H2-D2 equilibration by the Ag-K-O2 system

van Santen, R.A.; Moolhuysen, J.; Drent, E.; Sachtler, W.M.H.

Published in:
Proceedings of the seventh International Vacuum Congress and the Third International Conference on Solid Surfaces

Published: 01/01/1977

Document Version
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the author's version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

Citation for published version (APA):

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal

Take down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Download date: 12. Dec. 2018
H₂-D₂ EQUILIBRATION BY THE Ag-K-O₂ SYSTEM

R.A. van Santen, J. Moolhuysen, E. Drent, W.M.H. Sachtler
Koninklijke/Shell-Laboratorium, Amsterdam
(Shell Research B.V.)

Abstract: The rate of equilibration of an H₂/D₂ mixture over Ag films in the absence of oxygen decreases with increasing coverage of the surface with potassium. Addition of oxygen (in an amount in the order of a monolayer) prior to the addition of potassium results in a large enhancement of the rate constant. This increase in activity is due to the promotion of the catalytic activity of potassium by oxygen, as was demonstrated by experiments done in the absence of Ag.

INTRODUCTION

Ichikawa et. al. /1/ found that metallic potassium markedly enhances the catalytic activity of Ag for the H₂/D₂ equilibration reaction. This finding - which seemed to open up an avenue to an entirely new class of alloy catalysts - together with our basic interest in catalysis by alloys /2/, prompted us to make a more detailed study of the catalytic activity of the Ag-K system. Since this system is expected to be very sensitive to impurities, we used a UHV apparatus with a background pressure of 10⁻⁸ Pa.

EXPERIMENTAL

Once-distilled, high-purity grade potassium (Alfa Europe Products, purity ≥ 99.9 %) was contacted with Ag - evaporated from a tantalum filament onto the Pyrex glass wall of the UHV apparatus (wall surface area is 300 cm²) - by breaking a seal in the connection between reaction cell and potassium ampulla. Both ampulla and reaction cell were heated in an oil bath. The amount of potassium distilled into the reaction cell was controlled by varying the heating time.

At room temperature a mixture of equal volumes of H₂ and D₂ (total pressure 13 Pa) was contacted with the film deposited on the glass wall of the reaction cell. The reaction mixture was analysed in a mass spectrometer (Micromass 6 of Vacuum Generators) and from the kinetic data we calculated the rate constant K of equilibration. Particular care was taken to prevent artefacts due to the presence of the filaments in the reaction cell.

RESULTS

Table I gives the k values derived from two experiments performed in the absence of oxygen. Potassium had been distilled onto the silver for only 5 minutes, after which the surface coverage was about 0.7. This figure was obtained by comparing the amounts of H₂ desorbed below 300 K from the Ag film presintered at 380 K before and after deposition of the potassium. In either case the adsorption of hydrogen was carried out by atomising H₂ gas of 13 Pa at 77 K using a tungsten filament. The hydrogen thus adsorbed was desorbed from the silver film at 200 K, but from potassium no desorption took place below 300 K.

Table I shows that the equilibration rate had decreased after potassium admission.

<table>
<thead>
<tr>
<th>Film</th>
<th>k, 10⁻⁸ Pa⁻¹.s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>6.1 ± 0.6</td>
</tr>
<tr>
<td>Ag + K</td>
<td>3.7 ± 1.5</td>
</tr>
</tbody>
</table>

* mean value of two runs.

Table II shows the effect of preadsorption of oxygen onto Ag films different from the ones referred to in Table I.
TABLE II
EQUILIBRATION RATE CONSTANTS*  
<table>
<thead>
<tr>
<th></th>
<th>$k \times 10^{-8}$ Pa$^{-1}$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>blank</td>
<td>6.5</td>
</tr>
<tr>
<td>blank + $O_2$</td>
<td>5.6</td>
</tr>
<tr>
<td>Ag</td>
<td>$3.5 \pm 0.3$</td>
</tr>
<tr>
<td>$Ag + O_2$</td>
<td>$2.0 \pm 0.3$</td>
</tr>
<tr>
<td>$Ag + O_2 + K$</td>
<td>$16.5 \pm 5$</td>
</tr>
<tr>
<td>After 16 h</td>
<td>$67.5 \pm 2$</td>
</tr>
</tbody>
</table>

* mean value of two runs.

The presence of oxygen on the silver (in an amount in the order of a monolayer) decreased the equilibration rate, but subsequent admission of potassium induced a great enhancement, which increased with time.

Assuming that the potassium had reduced the silver and that the enhancement could thus have been due to promotion of the potassium by oxygen, we also decided to investigate the effects of oxygen on the equilibration activity of a pure potassium film. The results of this investigation are summarized in Table III, where $Q_t$ represents the total amount of $O_2$ added (mol) per mol K present in the reaction cell. Very large enhancements, increasing with time, were formed. At $Q_t = 2 \times 10^{-3}$ the appearance of the potassium film changed from metallic to dark blue and the film started to absorb hydrogen. Ultimately, a quantity of hydrogen was taken up which was approximately equal to the molar quantity of oxygen originally added to the potassium. The phenomenon that alkali metals become darkly coloured when contacted with a substoichiometric quantity of oxygen is not uncommon: e.g. sodium forms sodium black [3], which is a combination of solid solutions of sodium metal and sodium oxide, and a permanganate-coloured suboxide of Cs$_2$O$_2$ is known [4]. At $Q_t = 0.1$ the blue of potassium "suboxide" vanished and the film became inactive.

TABLE III
EFFECT OF OXYGEN ON EQUILIBRATION ACTIVITY OF POTASSIUM  
<table>
<thead>
<tr>
<th></th>
<th>$k \times 10^{-8}$ Pa$^{-1}$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>1.1$\pm$0.2</td>
</tr>
<tr>
<td>K</td>
<td>9$\pm$5</td>
</tr>
<tr>
<td>K + H</td>
<td>70$\pm$20</td>
</tr>
</tbody>
</table>

* mean value of two runs.

In a different series of experiments we studied the effect of hydrogen atomization on the equilibration activity of a potassium film. The results are given in Table IV.

TABLE IV
EFFECT OF ATOMIC HYDROGEN ON EQUILIBRATION ACTIVITY OF POTASSIUM*  
(Hydrogen (6.6 Pa) was atomized at 20 °C, 100 Pa l was adsorbed)  
<table>
<thead>
<tr>
<th></th>
<th>$k \times 10^{-8}$ Pa$^{-1}$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank</td>
<td>1.1$\pm$0.2</td>
</tr>
<tr>
<td>K</td>
<td>9$\pm$5</td>
</tr>
<tr>
<td>K + H</td>
<td>70$\pm$20</td>
</tr>
</tbody>
</table>

* mean value of two runs.

The strong positive effect of preadsorbed hydrogen on this metal suggests that equilibration takes place by a Rideal mechanism via intermediates such as: $\text{H} \rightarrow \text{K}$.

DISCUSSION AND CONCLUSION
Our experimental results clearly show that in the absence of oxygen potassium metal has no promoting effect on the H$_2$-D$_2$ equilibration activity of silver; this finding contrasts with the report by Ichikawa et. al. [1], who, however, did not work under UHV conditions. An experiment performed in the absence of Ag showed that oxygen promotes potassium. In an experiment in which prior to potassium deposition, oxygen was adsorbed onto the Ag, a substantial increase in activity was observed upon addition of potassium. The results of this experiment is in agreement with the finding that oxygen promotes potassium in the absence of Ag, if one assumes that potassium reacts with the $O_2$ preadsorbed on Ag, as has indeed been observed by others [5,6]. Marbrow and Lambert [7] likewise reported an increase in activity of NO upon incorporation of subsurface oxygen into a subsurface layer of sodium on the Ag (110) face.

Alkali oxides readily react with H$_2$ to form hydroxides and hydrides [8]:

$$\text{K}_2\text{O} + \text{H}_2 \rightarrow \text{KOH} + \text{KH}$$
We therefore propose the following mechanism to explain the promoting effect of oxygen on the activity of potassium:

1. The formation of an oxide or suboxide catalyses the formation of KH.
2. The KH species at a surface catalyse $H_2-D_2$ equilibration by a Rideal-type mechanism, probably via a surface complex in which at least two potassium atoms participate. Therefore, when too many potassium atoms become coordinated with oxygen the equilibration reaction will no longer be catalysed.

REFERENCES