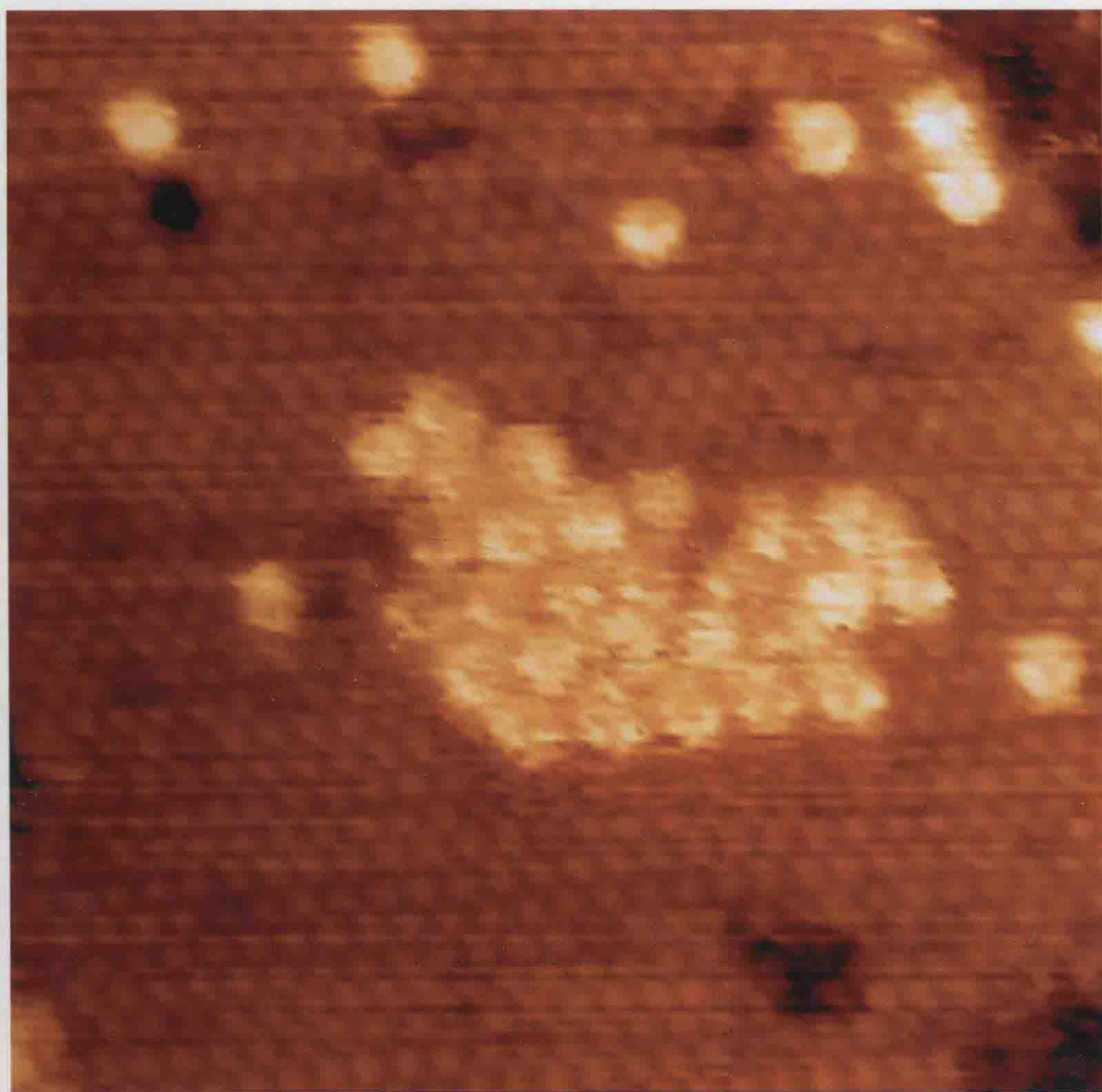


Fabrication, Structure and Reactivity of Anchored Nanoparticles

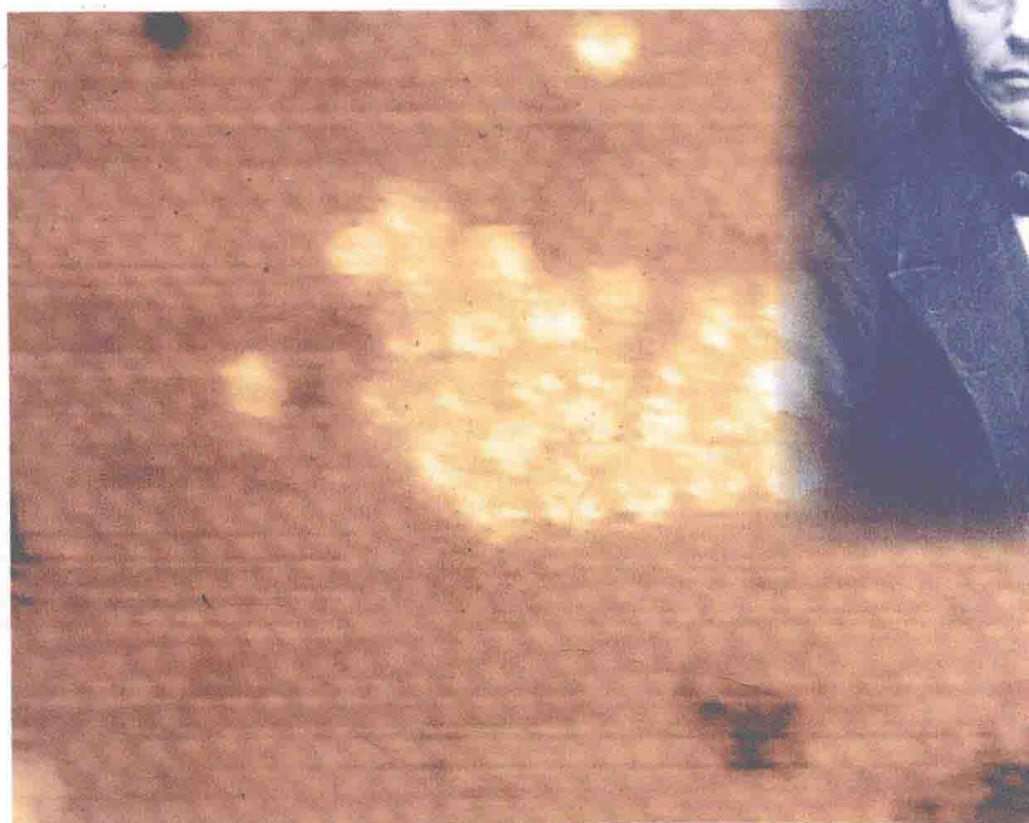


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Fabrication, Structure and Reactivity of Anchored Nanoparticles

Seminaris CampusHotel,
Berlin, Germany
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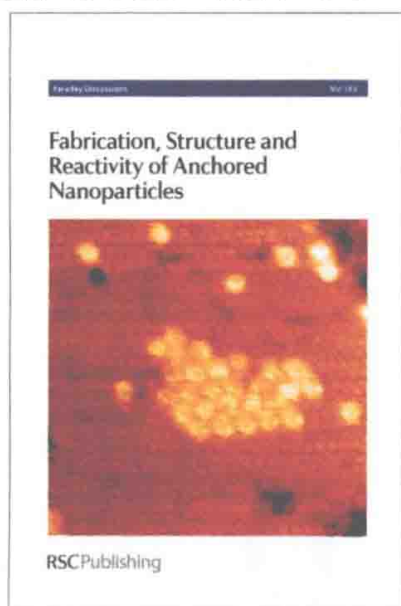
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See Bowker, Davies *et al.*, *Faraday Discuss.*, 2013, **162**, 201–212.

STM image after exposure of a clean Fe_3O_4 (111) single crystal surface to molybdenum oxide followed by annealing in oxygen at 10^{-7} mbar. The Mo oxide layer is seen as the bright islands consisting of Mo_3O_9 units organised in a (2×2) structure with respect to the iron oxide lattice underneath. The image size is 17×17 nm.

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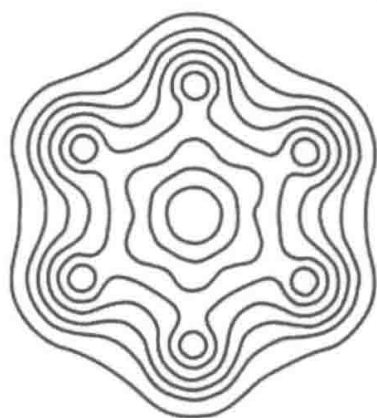
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Anchored metal nanoparticles: Effects of support and size on their energy, sintering resistance and reactivity

Charles T. Campbell* and Jason R. V. Sellers

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Many catalysts consist of metal nanoparticles anchored to the surfaces of oxide supports. These are key elements in technologies for the clean production and use of fuels and chemicals. We show here that the chemical reactivity of the surface metal atoms on these nanoparticles is closely related to their chemical potential: the higher their chemical potential, the more strongly they bond to small adsorbates. Controlling their chemical potential by tuning the structural details of the material can thus be used to tune their reactivity. As their chemical potential increases, this also makes the metal surface less noble, effectively pushing its behavior upwards and to the left in the periodic table. Also, when the metal atoms are in a nanoparticle with higher chemical potential, they experience a larger thermodynamic driving force to sinter. Calorimetric measurements of metal vapor adsorption energies onto clean oxide surfaces in ultrahigh vacuum show that the chemical potential increases with decreasing particle size below 6 nm, and, for a given size, decreases with the adhesion energy between the metal and its support, E_{adh} . The structural factors that control the metal/oxide adhesion energy are thus also keys for tuning catalytic performance. For a given oxide, E_{adh} increases with $(\Delta H_{\text{sub,M}} - \Delta H_{\text{f,MOx}})/\Omega_{\text{M}}^{2/3}$ for the metal, where $\Delta H_{\text{sub,M}}$ is its heat of sublimation, $\Delta H_{\text{f,MOx}}$ is the standard heat of formation of that metal's most stable oxide (per mole of metal), and Ω_{M} is the atomic volume of the bulk solid metal. The value $\Delta H_{\text{sub,M}} - \Delta H_{\text{f,MOx}}$ equals the heat of formation of that metal's oxide from a gaseous metal atom plus $\text{O}_2(\text{g})$, so it reflects the strength of the chemical bonds which that metal atom can make to oxygen, and $\Omega_{\text{M}}^{2/3}$ simply normalizes this energy to the area per metal atom, since E_{adh} is the adhesion energy per unit area. For a given metal, E_{adh} to different clean oxide surfaces increases as: $\text{MgO}(100) \approx \text{TiO}_2(110) \leq \alpha\text{-Al}_2\text{O}_3(0001) < \text{CeO}_{2-x}(111) \leq \text{Fe}_3\text{O}_4(111)$. Oxygen vacancies also increase E_{adh} , but surface hydroxyl groups appear to decrease E_{adh} , even though they increase the initial heat of metal adsorption.

1. Introduction

Metal nanoparticles dispersed across the surfaces of oxide and carbon supports form the basis for many catalysts and electrocatalysts of importance to future energy technologies, pollution prevention and environmental protection, all necessary for any sustainable technological infrastructure that maintains a high quality of life. The catalytic activity per surface metal atom and selectivity can vary with particle size when the metal particles are below about 7 nm in diameter,^{1–18} in some cases

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dramatically.^{7,8,19–28} Measurements have even shown that the activity depends on the nanoparticle shape for particles of the same size.²⁹ The activity can also depend strongly on the choice of support, even for particles of the same size,^{1,2,7–9,11,13,25,28,30–42} the extent of reduction if an oxide support,^{28,43–47} and oxidation if a carbon support.^{39,40,48} The proceedings of this Faraday Discussion include many examples of the effects listed above.

In general, these effects are poorly understood, largely due to the difficulty in structurally characterizing high-area catalysts with sufficient detail, resulting in an inability to analyze thoroughly any structure–reactivity relationships that control the effects, although the proceedings of this Faraday Discussion contain many papers that demonstrate that this situation is improving rapidly. Furthermore, the metal nanoparticles often sinter rapidly under catalytic reaction conditions, resulting in particle growth and loss of metal area during activity measurements, and thus challenging the ability to even measure area-specific activity let alone correlate it to size and support. The relationships of sintering kinetics to catalyst structure are also poorly understood.

In order to better understand structure–reactivity relationships in such catalysts and their sintering kinetics, a number of researchers including our own group have adopted a model catalysts approach whereby structurally well-defined samples of metal nanoparticles on oxides are prepared by vapor deposition of the metal onto single-crystal oxide surfaces.^{6,21–25,27,28,43,44,49–93} The deposited metal atoms generally nucleate small particles, whose size and number density can be controlled by the amount of deposited metal and the temperature. The aim of this approach is to correlate the metal's chemisorption, catalytic, sintering and/or electronic properties with the lateral diameter, thickness and composition of the nanoparticles and with the structure and extent of reduction of the oxide support upon which they sit.

Since we recently lost one of the most significant figures in this field, Professor D. Wayne Goodman, we wish to specifically recognize his contributions to this research area, especially his pioneering development of this model catalyst approach for studying structure–reactivity relationships in anchored nanoparticle catalysts. One can see the large impact of his contributions by looking at the very high frequency of citations to his papers in the paragraphs above. His creative approaches to establishing surface structure–function relationships in this area, and in the area of bimetallic catalysts, have paved the way for many others who later became active in this arena. His papers and talks in these areas eloquently outlined how one can approach industrially-important fundamental questions in catalysis using this model catalyst approach. Many researchers worldwide picked up on the infectious enthusiasm and clear-headed logic he projected, subsequently shifting their own research in directions he had set. Many of us who did that were also lucky enough to get to know him personally, and thus discovered his exceptionally enjoyable personality, intense competitiveness and unparalleled sense of humor.

In this paper, we review studies of well-defined model metal nanoparticle catalysts supported on clean, single-crystalline oxide surfaces, structurally characterized using a variety of ultrahigh vacuum surface science techniques. The main goal here is to relate the reactivity of late transition metal nanoparticles and the rates at which they sinter with the energies of metal atoms in these supported nanoparticles measured using unique adsorption calorimetry tools. To better understand how the choice of oxide support material affects the energies of metal atoms in nanoparticles, we also analyze temperature programmed desorption (TPD) measurements of metal desorption energies from metal nanoparticles anchored to clean oxide surfaces (from D. W. Goodman's group) as well as measurements of metal/oxide adhesion energies obtained from microscopic measurements of metal particle and molten metal droplet shapes.

We find that the concept of metal atom chemical potential is very powerful for predicting how chemisorption bond strengths and sintering rates depend on metal particle size for a given support, and on the support material for a given particle

size of late transition metal. We further show how this chemical potential depends on the structural properties of the catalyst including the metal particle size and the composition and extent of reduction of the oxide support surface.

2. The chemical potential of metal atoms in anchored nanoparticles

We will show below that in order to understand how anchored metal nanoparticles function with respect to surface reactivity, catalytic activity and sinter resistance, we must first understand how the chemical potential of the metal atoms in a nanoparticle depends on the structural details of the material. These structural details include: (1) the nature of the metal, (2) the composition and structure of the support surface upon which they sit, (3) the size of the metal nanoparticle, and (4) the shape of the metal nanoparticle. A metal atom's chemical potential is so important because it directly reflects how aggressive that atom will be in its chemical bonding to adsorbates, but at the same time it is also a direct measure of how unstable it is with respect to sintering into very large particles. We will limit this discussion of structural effects on metal chemical potential (μ , or partial molar Gibb's free energy) to a description of only the internal energy differences that arise due to these structural differences, since entropic differences are small and nearly constant in these respects, and since the difference between enthalpy (H) and internal energy (U) is also nearly constant from system to system. We will often refer to these simply as "energy".

The internal energy of a free metal (M) particle in vacuum relative to the bulk solid metal is:

$$U_M = \bar{U}_{M,\text{bulk}}n_M + \gamma_M A_M = \gamma_M A_M, \quad (1)$$

where $\bar{U}_{M,\text{bulk}}$ is the molar internal energy of the pure, bulk metal (which we set to the zero reference energy), n_M is the number of moles of metal atoms in the particle, γ_M is the surface energy of the metal–vacuum interface (which we will show depends on particle diameter below 6 nm), and A_M is the particle's surface area. When this same particle adheres to a support without any change in A_M , the system's total energy decreases by the adhesion energy (E_{adh}) times the total area of metal/support contact (A):

$$\Delta U = -E_{\text{adh}}A, \quad (2a)$$

so that the system's total energy is given by:

$$U = U_M + U_{\text{Sup}} - E_{\text{adh}}A = \gamma_M A_M + U_{\text{Sup}} - E_{\text{adh}}A, \quad (2b)$$

where U_{Sup} is the internal energy of the particle-free support before adhesion. The metal's chemical potential (μ_M , relative to the bulk metal reference state) is the partial derivative of this with respect to n_M (neglecting entropy differences, which are relatively small). Both A_M and A depend on n_M (typically varying as $n_M^{2/3}$), so μ_M will have a term that increases with γ_M and a second term that decreases with E_{adh} . As the adhesion energy increases, the metal's chemical potential decreases. So, to understand how the chemical potential of metal nanoparticles depends on a nanomaterial's structural properties, we must first understand how the adhesion energy depends on these properties. Note that both γ_M and E_{adh} can depend on particle size for particles below ~ 6 nm in effective diameter.^{94,95} We address in the next section how E_{adh} depends on the nature of the metal and of the support surface in the large-particle limit.

3. How metal/oxide adhesion energies depend on the metal and the oxide

Metal/oxide adhesion energies have mainly been measured for molten metal drops on flat oxide surfaces, using sessile drop/contact angle techniques, often under

controlled inert gas or H₂ atmospheres (although not under conditions of proven surface cleanliness). Two extensive compilations of such values have appeared,^{51,96} with much of these data coming from Chatain *et al.*^{97–100} There are similar measurements for faceted solid particles which instead of the contact angle use a ratio of distances that is similar to an aspect ratio (height/width) but which is specific to the Wulff construction of the particle shape (the ratio of the distance from the particle's center of symmetry or Wulff's point to the oxide surface divided by the distance from the Wulff's point to one exposed face of the particle).¹⁰¹ Some older values for solid particles that were collected on single crystal oxide surfaces but not under conditions of proven surface cleanliness have been summarized by Li.⁹⁶ The E_{adh} reported from such studies of molten drops and solid particles is directly proportional to the value for the bulk surface energy of the pure metal used in the data analysis, and many of the surface energy values originally used are now outdated. These E_{adh} values have been recalculated using the latest surface energies of the metals, as reported in ref. 102 and are presented in Table 1 along with the new surface energies used. More recently, such measurements have been extended to the clean conditions of ultrahigh vacuum (UHV) on single crystal oxide surfaces that were proven to be clean using surface spectroscopies. Table 2 lists many of those results.

Our group added another approach for determining adhesion energies, whereby we measure the heat of adsorption of metal atoms as they are vapor deposited onto the clean and ordered surface of a single-crystal oxide under UHV using single crystal adsorption calorimetry (SCAC). We derived the relationship between metal atom adsorption enthalpies on flat substrates and E_{adh} using a thermodynamic cycle.⁵¹ That cycle proved that the integral heat of adsorption per mole ($q_{\text{ad,int}}$) at some multilayer coverage where the differential heat of adsorption has just reached the bulk heat of sublimation of the metal per mole ($\Delta H_{\text{sub,M}}$) is given by:

$$q_{\text{ad,int}} = \Delta H_{\text{sub,M}} - [(1 + f_r)\gamma_{\text{M}} - E_{\text{adh}}]/(n_{\text{M}}/A), \quad (3)$$

where n_{M}/A is the coverage in moles of metal atoms per unit area of substrate covered by the metal and f_r is the roughness factor of the resulting multilayer metal film. We use here the convention that both $q_{\text{ad,int}}$ and $\Delta H_{\text{sub,M}}$ are positive, and neglected entropy. For metals which don't wet, $q_{\text{ad,int}} < \Delta H_{\text{sub,M}}$.⁵¹ This approach has also been applied to cases where the metal film is not continuous but instead the deposited metal assumes the form of large 3D particles.^{95,107,113} Table 2 lists all the values we have determined in this way.

Heats of adsorption of late transition metals on clean oxide single crystal surfaces have also been determined by temperature programmed desorption (TPD) in UHV, in a series of beautiful measurements made by the group of the late D. W. Goodman. We recently discovered that the leading-edge analysis used to analyze their TPD data, while usually quite valid, fails for these particular types of systems due to the simultaneous increase in particle size with time (due to both sintering and selective removal of the smaller particles by desorption).¹⁰⁶ We therefore reanalyzed much of their TPD data to get the heat of adsorption *versus* coverage for each system.¹⁰⁶ We then used those heats together with eqn (3) to extract adhesion energies (and equilibrium contact angles, assuming the solid particle shape can be approximated as a spherical cap to approximate the effect of surface roughness).¹⁰⁶ Those results are also listed in Table 2. However, we list these values here not as we originally reported them, but instead as upper limits. This is because we originally treated A in eqn (3) as if it were the full area of the oxide support surface. We recognize now that these multilayer metal films could have agglomerated into 3D particles that cover much less than 100% of the oxide during the heating of TPD prior to desorption. This is especially likely to happen on oxides with low adhesion energies. Decreasing A in eqn (3) leads to lower values of E_{adh} , thus the values we reported¹⁰⁶ should instead be considered as upper limits.

Table 1 Adhesion energies of metals on oxide surfaces measured by sessile drop/contact angle techniques for the liquid metal drops (top section) and by the shape of the particle for solid metals (bottom section). All data are from ref. 96, but the values marked with an asterisk have been recalculated based on newer values for the surface energies of the pure metals reported in ref. 102. Metals are ordered by their bulk heat of sublimation ($\Delta H_{\text{sub,M}}$) divided by the area per metal atom ($Q_{\text{M}}^{2/3}$). Also listed is the heat of formation of the bulk oxide support (per mole of oxygen atoms), $\Delta H_{\text{f,OXSup}}$

Liquid metal drops									
Metal	Oxide	Apparent θ_{contact}	$\gamma_{\text{M}}/(\text{J m}^{-2})$	$E_{\text{adh}}/(\text{J m}^{-2})$	$E_{\text{adh}}/2\gamma_{\text{M}}$	$\Delta H_{\text{sub,M}}/(\text{kJ mol}^{-1})$	$Q_{\text{M}}^{2/3}/(\text{\AA}^2)$	$-\Delta H_{\text{f,OXSup}}/(\text{kJ (mol O)}^{-1})$	Atmosphere
Pb	$\alpha\text{-Al}_2\text{O}_3(0001)$	$125 \pm 7^\circ$	0.44^{103}	$0.19 \pm 0.05^*$	0.22	195.2	6.01	558.6	Ar + H ₂
In	$\alpha\text{-Al}_2\text{O}_3(0001)$	124°	0.700	0.309*	0.22	243	8.79	558.6	Vacuum
Sn	$\alpha\text{-Al}_2\text{O}_3(0001)$	125°	0.709	0.302*	0.21	301.2	9.03	558.6	Vacuum
Ga	$\alpha\text{-Al}_2\text{O}_3(0001)$	118°	0.881	0.467*	0.27	271.96	7.27	558.6	Vacuum
Ag	$\alpha\text{-Al}_2\text{O}_3(0001)$	130°	1.22	0.436*	0.18	284.9	6.63	558.6	Ar + H ₂
Ge	$\alpha\text{-Al}_2\text{O}_3(0001)$	104°	0.555	0.421	0.38	372	8.01	558.6	Vacuum
Al	$\alpha\text{-Al}_2\text{O}_3(0001)$	$103 \pm 8^\circ$	1.14	$0.89 \pm 0.16^*$	0.39	330.9	6.51	558.6	Vacuum
Mn	$\alpha\text{-Al}_2\text{O}_3(0001)$	103°	1.54	1.19*	0.39	283.3	5.39	558.6	Ar
Au	$\alpha\text{-Al}_2\text{O}_3(0001)$	120°	1.51	0.77*	0.25	368.2	6.60	558.6	Vacuum
Si	$\alpha\text{-Al}_2\text{O}_3(0001)$	80°	0.745	0.875	0.59	450.0	7.37	558.6	He
Pd	$\alpha\text{-Al}_2\text{O}_3(0001)$	120°	2.00	1.00*	0.25	376.6	6.01	558.6	He
		104° *		1.52*	0.38				Vacuum
Cu	$\alpha\text{-Al}_2\text{O}_3(0001)$	128°	1.76	0.676*	0.19	337.4	5.18	558.6	Vacuum, Ar + H ₂
Fe	CaO	132°	2.42	0.806*	0.17	415.5	5.18	634.9	Ar
	BeO	127°		0.970*	0.20			609.4	He
	MgO	123°		1.11*	0.23			601.6	Vacuum
	UO ₂	123°		1.11*	0.23			542.5	Ar + H ₂
	ZrO ₂	115°		1.37*	0.28			550.3	Ar + H ₂
	$\alpha\text{-Al}_2\text{O}_3(0001)$	111°		1.55*	0.32			558.6	Ar + H ₂
		109°		1.63*	0.34				Ar + H ₂
	Cr ₂ O ₃	88°		2.52*	0.52			379.9	Ar
Co	ZrO ₂	118°	2.35	1.26*	0.27	426.7	4.96	550.3	Ar + H ₂
	$\alpha\text{-Al}_2\text{O}_3(0001)$	115°		1.36*	0.30			558.6	Ar + H ₂
		113°		1.53*	0.30				Ar + H ₂

Table 1 (Contd.)

Liquid metal drops									
Metal	Oxide	Apparent θ_{contact}	$\gamma_{\text{M}}/(\text{J m}^{-2})$	$E_{\text{adh}}/(\text{J m}^{-2})$	$E_{\text{adh}}/2\gamma_{\text{M}}$	$\Delta H_{\text{sub,M}}/(\text{kJ mol}^{-1})$	$\Omega_{\text{M}}^{2/3}/(\text{\AA}^2)$	$-\Delta H_{\text{f,OxSup}}/(\text{kJ (mol O)}^{-1})$	Atmosphere
Ni	CoO	70°		3.18*	0.68			237.9	Ar
	CaO	135°	2.38	0.697*	0.15	430.1	4.93	634.9	—
	MgO	132°		0.788*	0.17			601.6	Vacuum
	BeO	127°		0.965*	0.20			609.4	He
	SiO ₂	125°		1.02*	0.21			455.4	Vacuum
	ZrO ₂	121°		1.16*	0.24			550.3	Ar + H ₂
	UO ₂	112°		1.49*	0.31			542.5	Ar
	α -Al ₂ O ₃ (0001)	111°		1.52*	0.32			558.6	Ar + H ₂
		109°		1.61*	0.34				Vacuum, Ar, He, H ₂ , Ar + H ₂
	TiO ₂	105°		1.76*	0.37			472.0	Vacuum
Pt	NiO	60°		3.57*	0.75			244.3	—
	CoO	58°		3.64*	0.76			237.9	Ar
	α -Al ₂ O ₃ (0001)	98°	1.70	2.16*	0.43	565.7	6.10	558.6	Vacuum
Solid metal particles									
Metal	Oxide	Apparent θ_{contact}	$\gamma_{\text{M}}/(\text{J m}^{-2})$	$E_{\text{adh}}/(\text{J m}^{-2})$	$E_{\text{adh}}/2\gamma_{\text{M}}$	$\Delta H_{\text{sub,M}}/(\text{kJ mol}^{-1})$	$\Omega_{\text{M}}^{2/3}/(\text{\AA}^2)$	$-\Delta H_{\text{f,OxSup}}/(\text{kJ (mol O)}^{-1})$	Atmosphere
Ag	α -Al ₂ O ₃ (0001)	125°	1.22	0.51 ± 0.07	0.21	284.9	6.63	558.6	—
Au	α -Al ₂ O ₃ (0001)	125°	1.51	0.63 ± 0.09	0.21	368.2	6.60	558.6	—
Cu	α -Al ₂ O ₃ (0001)	131°	1.79	0.61 ± 0.11	0.17	337.4	5.18	558.6	—
Ni	α -Al ₂ O ₃ (0001)	130°	2.38	0.84 ± 0.09	0.18	430.1	4.93	558.6	—
Fe	α -Al ₂ O ₃ (0001)	124°	2.42	1.06 ± 0.17	0.22	415.5	5.18	558.6	—

Table 2 Adhesion energies of solid metals measured on clean oxide surfaces under ultrahigh vacuum conditions. Methods used are based either on the particle shape (HRTEM and GISAXS) or on the integral heat of adsorption of metal vapor at multilayer coverage (SCAC and TPD). All data are from the citations listed, but the values marked with an asterisk have been recalculated based on newer values for the surface energies of the pure metals reported in ref. 102. Also listed is the heat of formation of the most stable bulk oxide of that metal (per mole of metal atoms), $\Delta H_{f,MOx}$. Metals are ordered by their bulk heat of sublimation divided by the area per metal atom. (Table 1 lists these values.)

Metal	Oxide	Particle size/nm	Apparent θ_{contact}	$E_{\text{adh}}/(\text{J m}^{-2})$	$E_{\text{adh}}/2\gamma_{\text{v/m}}$	$\Delta H_{f,MOx}/(\text{kJ (mol M)}^{-1})$	Method	Citation
Pb	MgO(100)	10 + (4.75 ML)	72°	$0.57 \pm 0.20^*$	0.65	-219	SCAC	104
Ag	MgO(100)	6.6	$150 \pm 30^\circ$	0.30 ± 0.30	0.12	-15.1	SCAC	105
	$\alpha\text{-Al}_2\text{O}_3(0001)$ or $\gamma\text{-Al}_2\text{O}_3(111)$	—	$>70.8^\circ$	<1.6	<0.66		TPD	106
	CeO _{1.9} (111)	3.6	90°	2.3 ± 0.3	0.94		SCAC	95
	CeO _{1.8} (111)	3.6	90°	2.5 ± 0.3	1.0		SCAC	95
	Fe ₃ O ₄ (111)	3.6	90°	2.5 ± 0.3	1.0		SCAC	107
Au	MgO(100)	1-5	124°	0.67*	0.22	9.65	HRTEM	108
	TiO ₂ (110)	2-8	$130 \pm 5^\circ$	$0.54 \pm 0.10^*$	0.18 ± 0.03		GISAXS	159
	TiO ₂ (110)	>4	$122 \pm 5^\circ$	$0.71 \pm 0.11^*$	0.24 ± 0.04		HRSEM	160
	TiO ₂ (001)	—	$>79.1^\circ$	<1.8	<0.58		TPD	106
	Disordered SiO ₂	—	$>72.8^\circ$	<2.0	<0.65		TPD	106
Pd	MgO(100)	10-15	116°	1.11*	0.28	-85.4	HRTEM	109
		2-8	109°	1.34*	0.34		GISAXS	110
	Disordered SiO ₂	—	$>65.8^\circ$	<2.8	<0.70		TPD	106
Cu	MgO(100)	10 + (7 ML)	41°	1.92 ± 0.60	0.55	-168.2	SCAC	111
	Disordered SiO ₂	—	$>71.4^\circ$	<2.3	<0.65		TPD	106
	$\alpha\text{-Al}_2\text{O}_3(0001)$ or $\gamma\text{-Al}_2\text{O}_3(111)$	—	$>62.4^\circ$	<2.6	<0.74		TPD	106
Pt	MgO(100)	1-5	113°	1.51*	0.30	-54.3	GISAXS	112

Combining the adhesion energy data in Tables 1 and 2 reveals several important trends. As shown in Fig. 1, the adhesion energies for different metals on a given oxide (in this case $\alpha\text{-Al}_2\text{O}_3(0001)$) increase nearly linearly with the surface energy of the metal, and with its sublimation energy ($\Delta H_{\text{sub,M}}$) divided by the area per metal atom (approximated here as the atomic volume of the bulk metal, Ω_{M} , to the $2/3$ power). The adhesion energies for molten metal drops are larger than for solid particles by 50 to 100%, but both follow the same trend. We can summarize the results for solids in Fig. 1b by the relationship:

$$E_{\text{adh}} = m[(\Delta H_{\text{sub,M}}/N_{\text{A}})/\Omega_{\text{M}}^{2/3}] + b, \quad (4)$$

where N_{A} is Avogadro's number. The slope and y-intercept for $\alpha\text{-Al}_2\text{O}_3(0001)$ are $m = 0.15$ and $b = -0.43 \text{ J m}^{-2}$, respectively.

The trends in Fig. 1 can be easily explained as follows. Both the heat of sublimation and the surface energy of a metal reflect the strength of metal-metal bonding in that pure bulk metal. The same electronic properties that determine the strength with

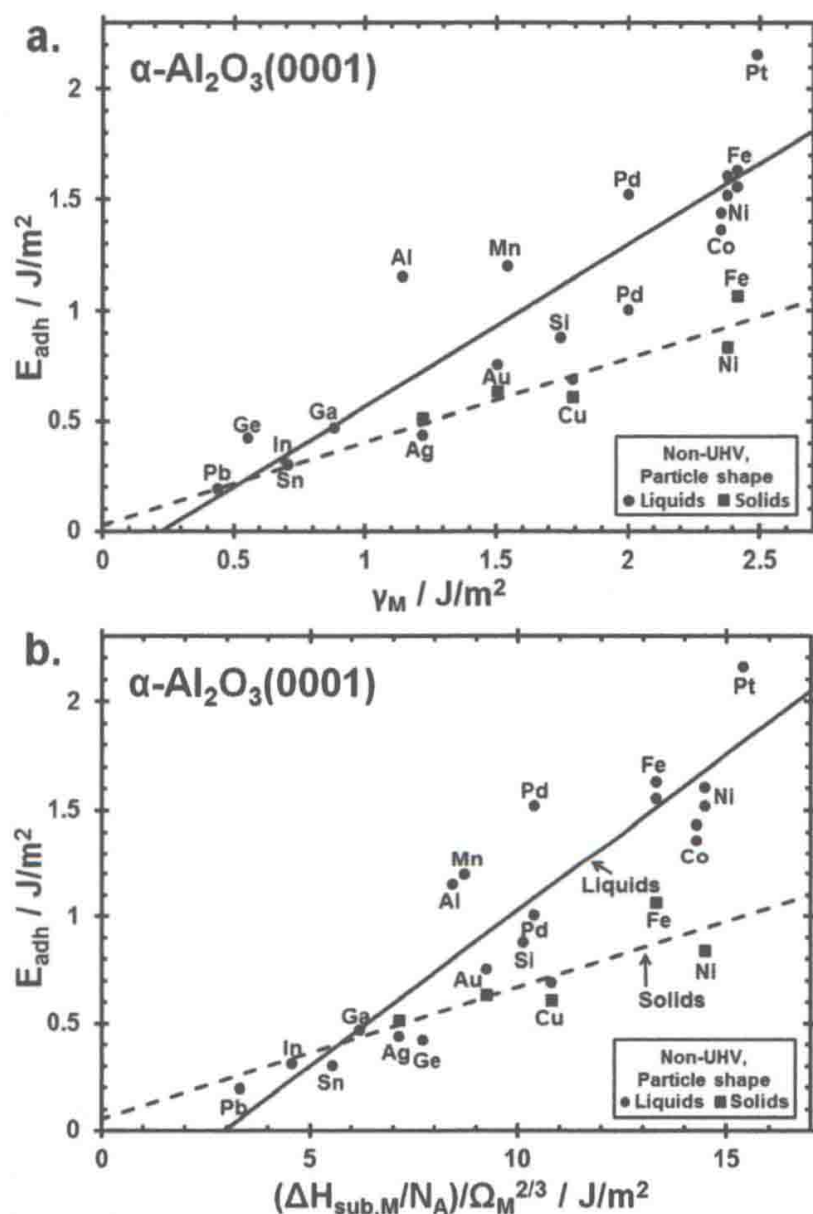


Fig. 1 Adhesion energies of different metals on $\alpha\text{-Al}_2\text{O}_3(0001)$ plotted *versus* the surface energy of the metal (a) and *versus* the bulk metal's sublimation enthalpy per atom ($\Delta H_{\text{sub,M}}/N_{\text{A}}$) divided by the area per metal atom ($\Omega_{\text{M}}^{2/3}$) (b). Black points are based on measurements of particle shapes for molten metal drops (round) and solid particles (squares) without verification of surface cleanliness, from Table 1. Lines through the subsets of data are the best linear fits.