JOURNAL OF CATALYSIS 92, 17–24 (1985)

Migration of Potassium on Iron and Alumina Surfaces as Studied by Auger Electron Spectroscopy

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Received August 1, 1984; revised October 23, 1984

The migration of potassium on model iron and alumina surfaces was studied with Auger electron spectroscopy. The extent of potassium migration at 670 K was found to be dependent on the gas-phase composition during treatment. In particular, the mobility of potassium was greater in hydrogen than in oxygen, and the mobility in either gas was increased by the addition of H_2O. The kinetics of migration are consistent with a surface-stabilized potassium species. After initial vapor-phase transport of volatile, bulk potassium species, surface diffusion controls the migration. Potassium appears to be bonded with comparable strengths to iron and alumina surfaces.

INTRODUCTION

Alkali metal compounds have been used widely as promoters of heterogeneous catalysts. Examples of the use of such compounds include promotion of iron-based catalysts for ammonia synthesis (*1*) and Fischer–Tropsch synthesis (*2*), and modification of sulfur-resistant water–gas shift catalysts composed of cobalt and molybdenum (*3*). The role of the alkali metal in these, and other catalysts, is generally believed to be that of a chemical promoter, i.e., an additive which modifies the catalytic properties per unit surface area. This is in contrast to the function of a textural promoter (such as alumina) which stabilizes a high surface area of the catalytically active phase. An important question related to understanding the mechanism by which an alkali metal functions as a chemical promoter is what is the proximity of the alkali metal to the catalytically active phase? Furthermore, the answer to this question may well be different for different catalysts and different reaction conditions. In this respect, the present paper focuses on model studies to probe the distribution of potassium on iron-based catalysts for ammonia and Fischer–Tropsch syntheses. In particular, emphasis is placed on studies of the migration of potassium on surfaces of iron and alumina.

The distribution of promoters in iron-based catalysts for ammonia and Fischer–Tropsch syntheses has been studied by a number of investigators (*4–9*). After reduction of these catalysts, the alumina and potassium are both segregated on the surface of the catalyst. Moreover, these promoters are distributed nonuniformly on the catalyst surface. For example, the alumina may exist as discrete crystallites of Al_2O_3 and as a thin surface phase on the iron particles. The potassium may be associated with the iron and with both of these two phases of alumina. Microprobe analysis (*7, 8*) showed that the majority of the potassium is associated with alumina crystallites at the grain boundaries of iron. However, since this technique probes regions of the catalyst which are ca. 1 μm in diameter, it is not sensitive to the presence of surface phases of potassium. Studies of the surface distribution of promoters have been conducted using scanning Auger electron spectroscopy (*4*), with a spatial resolution of ca. 100 nm. Prior to reduction of the catalyst the potassium was associated primarily with

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0021-9517/85 $3.00

alumina. In contrast, following reduction the potassium promoter was present on both the alumina and iron regions of the catalyst. In another study employing Auger electron spectroscopy (*6*), it was suggested that the potassium is associated exclusively with the alumina in iron-based ammonia synthesis catalysts. Indeed, since alumina is dispersed over the iron surface, it is not possible using Auger or scanning Auger electron spectroscopy (with a resolution of ca. 100 nm) to determine unambiguously whether potassium is associated with iron, alumina, or both.

The above results illustrate the complexity of the distribution and interactions between promoters in commercial iron-based catalysts. Furthermore, the distribution of promoters has been shown to change during the course of the reaction or during catalyst activation such as the reduction of an oxidized precursor. This is particularly true for the potassium, as described in the reviews by Mross (*9*), Dry (*2*), and Nielsen (*8*). Used styrene catalysts of iron oxide, for example, show gradients in the potassium distribution along the reactor length as well as within catalyst particles (*9*). It has also been shown that the potassium promoter can be added to the catalyst during the initial stages of catalyst preparation or added to an unpromoted catalyst as a separate potassium-containing phase (*2*). Both methods of potassium addition have similar effects on the catalytic properties of iron, suggesting that this promoter migrates over the surface during catalyst activation. However, it is not presently known at what stage of the catalyst activation the potassium promoter migrates over the catalyst surface. It should be noted that since potassium-promoted iron catalysts show long-term stability under reaction conditions (*2*), the potassium promoter is apparently not sufficiently volatile for all of it to be carried out of the reactor in the effluent stream.

The migration of potassium under various gaseous atmospheres was monitored in the present study using Auger electron spectroscopy. The samples used in these studies were model materials chosen to represent the iron and alumina regions of a promoted iron catalyst. These model samples were composed of iron overlayers on flat films of alumina, onto which potassium was deposited. Indeed, these "geometrically designed samples" illustrate a general methodology for studying surface migration phenomena in heterogeneous catalyst systems.

EXPERIMENTAL

Sample Preparation

High purity aluminum foils (Alfa-Ventron, 99.999%) 12.5 × 12.5 × 0.0125 mm were rinsed in acetone, methanol, and distilled water. The foils were then chemically polished in an orthophosphoric–nitric acid mixture at 350 K for 10 s (*10*). Subsequently, films of Al_2O_3 were grown anodically on these foils in a 3 wt% ammonium tartrate solution. The final applied voltage during anodization was 22.4 V, corresponding to a 30 nm thickness of the alumina film (*11*). The samples were then calcined in oxygen at 870 K for 24 h to convert the amorphous alumina film to γ-Al_2O_3, as described in the literature (*10*). Finally, a 20-nm iron overlayer was deposited onto one half of one side of the sample using a vacuum metal evaporator.

Potassium was deposited onto the above samples by atomization of an aqueous solution containing 1.1 wt% KOH. This was accomplished with 75 sprays at a distance of 10 cm from the sample. During this process, one-half of the sample was masked, the orientation of this mask being perpendicular to the mask used to cover one-half of the sample surface during deposition of the iron overlayer. In this way, a sample with four distinct quadrants was prepared. This is shown schematically in Fig. 1. Quadrants I and II are alumina surfaces, with and without the presence of KOH, respectively. Quadrants III and IV represent unpromoted and potassium-promoted iron surfaces,

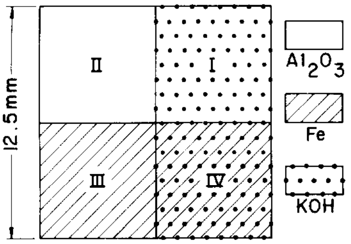

FIG. 1. Sample geometry. Quadrant I: Al_2O_3 + KOH; II: Al_2O_3; III: Fe; IV: Fe + KOH.

respectively. Auger electron analyses of these samples prior to thermal treatments indicated that the atomization procedure produced an uneven deposition of potassium due to the presence of droplets in the atomized spray which subsequently formed KOH crystallites on the sample upon drying. In addition, the atomized spray was not always evenly distributed over quadrants I and IV. For example, more potassium was deposited on alumina than on iron for the samples presented in this paper; however, other samples were prepared where the reverse was observed. The important point for the present paper is that the masking procedure was effective in eliminating the deposition of potassium on quadrants II and III during atomization.

Sample Treatments

Four different treatments of the above model samples were studied. The effects of each different treatment were investigated using a fresh sample for each experiment. All treatments were carried out at atmospheric pressure and, except where noted, were performed in a 1.9-cm-i.d. stainless-steel tube with a linear gas velocity of ca. 0.7 cm/s. The temperature of each treatment was 670 K, and the time of treatment was normally 72 h unless stated otherwise. The details of the four treatments are outlined below.

Treatment 1. The sample was treated in flowing hydrogen. A pyrex cell was used instead of the above stainless steel tube in order to eliminate the formation of water from the reduction of chromates present in the steel. The hydrogen was purified by passage through a palladium thimble (Sasafras).

Treatment 2. The sample was treated in an H_2O/H_2 gas mixture. The hydrogen was first passed through a deoxo purifier (Engelhardt) to remove oxygen, followed by an activated molecular sieve (13X) at room temperature. Approximately 530 Pa of water (i.e., 0.53 mole% H_2O in H_2) was then introduced into the gas stream by passing the hydrogen through a water saturator at 273 K.

Treatment 3. The sample was treated in oxygen. The oxygen was purified by passage through an activated molecular sieve (13X) at 195 K.

Treatment 4. The sample was treated in an H_2O/O_2 gas mixture. This gas mixture was prepared by passing purified oxygen through a water saturator at 273 K, giving a water pressure of 530 Pa.

Finally, a sample of iron on alumina which did not contain potassium was treated in a separate experiment. This sample was placed in the stainless-steel tube approximately 5 cm downstream from a titanium boat which contained 0.08 g KOH. The sample was heated in an H_2O/H_2 gas mixture (see Treatment 2) for 8 h at 670 K. This will be denoted as *Treatment 5.* A blank experiment was also carried out in which an iron on alumina sample was treated in H_2O/H_2 in the absence of the boat containing KOH.

Auger Electron Spectroscopy (AES)

Auger electron spectra were collected using a Physical Electronics (model 548 ESCA/Auger) spectrometer. All samples were exposed to air prior to study by AES. Spectra were collected, with a beam current of 20 μA and beam energy of 3 keV, in all four quadrants of each sample. Multiple scans of the potassium peak at 252 eV were taken as the beam was moved across the sample surface, from one quadrant to another. The size of the spot analyzed in each Auger electron spectrum is about 0.2 mm.

RESULTS

Figures 2 and 3 show the potassium peak-to-peak height for Auger electron spectra collected as a function of position on samples subjected to the various treatments outlined above. These peak heights have been normalized to the maximum height of the potassium peak for each sample. In this way motion of the potassium between the alumina and iron regions of the sample, as well as motion across each region individually, can be monitored. Since the electron beam was moved manually across the sample to collect these data, the distances shown in these figures are approximate only (±0.3 mm). It should be noted that while each of the curves shown in Figs. 2 and 3 represents data from a single experiment, the shapes of each of these curves have been reproduced by a number (ca. 3–5) of repetitive experiments. Finally, the approximate potassium to aluminum atomic ratios given in the figure captions are based on standard sensitivity factors of 0.82 for K at 252 eV, 0.5 for O at 503 eV (*12*), and a factor of 0.156 for Al at 1378 eV chosen to give the proper stoichiometry for Al_2O_3. These K : Al ratios are given for qualitative purposes only.

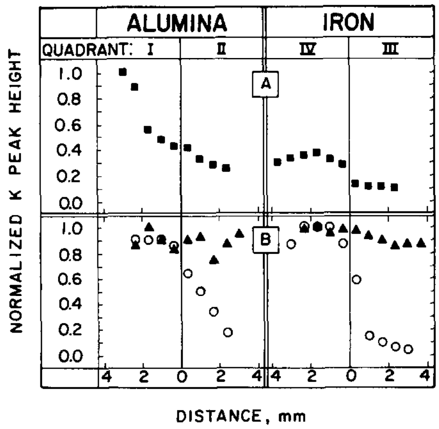

FIG. 2. Potassium distribution by quadrant versus distance from the quadrant boundary. (A) After treatment in H_2 for 72 h at 670 K, K : Al = 2.5; (B) after treatment in H_2O/H_2 at 670 K for (▲) 80 h, K : Al = 1.2, and (○) 1 h, K : Al = 1.2.

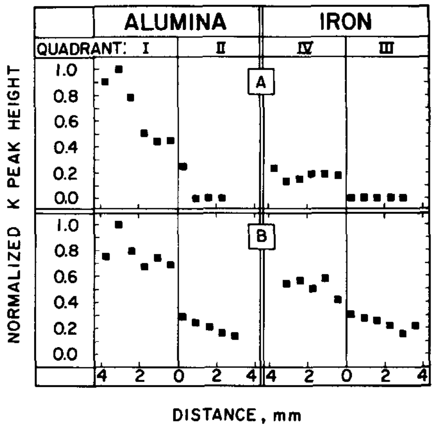

FIG. 3. Potassium distribution by quadrant versus distance from the quadrant boundary. (A) After treatment in O_2 for 72 h at 670 K, K : Al = 1.1; (B) after treatment in H_2O/O_2 for 72 h at 670 K, K : Al = 2.2.

The data of Fig. 2A show the distribution of potassium on the iron/alumina surface after treatment in hydrogen (Treatment 1). The maximum K : Al ratio is 2.5. A surface concentration gradient exists on both the iron and alumina halves of the sample. Apparently, an equilibrium distribution of potassium over the surface has not been established after this 72 h treatment. It is also noteworthy that the AES peak height of potassium is greater on the alumina half of the sample. This is due largely to the greater potassium peak height on this half of the sample prior to thermal treatment; however, this difference persists on the alumina and iron halves of the sample which did not contain potassium prior to Treatment 1.

The distribution of potassium on the sample subjected to the treatment in H_2O/H_2 (Treatment 2) is shown in Fig. 2B. The upper curves (filled triangles) in each half of this figure were obtained after treatment for 80 h, whereas the lower curves (open circles) were collected after a 1 h treatment. The maximum K : Al ratios are both 1.2. It can be seen that the distribution of potassium over the surface is fairly uniform after the 80 h treatment. Indeed, the initially higher concentration of K in quadrant I over quadrant IV, as well as the concentration gradients across iron (quadrants III and IV) and alumina (quadrants I and II) have been eliminated by this treatment. Hence, high mobility of potassium with no preference for alumina or iron is evident. Comparison of the results of Figs. 2A and B indicates that the presence of 0.53 mole% water in hydrogen markedly increases the mobility of potassium. Additional studies at a lower water concentration of 0.005 mole% also showed increased potassium mobility compared to dry hydrogen but decreased mobility compared to the higher water concentration in hydrogen. Specifically, the smallest potassium AES signal on the sample after treatment in 0.005 mole% H_2O for 72 h was 0.5 of the maximum AES signal on the sample, compared to values of 0.2 in the absence of water and 0.9 at the higher water concentration. Finally, the AES data in Fig. 2B collected after treatment in H_2O/H_2 (0.53 mole% H_2O) for 1 h show that a potassium concentration gradient exists on the alumina and the iron halves of the sample. These data will be used to estimate the rate of potassium migration.

Figure 3A shows the potassium distribution on the surface after treatment in oxygen (Treatment 3). The maximum K : Al ratio is 1.1. It is clear that essentially no migration of potassium takes place during this treatment. The concentration of potassium on the iron half of the surface prior to the treatment in oxygen was particularly small for this sample. All samples studied, however, showed the absence of potassium on either the alumina or iron halves of the surface following treatment in oxygen. In contrast to this behavior, Fig. 3B shows that the addition of water to oxygen (Treatment 4) increases the mobility of potassium. For this sample the maximum K : Al ratio is 2.2. This is evidenced by the presence of potassium on the portions of the sample which did not contain potassium prior to this treatment. In fact, the potassium concentration gradient after treatment in H_2O/O_2 is similar to that after treatment in H_2 for the same period of time (i.e., 72 h).

The above results indicate that the mobility of potassium is greater in the H_2O/H_2 gas mixture than it is in H_2, O_2 or the H_2O/O_2 gas mixture. Treatment 5 was designed to test whether gas-phase transport of potassium took place in this H_2O/H_2 gas mixture (i.e., from the KOH in the titanium boat to the iron-alumina sample). In short, a measurable amount of potassium was detected on the sample after this treatment (e.g., K : Al atomic ratio of about 0.3 on the alumina half of the sample). In addition, the potassium appeared to be deposited without preference on either alumina or iron. No potassium was present on a sample after treatment in H_2O/H_2 but in the absence of the boat containing KOH.

DISCUSSION

The results of this study have confirmed the mobility of potassium at 670 K on model surfaces of iron and alumina. This migration appears to be most extensive in H_2O/H_2 gas mixtures. The possible mechanisms for transport of potassium will be discussed below.

Bulk thermodynamic calculations are useful to provide insight into the possible nature of the potassium phases present as a function of the gas atmosphere over the sample. The following potassium phases were considered in these calculations: $K_{(l)}$, $K_{(g)}$, $K_{2(g)}$, $KH_{(s)}$, $KOH_{(s)}$, $KOH_{(l)}$, $KOH_{(g)}$, $K_2O_{(s)}$, $KO_{(g)}$, $K_2O_{2(s)}$, $K_2O_{3(s)}$, $KO_{2(s)}$, and $KO_{3(s)}$. Values of ΔG_f at 670 K were obtained from tabulations of thermodynamic data (*13*, *14*). These values are summarized in Table 1.

In hydrogen at atmospheric pressure and 670 K, the thermodynamically stable form of potassium is $K_{(l)}$ if the partial pressure of water is lower than ca. 10^{-4} Pa. Under these conditions, the vapor pressure of metallic potassium is approximately 530 Pa (*13*). If the partial pressure of water becomes greater than ca. 10^{-4} Pa, then $KOH_{(l)}$ becomes the stable phase of potassium. The vapor pressure of KOH at 670 K

TABLE 1

Free Energy of Formation of Potassium Phases at 670 K[a]

Phase	ΔG_f (kJ/mol)	Phase	ΔG_f (kJ/mol)
$K_{(l)}$	0.0	$KO_{(g)}$	0.80
$K_{(g)}$	29.2	$K_2O_{2(s)}$	−345.5
$K_{2(g)}$	55.3	$K_2O_{3(s)}$	−310.8[b]
$KH_{(s)}$	1.53	$KO_{2(s)}$	−201.98
$KOH_{(s)}$	−324.71	$KO_{3(s)}$	(−104)[b,c]
$KOH_{(l)}$	−324.52	$H_2O_{(g)}$	−210.40
$KOH_{(g)}$	−232.09	$H_{2(g)}$	0.0
$K_2O_{(s)}$	−268.51	$O_{2(g)}$	0.0

[a] Reference (*13*).

[b] Reference (*14*).

[c] Extrapolation from an equation valid only from 336 to 500 K.

can be estimated to be about 10^{-2} Pa (*13, 15*). The above statements regarding the effect of the water pressure in determining the stable phase of potassium are in agreement with the calculations of van Ommen *et al.* (*16*). In oxygen at 670 K, the most stable phase of potassium is $KO_{2(s)}$. The vapor pressure of this phase at 670 K is not known. If the partial pressure of water in oxygen exceeds 200 Pa, then the stable phase of potassium becomes KOH.

Order of magnitude estimates of the rate of potassium migration can be made by analyzing the experiments carried out in H_2O/H_2 for the two different lengths of time, i.e., 1 and 80 h. The mobility of potassium under these conditions was more extensive than under H_2, O_2, or H_2O/O_2. It can be seen in Fig. 2B that a characteristic distance, L, for the migration of potassium (e.g., the distance over which the potassium surface concentration decreases to one half of its maximum value) is about 0.2 cm over a period time, t, of 1 h. This corresponds to an apparent diffusivity of 10^{-5} cm²/s (L^2/t). The diffusion coefficients for migration of potassium in H_2 or H_2O/O_2 are approximately 10 to 100 times smaller than this value, while the migration in O_2 was too slow to be measured in the present study. Diffusion coefficients for transport in the gas phase are typically 0.1–1 cm²/s (*17*), while diffusion coefficients for surface diffusion are typically in the range from 10^{-9}–10^{-4} cm²/s (*18*). The diffusivity estimated in the present study, therefore, suggests that (i) the transport of potassium takes place via surface diffusion, and/or (ii) the vapor pressure of the species which diffuses through the gas phase is very low. Concerning this second possibility, the surface of the sample would become covered with a monolayer of potassium in 1 s if the vapor pressure of potassium were 10^{-4} Pa and the sticking coefficient of potassium were unity. Since the potasium coverage in quadrants II and III remains significantly less than one monolayer after treatment for 1 h, the effective vapor pressure of potassium can be estimated to be less than ca. 10^{-7} Pa under the conditions of this study.

In general, one may anticipate that the primary mode of potassium transport may be dependent on the state of potassium on the sample. For example, potassium may well be bonded more strongly to the iron and alumina surfaces than it is bonded on the surfaces of bulk potassium compounds (*19, 20*). Accordingly, for submonolayer quantities of potassium on iron and alumina, the vapor pressure of potassium may be lower than that over bulk potassium phases. This has been used in the literature to explain the observation that potassium is not lost from iron-based catalysts under reaction conditions for prolonged periods of time (*20*). This would also suggest that the primary mode of potassium migration is via surface diffusion. During the initial stages of catalyst preparation, however, the potassium may not be uniformly dispersed over the iron and alumina surfaces in sub-monolayer amounts. Instead, crystallites of bulk potassium phases may exist (e.g., K, KOH). This applies for both high surface area samples and the model samples of the present study. The primary mode of transport of potassium associated with these crystallites may be via the gas phase. This is demonstrated in the present study by the experiments in H_2O/H_2 which showed the gas-phase transport of potassium from a titanium boat filled with KOH to a sample of iron on alumina.

The differences between the rates of potassium migration during the various sample treatments must now be explained. The order of decreasing rates of potassium migration in the various gas atmospheres was:

$$H_2O/H_2 > H_2,\ H_2O/O_2 > O_2$$

In short, the mobility of potassium is greater in H_2 than in O_2, and the presence of water increases the mobility of potassium in both H_2 and O_2. It should be noted that this latter observation is in agreement with other studies which have shown that sintering of metallic particles (a process which also involves surface migration) is facilitated by the presence of water (*18, 21*).

The lower mobility of potassium in O_2 compared to H_2 indicates stronger bonding of potassium to the surface under oxidizing conditions. During the treatment in O_2, the iron and aluminum are both present as oxides (Fe_2O_3 and Al_2O_3). In addition, the potassium is present in an oxidized state (e.g., KO_2). Indeed, a K to O ratio of 0.5 was found on the (111) face of Pt (22). The surfaces of iron and aluminum oxides apparently provide sites for strong bonding of potassium oxide. In hydrogen, iron is present in the metallic state, and potassium may exist in the metallic state or as a reduced oxide (e.g., as KO_x, with x less than two). Removal of oxygen from the system now apparently leads to a decrease in the strength of potassium bonding to the surface. This is in agreement with other studies which have indicated that the presence of oxygen increases the strength of potassium bonding to iron surfaces (*19, 20, 23*).

The increase in potassium mobility observed upon introduction of water into either H_2 or O_2 can be explained by the formation of hydroxylated (or hydrated) forms of potassium on the surface. Upon addition of water to either oxygen or hydrogen under the conditions of this study, the stable phase of potassium becomes KOH. Thus, the presence of water may disrupt the bonding of potassium to the surface by insertion of hydroxyl groups. For the case of water addition to oxygen, the surfaces of Al_2O_3 and Fe_2O_3 will also become hydroxylated, further reducing the strength of the potassium-surface bonding. During the treatments in H_2O/H_2 employed in the present study, the stable phases of iron and aluminum are metallic iron and Al_2O_3, i.e., addition of H_2O to H_2 did not change the bulk states of iron and aluminum. However, the metallic iron surface may contain adsorbed water and the surface of alumina will become hydroxylated during treatment in H_2O/H_2, and this may be another origin of increased potassium mobility in the presence of water. Comment must also be made regarding the observation that the mobility of potassium in H_2O/H_2 is significantly greater than that in H_2O/O_2. This is probably related to the greater ease of hydroxylation of potassium in the former gas mixture, since the formation of bulk KOH occurs at much lower partial pressures of water in the presence of H_2 (10^{-4} Pa) than in the presence of O_2 (200 Pa), as discussed earlier.

Finally, within the experimental limits of this study, no particular preference of potassium for either iron or alumina could be discerned. That is, the mobilities of potassium on both of these surfaces appear to be similar in each of the gas atmospheres investigated. In addition, the amounts of potassium which were transported onto these surfaces were comparable after the various treatments.

CONCLUSIONS

A model sample was prepared by depositing iron and potassium onto different regions on an alumina surface. This "geometrically designed sample" was effective in monitoring the migration of potassium on iron and alumina during treatments at 670 K in H_2, H_2O/H_2, O_2, and H_2O/O_2. The results of this study confirm the suggestions from previous studies of potassium promoted catalysts that potassium can become highly mobile during catalyst activation at elevated temperatures. Moreover, potassium was found in this study to be more mobile in hydrogen than in oxygen, and the presence of water was observed to increase the mobility of potassium in both gases. Potassium transport via the gas phase and by surface diffusion were both demonstrated. The predominant mode of transport is believed to depend on the dispersion of potassium promoter phase, larger crystallites of the potassium promoter favoring gas-phase transport.

ACKNOWLEDGMENTS

We would like to thank Amoco for providing a graduate fellowship to one of us (G.C.) during the course of this study. Financial support from the National Science Foundation is gratefully acknowledged.

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