles of both surface structure and
bonding modifiers. They cause the restructuring of iron oxide or
prevent the alumina induced restructuring of iron when coadsorbed
with Al_2O_3. Coadsoption with adsorbates that are also electron
donors to transition metals produces disordered monolayers while
coadsorption with electron acceptors leads to ordering. Repulsive
donor-donor and attractive donor-acceptor interactions strongly
influence the bonding and reactivity of co-adsorbed molecules. The
effect of alkali metals on the bonding and reactivity of ammonia,
nitrogen, carbon monoxide, and small organic molecules, is reviewed
and discussed.

1. INTRODUCTION

Alkali metals and alkali metal ions have rich surface chemistry that is
responsible for many diverse phenomena and applications. Because of their
low surface energy they segregate onto surfaces of metals and oxides, thus,
they modify their chemisorption and reactivity behavior. The low melting
points of alkali ion and transition metal ion mixed salts or mixed oxides
permits their use as molten phase catalysts (sodium-vanadium oxides for SO_2
oxidation, for example). Because of their electron donating ability (on
account of their low work function and ionization potentials) they are used
for free radical polymerization (polymerization of butadiene for example).
Their small ion sizes, especially that of lithium, Li^+, provide utility as
ion transport agents in solid state batteries as they readily intercalate and
diffuse in layer compounds such as TaS_2 or graphite.

Perhaps the most widespread use of alkali metals in surface chemistry is
for bond activation. Because of the ease of charge transfer and their strong
electrostatic interaction with neighboring molecules, they strongly polarize
them. As a result, molecules that are co-adsorbed with alkali metals on
transition metal surfaces experience weakening or strengthening of their
chemical bonds within the molecule and to the transition metal. Thus, alkali
metals catalyze the dissociation of N_2 and CO bonds under proper

---

*Dept. of Chemistry, Rutgers University, New Brunswick, NJ 08903

circumstances and modify the bonding of hydrogen, ammonia and of small organic molecules. Alkali metals, therefore, are frequently used as bonding modifiers or promoters in catalytic reactions [1].

In this paper we give several examples based on recent experimental results from surface science and catalysis studies of the effects of alkali metals on the bonding and catalytic behavior of adsorbed molecules.

2. THE ALKALI METAL COADSORPTION BOND

It is frequently found in chemisorption studies that there are large changes in the isosteric heat of adsorption with increasing coverage which lead to marked reduction in the average heat of adsorption per molecule [2]. This is commonly caused by a repulsive (predominantly dipolar) adsorbate-adsorbate interaction that becomes larger as the interadsorbate separation decreases at higher coverages and results in the weakening of the bonding of the molecules to the surface.

A good example of this type of repulsive adsorbate-adsorbate interaction is the variation of the heat of adsorption of potassium as a function of coverage on the Pt(111) surface (Fig. 1). At low coverages the heat of
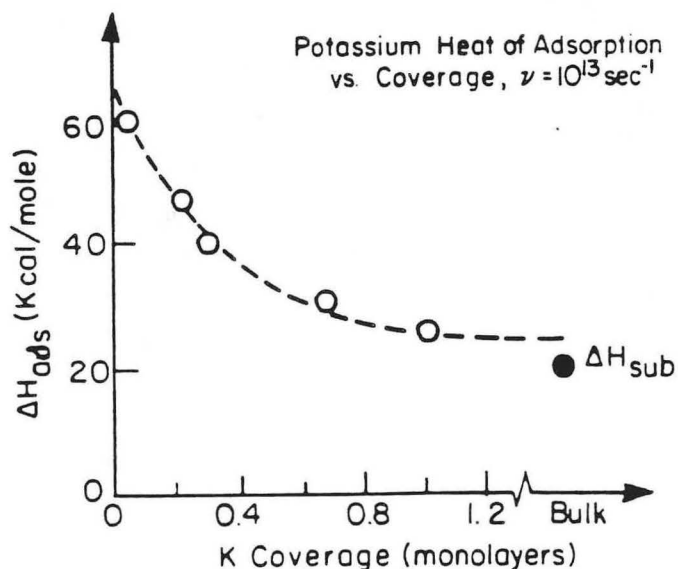
FIGURE 1

Heat of adsorption of potassium on the platinum(111) crystal face as a function of potassium coverage.

adsorption can be as much as 62 kcal/mole because of electron transfer from the alkali metal to the transition metal that stabilizes the ionized alkali species [3]. At higher coverages depolarization effects due to repulsive

interaction among alkali ions leads to a rapid decline of the average heat of adsorption until its value reaches about 23 kcal/mole above 50% of a monolayer coverage, that is equal to the heat of sublimation of the alkali metal.

Similar repulsive adsorbate-adsorbate interaction occurs when two different molecules are coadsorbed on metal surfaces if both molecules are electron donors to the metal or are electron acceptors [4]. For example Fig. 2 shows the thermal desorption curves of ammonia from the iron(111)

FIGURE 2

Temperature programmed desorption spectra of ammonia on the Iron(111) crystal face when clean and when coadsorbed with different amounts of potassium.

crystal surface [5]. When coadsorbed with potassium, ammonia desorbs at lower temperatures due to weakening of the ammonia-iron bond by potassium. Since both ammonia and potassium are electron donors to iron, this effect can be explained by the repulsive dipolar interaction between the two molecules. Similar effects were observed upon the coadsorption of potassium and benzene on Pt(111), both electron donors [6].

3

Attractive adsorbate-adsorbate interaction upon coadsorption of two different molecules on metals may lead to stronger chemical bonding to the metal [7]. This is well documented by many studies of the potassium and carbon monoxide coadsorption system (Fig. 3). The heat of adsorption of CO

Saturation CO Exposure
TDS for Various K Coverages

$\theta_K = 0$
~0.05
~0.2
~0.3
~0.5
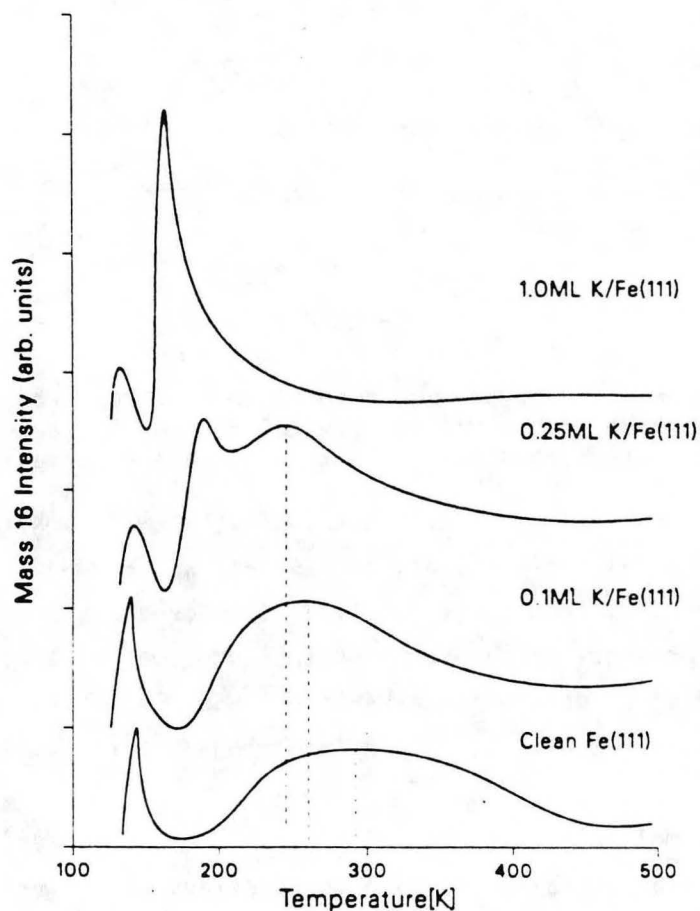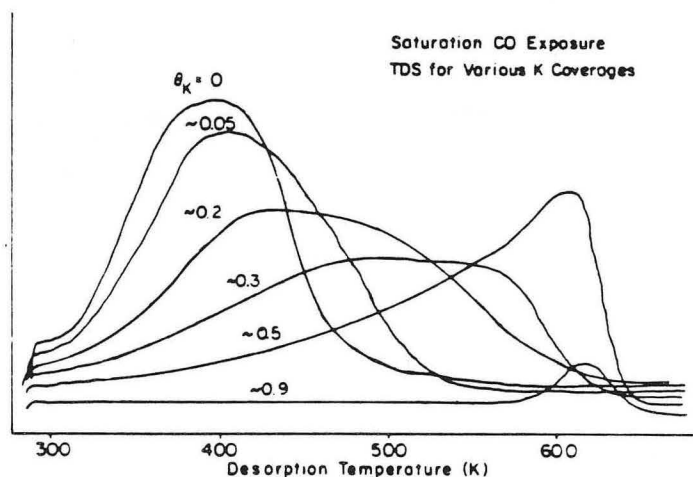~0.9

Desorption Temperature (K)

FIGURE 3

Temperature programmed desorption spectra of carbon monoxide on the Pt(111) crystal face when clean and when coadsorbed with different amounts of potassium.

increases by as much as 10-15 kcal when coadsorbed with alkali metals [8] on most transition metal surfaces that include Pt, Rh, Ni, and Fe. For example, CO desorbs completely from a clean Cu(110) surface at temperatures below 200K whereas in the presence of coadsorbed potassium, two new binding sites are populated yielding CO desorption at 480K and 550K [9]. This corresponds to an increase in the heat of adsorption from around 11 kcal/mol to greater than 28 kcal/mol.

Not only the molecular bond energies are altered by coadsorption of alkali on transition metal surfaces but also the ordering characteristics and the structure of the adsorbed monolayer [10]. LEED and HREELS studies show that benzene molecularly adsorbs at 300K in a disordered manner on a clean Rh(111) surface. However, it can be readily ordered [11] by coadsorption with other molecules, such as CO and NO, that are electron acceptors. Like most organic molecules, benzene is a strong electron donor to metal surfaces. Therefore, the presence of electron acceptor-donor interactions apparently induce ordering and the formation of surface structures containing both benzene and CO molecules in the same unit cell.

This is not an isolated phenomenon: Table 1 gives examples of several systems including those containing alkali metals where the coadsorption of an

electron donor and an acceptor leads to the formation of ordered structures while the coadsorption of two electron donors or two electron acceptors yields disordered surface monolayers [12].

TABLE 1
Coadsorption of Adsorbates on Rh(111)

Adsorbates	Ratio	Coadsorbed LEED Pattern
$NO + \equiv C.CH_3$	1:1	c(4x2)
$CO + C_2H_2$	1:1	c(4x2)
$CO + \equiv C.CH_3$	1:1	c(4x2)
$CO + C_6H_6$	2:1	(3x3)
$CO + C_6H_6$	1:1	c(2√3x4)rect
$CO + C_6H_5F$	2:1	(3x3)
$CO + C_6H_5F$	1:1	c(2√3x4)rect
$CO + Na$	1:1	c(4x2)
$CO + NO$		Disorder
$Na + C_2H_2$		Disorder
$Na + \equiv C.CH_3$		Disorder
$Na + C_6H_6$		Mixed*

* – 2 patterns characteristic of individual adsorbates observed suggesting phase separation into independent domains.

3. ALKALI METAL INDUCED BOND DISSOCIATION

3.1. CO Activation

Perhaps the most frequently studied molecule whose co-adsorption with alkali metals on transition metal surfaces leads to bond dissociation is carbon monoxide. A typical CO bond dissociation yield as a function of alkali metal coverage is shown in Fig. 4. CO does not dissociate at low pressures on the Rh(1111) surface. Upon coadsorption with potassium, dissociation of the molecule occurs and at 20% of a monolayer potassium coverage, three CO molecules disssociate per potassium atom. As the K surface coverage increases, the CO dissociation probability rapidly decreases and becomes zero over a potassium monolayer. In these studies the CO dissociation is monitored by the scrambling of doubly labelled $^{13}C^{16}O$ and $^{12}C^{18}O$ isotopes [13].

Increases of the CO dissociation probability by alkali coadsorption were also observed by Broden et al. [14], Benziger and Madix [15], Kiskinova [16], Kelemen [17], Berko [18], de Paola et al. [19], Luftman and White [20], Hoffman et al. [21], Weimer et al. [22], Lackey et al. [9], Whitman et al. [23], and others [24,25]. Usually spectroscopic studies provide convincing evidence for CO bond breaking. These include studies by both vibrational and electronic surface spectroscopies.

CO does not adsorb on potassium at low pressures ($<10^{-5}$ torr) when the alkali metal is deposited as a completed overlayer on a transition metal surface.
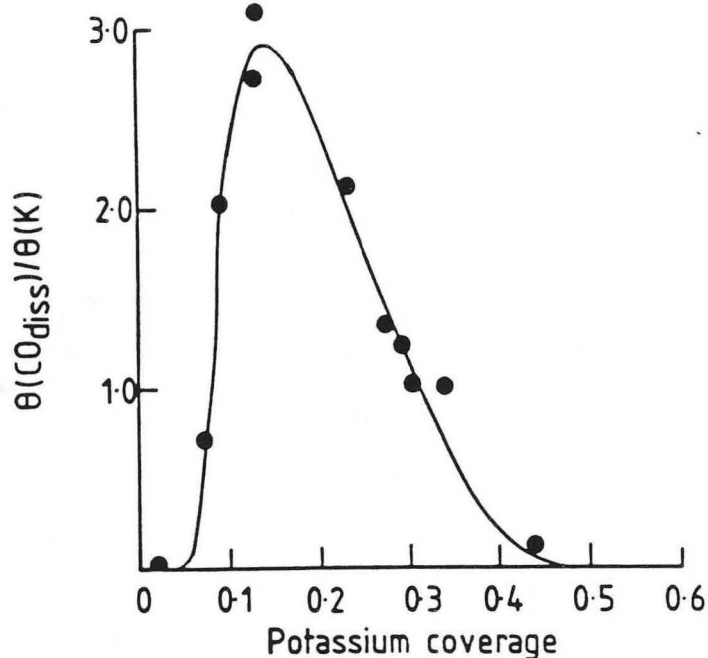

FIGURE 4

The number of dissociated CO molecules per potassium atom as a function of potassium coverage on the Rh(111) crystal face.

3.2. N_2 and NO Bond Activation

In their study Ertl and his co-workers [26] showed that on iron single crystal surfaces the rate of dissociative nitrogen adsorption increased by at least two orders of magnitude when submonolayer amounts of potassium were present. This was the result of both an increase in the heat of adsorption of molecularly adsorbed nitrogen by at least 3 kcals and a decrease in the activation barrier for dissociation.

During investigations of the coadsorption of N_2 or CO with alkali metals on transition metal surfaces, it was the transition metal that chemisorbed the molecules and the alkali metal acted only as a bonding modifier. This was not the case when NO was coadsorbed with potassium on the platinum (111) crystal face [27]. In this circumstance NO chemisorbed on both the platinum and the adsorbed potassium. While it is bound mostly molecularly on the transition metal, it dissociated over potassium to produce mostly N_2 and also some N_2O. In fact the dissociation probability of NO was directly proportional to the potassium coverage.

6

4. ALKALI ADSORPTION INDUCED RESTRUCTURING OF SURFACES

Iron oxide ordered thin films that are epitaxially grown on Pt(111) single crystal substrates are found to restructure by alkali metal adsorbates [27]. When four monolayers of sodium oxide, lithium oxide or potassium oxide are deposited on the iron oxide, ion scattering spectroscopy studies indicate that the alkali ion resides in the outermost layer. Heating the sodium oxide covered surface to 850K induces restructuring of the iron oxide film as shown in Fig. 5. Lithium oxide and potassium oxide restructure the iron oxide to a

```
┌─────────────────────┐      ISS: Fe, O
│   1 ML Fe O         │      AES: Pt, Fe, O
└─────────────────────┘
////// Pt(111) //////

        │
        │  4 ML Na + O
        ▼

┌─────────────────────┐      ISS: Na
│   4 ML Na + O       │      AES: Pt, Fe,
├─────────────────────┤           4 ML Na, O
│      Fe O           │
└─────────────────────┘
////// Pt(111) //////

        │
        │  850 K
        ▼

┌───┐   ┌───┐   ┌───┐        ISS: Pt, Na
│   │   │   │   │   │        AES: Pt, Fe,
└───┘───┘───┘───┘───┘             2 ML Na, O
////// Pt(111) //////
```
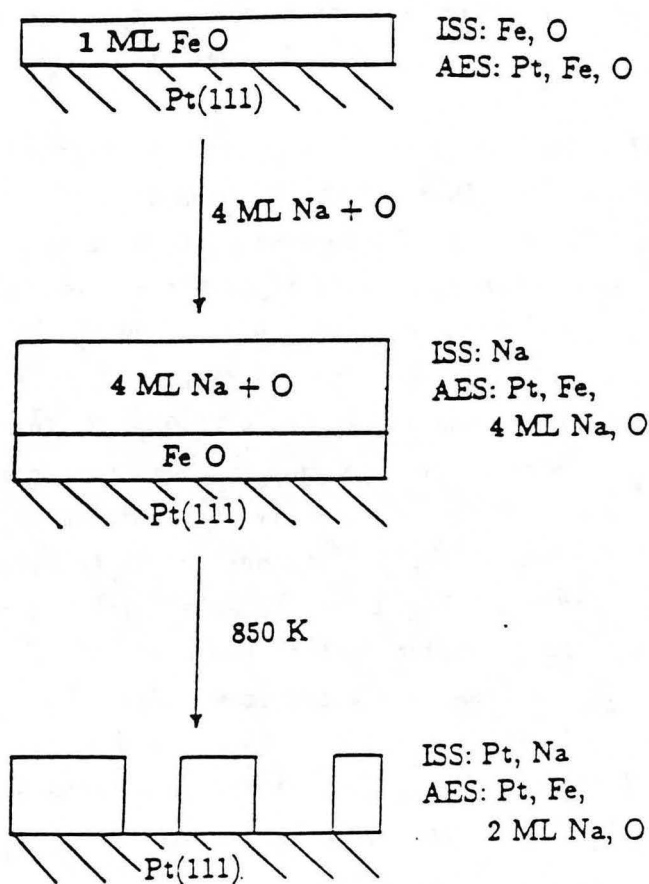
FIGURE 5

Model of alkali induced restructuring of iron oxide overlayers grown on Pt(111).

lesser extent than sodium oxide. The restructuring of the iron oxide appears to occur by dissolution in the alkali phase.

5. ALKALI METAL PROMOTED CATALYTIC REACTIONS

5.1 Ammonia Synthesis

Potassium and alumina are the most frequently used promoters for ammonia synthesis over iron [28]. The addition of alkali can increase the rate of

the reaction by as much as a factor of three even though it reduces the surface area of the iron catalyst by a factor of two [29]. Surface science studies verify three important effects of potassium in this reaction. It increases the heat of adsorption of dinitrogen and reduces its activation energy for atomization [26]. Potassium also decreases the heat of adsorption of ammonia thereby decreasing its surface concentration during the reaction [5]. Since the adsorbed ammonia product molecule blocks the sites that are active for the dissociation of N_2, a reduction in its surface concentration increases the reaction rate. This is seen by the change in the ammonia pressure dependence of the reaction rate that becomes less negative when potassium is added to the iron catalyst [5].

The third effect is due to the interaction of potassium with alumina to form $KAlO_2$, potassium aluminate [30]. Alumina is a "structural promoter" of iron for the ammonia synthesis because it catalyzes the restructuring of iron to produce predominantly Fe(111) crystal faces which are the most active in this structure sensitive reaction. This occurs by the formation of an iron aluminate phase that provides the substrate on which iron can grow with (111) orientation during ammonia synthesis [31]. The formation of potassium aluminate, $KAlO_2$, a very stable compound inhibits the promoter actions of both potassium and alumina by effectively neutralizing the two constituents. In addition, by covering a fraction of the iron surface by a chemically inert layer, it reduces the active iron surface area. Thus, care should be exercized to avoid the formation of this compound in the doubly promoted (potassium and alumina) iron catalyst system [32].

5.2 Carbon monoxide hydrogenation

Potassium is utilized as a promoter to produce methane over nickel and to produce higher molecular weight hydrocarbons over iron [33], ruthenium [34], and cobalt [35]. Surface science studies reveal that potassium has several important effects. It catalyzes the dissociation of carbon monoxide that increases the supply of reactive surface carbon, a reaction intermediate [2] ($2CO \rightarrow$ "C" $+ CO_2$) [36]. It also reduces the heat of adsorption of hydrogen on some of the transition metals, iron for example. As a result, there is a greater carbon to hydrogen ratio under the reaction conditions that increases the probability to produce higher molecular weight hydrocarbons (more C-C bonds) that contain less hydrogen (more olefins instead of saturated hydrocarbons). There is evidence that the alkali promoter slows down the conversion of the active "carbidic" carbon to the inactive graphitic form [2]. Potassium also acts as a promoter for the water-gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$) presumably through its ability to dissociate water. As a consequence, the ratios of CO to CO_2 and

8

H_2 are altered. Because of their important effects, alkali metals are additives in most catalytic processes involving CO hydrogenation.

5.3 Steam Gasification of Carbon Solids

Potassium catalyzes the gasification of graphite, chars or coal to hydrogen, CO_2, and CO using steam [37]. One of the important properties of the alkali that is utilized in this reaction is its ability to dissociate water to OH^- and H^+ ions and then to H_2 and O_2. In this reaction the oxygen is used to oxidize the carbon to produce stable phenolate, carboxyl, and lactate groups at the surface [38]. The rate limiting step in the gasification reaction is the carbon-carbon bond scission next to these carbon oxide species to form CO_2 or CO [39]. Potassium also catalyzes this reaction.

Often CaO or a transition metal oxide is added to the alkali metal oxide to produce a molten salt at the gasification temperatures of 500-700°C [40]. This way wetting of the carbon solid occurs which provides a higher catalyst-solid reactant contact area where the gasification reaction occurs.

5.4 Other Alkali Promoted Catalytic Reactions

There are many other reactions that are promoted by the presence of alkali metals. The partial oxidation of ethylene to ethylene oxide that occurs over silver catalysts is one of the most important processes [41]. The alkali metal (Cr, K, Na) is thought to increase the dissociation probability of molecular oxygen, thereby increasing the surface concentration of the oxygen species that are active in epoxidation. In recent years similar silver catalyst formulation with alkali metals is used for the production of propylene oxide from propylene.

Alkali metals are also used as promoters for the water-gas shift reaction over copper or iron oxide catalysts. Recent surface science studies explore the importance of alkali metal ions in dissociating water and stabilizing ionic intermediates by electrostatic interactions.

Alkali ions are utilized in ion catalyzed chemical reactions; in acid-base catalysis [42]. By ionizing or polarizing the reactant molecules, reactions can occur over different reaction paths. Surface science studies to identify the role of alkali metals in these reactions are just being initiated in several laboratories.

It should be mentioned that alkali metals are usually inhibitors of transition metal catalyzed hydrocarbon conversion reactions [43]. They uniformly slow down hydrocarbon conversion (dehydrogenation, hydrogenation, isomerization, and cyclization) by altering the bonding of the reaction intermediates, organic fragments, and of hydrogen. Surface science studies indicate that the activation energy for dehydrogenation increases and the heat of adsorption for hydrogen decreases in the presence of potassium.

REFERENCES

[1] Somorjai, G.A., The Building of Catalysts: A Molecular Surface Science Approach, in: Catalyst Design, Progress and Perspectives Chapter 2 (John Wiley & Sons, NY, 1987) pp. 11-69.

[2] Somorjai, G.A., Chemistry in Two Dimensions: Surfaces (Cornell University Press, 1981).

[3] Somorjai, G.A. and Garfunkel, E.L., Surf. Sci. 115 (1982) 441.

[4] Somorjai, G.A., C.M. Mate, and C.-T. Kao, Surf. Sci. 206 (1988) 145-168.

[5] Somorjai, G.A. and Strongin, D.R., J. of Catal. 109 (1988) 51-60.

[6] Somorjai, G.A., Garfunkel, E.L., Maj, J.J., Frost, J.C., and Farias, M.H., J. Phys. Chem. 87 (1983) 3629.

[7] Somorjai, G.A., Garfunkel, E.L., and Crowell, J.E., J. Phys. Chem. 86 (1982) 310.

[8] Somorjai, G.A., Crowell, J.E., and Garfunkel, E.L., Surf. Sci. 121 (1982) 303.

[9] Lackey, D., Surman, J., Jacobs, S., Grider, D., King, D.A., Surf. Sci. (1985) 152/153.

[10] Mate, C.M., and Somorjai, G.A., Surf. Sci 160 (1985) 542.
Blackman, G.S., Lin, R.F., Van Hove, M.A. and Somorjai, G.A., Acta Cryst B43 (1987) 368.
Van Hove, M.A., Lin, R.F., and Somorjai, G.A., J. Am. Chem. Soc. 108 (1986) 2532.

[11] Somorjai, G.A., Ohtani, H., Bent, B.E., Mate, C.M., and Van Hove, M.A., Applied Surface Science 33/34 (1988) 254-260.

[12] Somorjai, G.A. and Bent, B., J. of Advances in Colloid and Interface Science 29 (1989) 223.

[13] Somorjai, G.A., Crowell, J.E., and Tysoe, W.T., J. Phys. Chem. 89 (1986) 1598-1601.

[14] Broden, G., Gafner, G., and Bonzel, H.P., Surf. Sci. 84 (1979) 295.

[15] Benziger, J., and Madix, R.J., Surf. Sci. 94 (1980) 119.

[16] Kiskinova, M., Surf. Sci. 111 (1981) 584.

[17] Kelemen, S.R., Kaldor, A., and Dwyer, D.J., Surf. Sci. 121 (1982).

[18] Berko, A. and Solymosi, F., Surf. Sci. 171 (1986) L498.

[19] dePaola, R.A., Hrbek, J., and Hoffmann, F.M., J. Chem. Phys. 82 (1985) 2484.

[20] Luftman, H.S., Sun, Y.M., and White, J.M., Surf. Sci. 141 (1983) 82.

[21] Hoffmann, F.M. and dePaola, R.A., Physical Review Letters 52 (1984) 1697.

[22] Weimer, J.J., Umbach, E., and Menzel, D., Surf. Sci. 155 (1985) 132.

[23] Whitman, L.J. and Ho, W. J. Chem. Phys. 83 (1985) 4808.

[24] Solymosi, F. and Berko, A., J. Catalysis 101 (1986) 458.
Solymosi, F. and Pasztor, M., J. Phys. Chem. 90 (1986) 5312.

[25] Uram, K.J., Ng, L., Folman, M., and Yates, J.T., J. Chem. Phys. 84 (1986) 2891.

[26] Ertl, G., Weiss, M., and Lee, S.B., Chem. Phys. Lett. 60 (1979) 391.

[27] Somorjai, G.A., Vurens, G.H., Strongin, D.R., and Salmeron, M., Surf. Sci. 199 (1988) L387-L393.

[28] Ozaki, A., Catalysis, Science and Technology I, Chapter 3 (Springer-Verlag, Berlin, 1981).

[29] Somorjai, G.A. and Strongin, D.R., A Surface Science and Catalytic Study of the Effects of Aluminum Oxide and Potassium on the Ammonia Synthesis Over Iron Single Crystal Surfaces, iin :Jennings, J.R., Catalytic Ammonia Synthesis: Fundamentals and Practice (Plenum. Pub. Co. 1987)

[30] Somorjai, G.A., Baer, S.R., and Strongin, D.R., J. of Phys. Chem. 90 (1986) 4726.

[31] Somorjai, G.A., Strongin, D.R., and Bare, S.R., J. of Catal. 103 (1987) 289-301.

[32] Somorjai, G.A. and Strongin, D.R., Catalysis Letters 1 (1988) 61-66.

[33] Dry, M.E., Shingles, T., Boshoff, L.J., and Oosthuizen, G.J., J. Catalysis 15 (1969) 190.

[34] Dry, M.E., The Fischer-Tropsch Synthesis, in: Anderson, J.R. and Boudart, M., (eds), Catalysis Science and Technology (1981).

[35] Olive, G.H. and Olive S., J. Mol. Catalysis 16 (1982) 187.

[36] Peebles, D.E., Goodman, D.W., and White, J.M., J. Phys. Chem. 87 (1983) 4378.

[37] Somorjai, G.A., Carrazza, J., Tysoe, W., and Heinemann, H., J. of Catal. 96 (1985) 234-241.

[38] Somorjai, G.A., Carrazza, J., and Heinemann, H., Am. Chem. Soc., Div. Fuel Chem. 31 (1986) 158-165.

[39] Somorjai, G.A., Marchon, B., Tysoe, W.T., Carrazza, J., and Heinemann, H., J. Phys. Chem. 92 (1988) 5744-5749.

[40] Somorjai, G.A., Heinemann, H., Pereira, P., and Carrazza, J., ACS Div. Fuel Chem. 34 (1989) 121.

[41] Somorjai, G.A. and Spencer, N.D., Rep. Prog. Phys. 46 (1983) 1.

[42] Ward, J., IR Studies of Zeolite Surfaces, in: Rabo, J.A., (ed.), Zeolite Chemistry and Catalysis (ACS , 1976) pp. 201 & 268 Gallezot, P. and Bergeret, G.., Metal Catalysts Supported in Molecular Sieves, in: Petersen, E.E. and Bell, A.T., (eds), Catalyst Deactivation (Marcel Dekker, Inc., 1987) p. 267.

[43] Somorjai, G.A. and Zaera, F., J. Catal. 84 (1983) 375.

LAWRENCE BERKELEY LABORATORY
CENTER FOR ADVANCED MATERIALS
1 CYCLOTRON ROAD
BERKELEY, CALIFORNIA 94720