JOURNAL OF CATALYSIS 13, 328–336 (1969)

NOTES

Influence of Oxygen and Carbon Monoxide Chemisorption on the Effective Thickness of Thin Copper Films

In a previous paper (*1*) we have shown that Sachtler and Dorgelo's hypothesis (*2*) referring to the thickness decrease of thin metallic films during gas chemisorption, is supported qualitatively as well as quantitatively by our results concerning the oxygen chemisorption on thin silver films (*3–5*). Other experiments performed by us dealt with the influence of oxygen and carbon monoxide chemisorption on the electric properties depending on thickness, of thin copper films, such as electric resistance (*6–8*), temperature coefficient of the electric resistance (TCR) (*9*) and Hall voltages (*7, 8*). In this note we will point out that also these experimental results quantitatively check up Sachtler and Dorgelo's hypothesis and, moreover, that they emphasize the specific character of the thickness decrease.

The experimental technique was similar to that used for silver. Copper films, thinner than 100 Å, were deposited at a residual gas pressure of 10^{-8} torr, on a glass support cooled to 77°K. After deposition the films were annealed in order to obtain stable structures with metallic conductivity, to which Fuchs's relation can be applied. During the oxygen chemisorption on such copper films, an increase in the electric resistance (*6–8*) and a decrease in both the TCR (*9*) and the Hall voltages (*7, 8*) were recorded in the temperature range 77–273°K. During carbon monoxide chemisorption at 200°K, besides the resistance increase we noticed an increase in the Hall voltages for small coverage degrees and a decrease in it for greater ones (*8*).

The resistance increase and the TCR decrease, as well as the variation in the Hall voltages may be interpreted on grounds of Sachtler and Dorgelo's hypothesis. For the Hall voltages this becomes obvious if one takes into account the thickness dependence of the Hall coefficient of very thin copper films (*10*).

Assuming that the changes of the electric parameters are entirely brought about by a decrease in the effective film thickness and that the structure of the copper film is bulk-like and does not change through chemisorption, we computed—on grounds of TCR and electric resistance measurements by using the relationships given in paper (*1*)—the magnitude δ of the decrease in the effective film thickness. In Table 1, besides these values, there are also listed the previously obtained (*1*) data for the silver-oxygen system, as well as the lattice constants of copper and silver.

TABLE 1

δ-VALUES

Adsorban / adsorbed system	δ(Å)		Lattice constant (Å) (*11*)
	From the resistance variation (*8, 4*)	From the TCR variation (*9, 5*)	
Cu/O_2	6.05 ± 0.13	7.25 ± 1.25	3.608
Cu/CO	4.20 ± 0.50		
Ag/O_2	4.16 ± 0.25	3.58 ± 0.22	4.072

By comparing the δ-values for the Cu/O_2 and Cu/CO systems with the lattice constant of copper, it follows that in the chemisorptive copper-oxygen bond two layers of copper atoms are involved, whereas in the copper-carbon monoxide bond only one. As the measurements have been carried out at approximately the same coverage degree (at saturation), it results that the thickness decrease shows a specificity function of the chemical nature of the adsorbant/adsorbed system. The same conclusion may be drawn from the comparison of the data referring to the copper-oxygen and silver-oxygen systems, the values for the thickness decrease being in agreement with the chemical properties of the two metals.

Table 2 contains the values of the thickness decrease, δ', computed from the resistance increase by assuming not only a thickness variation but also a change in the number of conduction electrons (*5, 9*).

TABLE 2
δ'-VALUES

Adsorbant/adsorbed system	δ'(Å) (*9, 5*)
Cu/O_2	5.91 ± 0.46
Ag/O_2	3.08 ± 0.24

As it may be noticed this assumption affects neither the magnitude order nor the specific character of the thickness decrease. In other words, even by yet admitting another mechanism for the interpretation of the resistance variation in thin metallic films during oxygen chemisorption, Sachtler and Dorgelo's hypothesis remains valid.

REFERENCES

1. MURGULESCU, I. G., COMSA, GERDA H., AND IONESCU, N. I., *J. Catalysis* **12,** 102 (1968).

2. SACHTLER, W. M. H., AND DORGELO, G. J. H., *Z. Physik. Chem.* (Frankfurt) **25,** 69 (1960).

3. MURGULESCU, I. G., AND IONESCU, N. I., *Rev. Roumaine Chim.* **11,** 1035 (1966).

4. MURGULESCU, I. G., AND COMSA, GERDA, *Rev. Roumaine Chim.* **13,** 1261 (1968).

5. MURGULESCU, I. G., AND IONESCU, N. I., *Rev. Roumaine Chim.* **11,** 1267 (1966).

6. MURGULESCU, I. G., AND IONESCU, N. I., *Rev. Roumaine Chim.* **13,** 1533 (1968).

7. MURGULESCU, I. G., AND COMSA, GERDA, *Rev. Roumaine Chim.* **11,** 1253 (1966).

8. MURGULESCU, I. G., AND COMŞA, GERDA, *Rev. Roumaine Chim.* **12,** 1171 (1967).

9. MURGULESCU, I. G., AND IONESCU, N. I., *Rev. Roumaine Chim.* **14,** (1969) (in press).

10. COMŞA, GERDA, *Rev. Roumaine Chim.* **13,** 1003 (1968).

11. MOELWYN-HUGHUES, E. A. *in* "Physical Chemistry" (2nd revised edition) p. **644.** Pergamon, 1964.

I. G. MURGULESCU
N. I. IONESCU
GERDA H. COMŞA

Institute of Physical Chemistry
Academy of the Sociaist Republic of Romania
Bucharest 9, str. Dumbrava Rosie 23
Romania

Received October 22, 1968

Cage Effect on Product Distribution from Cracking over Crystalline Aluminosilicate Zeolites

Previous publications (*1, 2*) described the hydrocarbon cracking activity of various zeolites for *n*-hexane. Zeolite catalysts have been shown to have one to more than four orders of magnitude higher activity than that of conventional cracking catalysts.

With these zeolites it is possible to carry out hydrocarbon cracking reactions at temperatures considerably below the conventional cracking temperatures of ~500°C. As previously noted, temperature has a pronounced effect on product pattern in hexane cracking (*2*). The products are rich in C_4–C_5 at 316°C (600°F), and due to secondary reactions they shift toward predominantly C_3 hydrocarbons at 480°C (900°F).

Of particular interest is the study of the primary product pattern from cracking with shape-selective zeolites. It has previously been shown that when cracking