

Preparation of Metallic Powders and Alloys in Polyol Media: A Thermodynamic Approach

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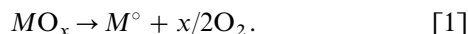
Through simple thermodynamic considerations, the metal oxides reduction reaction in polyol medium (ethylene glycol) has been addressed with the assumptions that the reaction takes place at the boiling point of the alcohol, and that the polyol is totally oxidized with formation of CO₂ and H₂O. By considering the initial (MO_x+ethylene glycol) and final (M+CO₂+H₂O) states, we estimated the Gibbs free energies (ΔG_{red}) for the reduction of numerous oxides, and found a good correlation with the experimental results. Without any exception, oxides leading to metallic powder when reacted in boiling polyol medium have a negative calculated ΔG_{red} . However, a few oxides with negative calculated ΔG_{red} could not be reduced to metal, likely for kinetics limitations and/or solubility issues. This strategy has been extended with similar success to both hydroxide precursors and other alcohols having longer backbones (e.g., glycerol). Finally, we show that this basic thermodynamic approach opens new insights for the synthesis of alloys, obviously represents a useful prediction tool for the preparation of metals, and could be easily extended to the preparation of oxides. © 2000 Academic Press

Key Words: Gibbs free energy; polyol process; metal powder; alloys; oxides.

Although much less investigated, the preparation of powdered metallic Cd, Ir, Bi, Pb, Rh, Ru, Os, and Se in alcoholic medium has also been reported (1, 13, 18, 20). The polyol medium composition itself, the reaction temperature, the nature of the precursors, the use of additives (surfactants, foreign nuclei), the pH of the medium, and the reaction time are some of the parameters that can be separately or simultaneously adjusted, depending on the system and on the desired characteristics of the final product.

Despite an impressive number of studies devoted to this synthetic route it still remains highly empirical, and to our knowledge, no successful approach has been proposed in order to theoretically understand the accumulated sum of experimental findings or to predict its potentialities. However, recent accurate electrochemical investigations, mainly based on the study of the redox potentials in alcoholic medium, successfully gave rise to a better fundamental understanding of the reduction mechanism for the preparation of noble metal (Au, Pt, Pd, and Ag) (10).

Even some basic chemical aspects of the reaction process are seldom studied and not well understood. The reduction of an oxide MO_x to the metal M⁰ can be expressed as



INTRODUCTION

Besides the various physical and chemical methods commonly used for the preparation of metallic powders (e.g., atomization, electrolysis, reduction by hydrogen or hydride), the polyol process presents large advantages. It consists of the reduction in a liquid alcohol medium, at moderate temperatures, of metallic compounds such as oxides, hydroxides, and salts. The organic liquid (e.g., ethylene glycol, glycerol, diethylene glycol) acts as a reducing and dissolving medium. This method enables an accurate control of the size distribution and shape of the particles from the micrometric to the colloidal scale. Over the past two decades, the polyol process has been largely studied and well adapted to the preparation of divided powders such as Co, Ni, Cu, Ag, Au, Pt, and Pd (1–10) and also to the synthesis of binary alloys (Co–Ni, Ag–Pd, Au–Pt) (9, 11, 12).

When this reaction is performed in an alcohol medium, an oxidation of the polyol does occur at the same time. Although the chain products for a moderated oxidation of ethylene glycol have been well known for more than a century (14) (glycoaldehyde, glyoxal, glycolic acid, glyoxylic acid, oxalic acid, formic acid, and CO₂), the nature of the product(s) formed in the course of such metal-precursor reduction has been the subject of a few investigations.

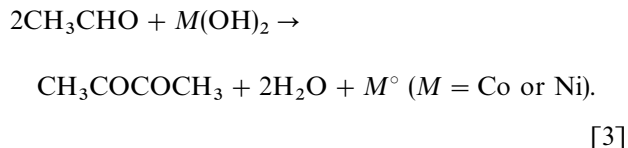
For the reduction by ethylene glycol of Ni(OH)₂ or Co(OH)₂ into metallic Ni or Co, acetaldehyde and diacetyl have been detected as the main products of degradation (15). None of these compounds appear in the above-listed organics, first clue to a distinct mechanism. A close comparison between the phases present in the solid and the nature of the organic compounds simultaneously formed in the liquid



leads to the conclusion that the degradation of ethylene glycol (EG) takes place in two steps. The first one is a dehydration of EG giving rise to acetaldehyde:



The second is a duplicative oxidation of the acetaldehyde with formation of diacetyl. This transformation was found to take place at the same time as the formation of metallic powder:



When dealing with the Ag formation from easily reducible AgNO_3 , the products of a moderated oxidation are identified together with methanol and acetic acid, indicating a different oxidative process (11, 15). As illustrated from these two examples, no general scheme of EG oxidation can be drawn, thus the need to consider specific reaction paths driven by energetic and thermodynamic characteristics of the $\text{MO}_x \rightarrow M^\circ + x/2\text{O}_2$ reaction.

In this paper we propose a simple thermodynamic approach mainly devoted to the preparation of metallic powders from oxide and hydroxide precursors treated in boiling alcohols. Through this study we assumed that the reduction of the precursor into metal comes with a total oxidation of EG into CO_2 and H_2O , this situation corresponding to the maximum reducing power of the alcohol. These theoretical results are compared to experimental observations, and further punctually extended to varied temperatures and other polyols.

EXPERIMENTAL

Typical reactions are done as follows. In a glass vessel, the precursor (1 to 5 g) is suspended in 200 ml of polyol under constant magnetic stirring, and heated up to the boiling point under reflux. The heating rate is fixed to $1-2^\circ\text{C}/\text{min}$ and the temperature is electronically regulated. Reactions are always performed under air. Intermediate withdrawals (5 ml) are performed in the course of the heating and while the boiling point is reached. The withdrawn suspensions are rapidly cooled down to room temperature, washed several times with acetone and/or water, centrifuged, and dried at 50°C for a few hours. The resulting powders are characterized by X-ray diffraction on a Philips PW 1729 apparatus ($\text{CuK}\alpha$: 1.5418 \AA) equipped with a back monochromator. The reaction is pursued until crystallized metal powder is detected or maintained for a maximum period of one week. All the precursors and alcohols used are reagent grades

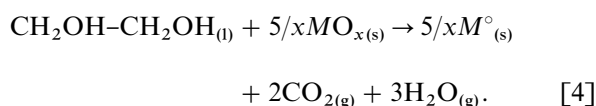
(purity > 99%). $\text{Fe}(\text{OH})_3$ was prepared by progressive addition of a M KOH solution to a $M/10$ FeCl_3 aqueous solution at 25°C as described in (16). Fine $\text{Mn}(\text{OH})_2$ powder was prepared as described in (17) and kept under inert Ar atmosphere until used. After one week of reaction, the final product was also characterized by means of X-rays diffraction.

In this paper, we compiled our experimental results with others well documented in the literature (1-13, 18-21).

RESULTS AND DISCUSSION

Pure Metals

The overall reduction reaction of metal oxides in boiling EG can be written as



The Gibbs free energies of formation of $\text{CO}_{2(g)}$, $\text{MO}_{x(s)}$, $\text{H}_2\text{O}_{(g)}$, and $\text{EG}_{(l)}$ at 200°C can be either found or easily calculated from the data in these references (22-29). The ΔG_f for M° is taken to be zero at any temperature. When different crystallographic modifications were reported, only one stable oxide was considered (e.g., $\alpha\text{-Fe}_2\text{O}_3$, red $\alpha\text{-PbO}$, anatase TiO_2). Due to the azeotropic behavior of the polyol-water systems, we could have also assumed that water, near the EG boiling point, was primarily formed in liquid state, and progressively evacuated from the medium through vaporization. Nevertheless, we found that considering the formation of either liquid or gaseous water resulted in only small deviations in the overall ΔG_{red} calculated as

$$\Delta G_{\text{red}} = 2\Delta G_f(\text{CO}_2) + 3\Delta G_f(\text{H}_2\text{O}) - 5/x\Delta G_f(\text{MO}_x) - \Delta G_f(\text{EG}).$$

As an example, we estimated the ΔG_{red} of NiO ($x = 1$) at 200°C to be equal to -55 kcal/mol from $\Delta G_f(\text{H}_2\text{O}) = -53 \text{ kcal/mol}$, $\Delta G_f(\text{CO}_2) = -94 \text{ kcal/mol}$, $\Delta G_f(\text{NiO}) = -46 \text{ kcal/mol}$, and $\Delta G_f(\text{EG}) = -62 \text{ kcal/mol}$. We experimentally verified that NiO was reduced to Ni° in EG at boiling point. In Fig. 1 are reported the calculated ΔG_{red} values for various oxides. The vertical bars indicate the ranges of the ΔG_{red} values, taking into account the discrepancies in thermodynamics values listed in the literature for the various ΔG_f values. The shadowed labels correspond to oxides that have not been successfully reduced to metal in EG at boiling point. From this graph, it can be clearly observed that none of the oxides with $\Delta G_{\text{red}} > 0$ is reducible according to our experimental conditions. In contrast, all the oxides experimentally reduced to metal (not shadowed in Fig. 1) show a negative ΔG_f . It is necessary to keep in

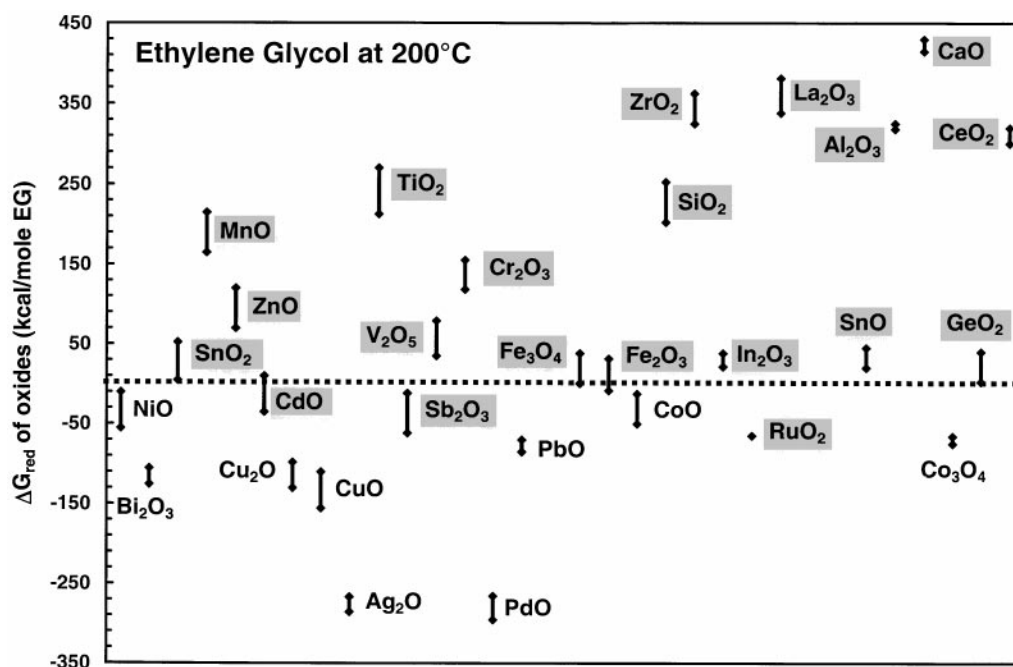


FIG. 1. Calculated ΔG of reduction (ΔG_{red}) by ethylene glycol at 200°C for various oxides assuming a total oxidation of the alcohol and the formation of the metal according to reaction [4]. The shadowed and nonshadowed labels indicate experimentally nonreduced and reduced oxides, respectively.

mind that these calculations have been performed assuming a total oxidation of EG (i.e., formation of CO_2). Practically, this reaction path could be invalid. Nevertheless, any intermediate oxidation product of EG would correspond to a lower reduction power of the alcohol. Therefore, if the reduction of an oxide does not theoretically occur with our extreme computational assumptions, there are no chances for it to occur under milder conditions of EG oxidation.

Note in Fig. 1 that three oxides (CdO , Sb_2O_3 , and RuO_2) do not lead to metallic powder, although their ΔG_{red} values are close to those calculated for NiO (CdO , Sb_2O_3) or even more negative (RuO_2). Experimentally, CdO is unmodified when reacted in boiling EG, Sb_2O_3 dissolves totally without any subsequent precipitation, and RuO_2 is partially reduced into RuO_x . In order to provide some insights on this point, specific aspects of the reactivity of oxides in alcohols must be kept in mind. The formation of the metal generally comes with the formation of intermediate reactive phases, such as reduced oxides and/or alkoxides (see Fig. 2). For example, the formation of Cu from CuO is known to be a multistep reaction involving the formation of Cu_2O and Cu-based alkoxide intermediates (5). When the metal is initially at its lowest stable oxidation state, the formation of intermediate reduced oxide is bypassed and the initial oxide dissolves. Then the metal is formed either directly (e.g., Ag_2O , PdO , Cu_2O) or after the precipitation of alkoxide (e.g., PbO , NiO , CoO). When the metal is not finally obtained, we observe either no modification of the precursor (e.g., TiO_2 , In_2O_3 ,

SiO_2) only a partial reduction (e.g., $\text{RuO}_2 \rightarrow \text{RuO}_x$), or precipitation of alkoxides. This last step can be direct (e.g., MnO , SnO) or be preceded by a partial reduction (e.g., $\text{MnO}_2 \rightarrow \text{MnO}_x \rightarrow \text{Mn-alkoxide}$). The solid state reduction of oxide under the effect of alcohol is generally accompanied by the insertion of cations (30), and will be studied further in a forthcoming paper (31). All these reaction paths are summarized in Fig. 2. From this graph and the above detailed examples, it is obvious that each reaction step could be slowed down or even blocked by solubility and/or kinetics

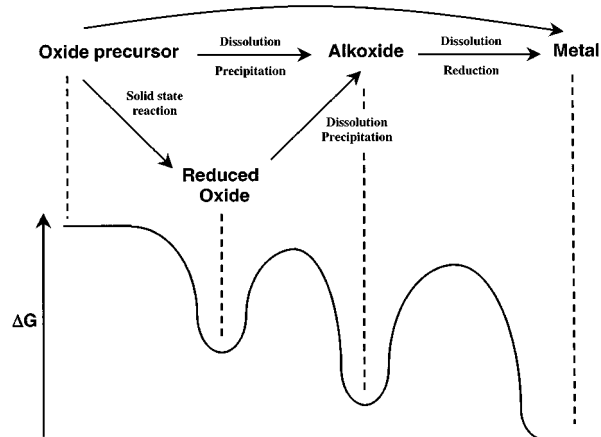


FIG. 2. Reaction steps and intermediate phases observable during the reaction of various oxides in EG.

issues. We believe that the nonformation of metallic Ru, Cd, and Sb from their oxides could originate from these limitations. Likely, each scenario is specific to each oxide, and cumulated limitations can be envisaged. Nevertheless, the existence of these intermediates along the path of the reaction does not make invalid the calculation of ΔG_{red} for the overall reaction since we only considered the initial and final states. In order to be perfectly consistent with our assumptions, we should have performed our experiments by directly adding the precursor into boiling EG, thus bypassing the slow heating step. Actually, we observed that this procedure could occasionally prevent, to some extent, the formation of stable intermediate phases, and therefore minimize the kinetics limitations. It is also worth pointing out that metallic cationic species and metal powder can act as catalysts onto some reactions of transformation of organic compounds. Some EG-based alkoxides (Ni, Co, Mn, V) have already been thoroughly studied and characterized (17, 32–36).

Our present thermodynamic approach raises now the question of whether it is possible to modify some synthetic parameters in order to push down the ΔG_{red} below 0, *sine qua non* thermodynamic condition to possibly observe the formation of metal. Since the values of ΔG_f for H_2O , CO_2 , EG and oxides are dependent on the temperature, we first studied the effect of this parameter. In Fig. 3 is plotted the evolution of ΔG_{red} for Fe_2O_3 and ZnO as a function of the reaction temperature. EG is supposed to remain liquid within the whole scanned thermal range. Only two examples are shown to convey the message since similar trends/slopes were observed for other oxides. We selected Fe_2O_3 because it has the smallest mean ΔG_{red} value, and is therefore the best candidate to be made reducible. Obviously the ΔG_{red} values slowly decrease as the temperature increases. For Fe_2O_3 , a temperature of about 850 K (not achievable by

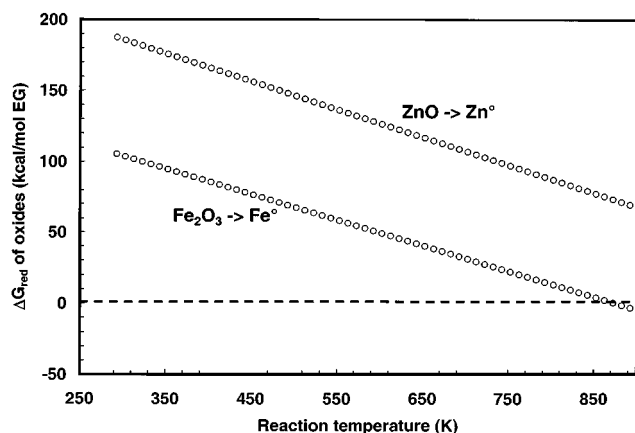
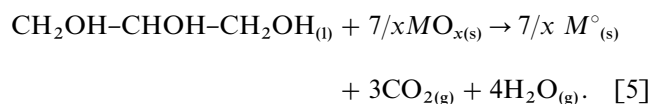


FIG. 3. Evolution of the ΔG_{red} by ethylene glycol for Fe_2O_3 and ZnO as a function of the temperature. Ethylene glycol is considered liquid in the whole temperature range.

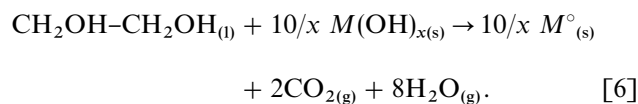
solution chemistry) is necessary to force ΔG_{red} to cross the zero line and become negative, and a much higher temperature is even required in the case of ZnO . Practically, the treatment of EG at boiling point in an autoclave device resulted in the degradation of the alcohol and the formation of tar even at moderate pressure, making so far any practical verification of our calculation impossible.

In a second step, we modified the nature of the polyol and embarked on similar calculations as performed for EG. The reaction of reduction by glycerol is written as



The results obtained for the reduction of the oxides in this medium at boiling point (290°C) are shown in Fig. 4. The ΔG_f of glycerol is taken equal to -77 kcal/mol at 290°C . We observed that the relative ΔG_{red} values are not drastically modified when compared to the results shown in Fig. 1 (EG at 200°C). From these two sets of calculations, none of the theoretically nonreducible oxides in EG at 200°C appears to be clearly reducible in glycerol at 290°C . The same symbolism has been used in both graphs to indicate the experimental results (shadowed oxides when the metal is not obtained). Again, a perfect agreement is observed with the experiment, a positive ΔG_{red} never leading to metallic powder. As already observed for EG, some oxides are not reduced despite negative ΔG_{red} values (PbO , CdO , CoO , and RuO_2) but here Sb is obtained from Sb_2O_3 . Similarly to EG, solubility and/or kinetics limitations can also be proposed to explain these apparent deviations. As reactive intermediates or final products, numerous glycerol-based alkoxides have indeed been detected throughout this study, most of them having been intensely studied over the past decades (18–21, 37).

In a last attempt, we checked the effect of the nature of the precursors by using hydroxides in place of oxides. For such a change, we assumed that the reaction of direct reduction in EG proceeds as in



Here, two situations can be encountered: hydroxides either are stable upon heating or dehydrate to form oxides, and we then fall into the already investigated situation. For examples, $\text{Zn}(\text{OH})_2$ dehydrates to ZnO at 125°C and $\text{Cu}(\text{OH})_2$ dehydrates to CuO at 160°C .

Results of the computation for hydroxides are shown in Fig. 5. Here again, we observe that a negative ΔG_{red} experimentally comes with the formation of the metal (Cu, Ni, Co, Cd), although a positive value of ΔG_{red} does not (Mn, Mg,

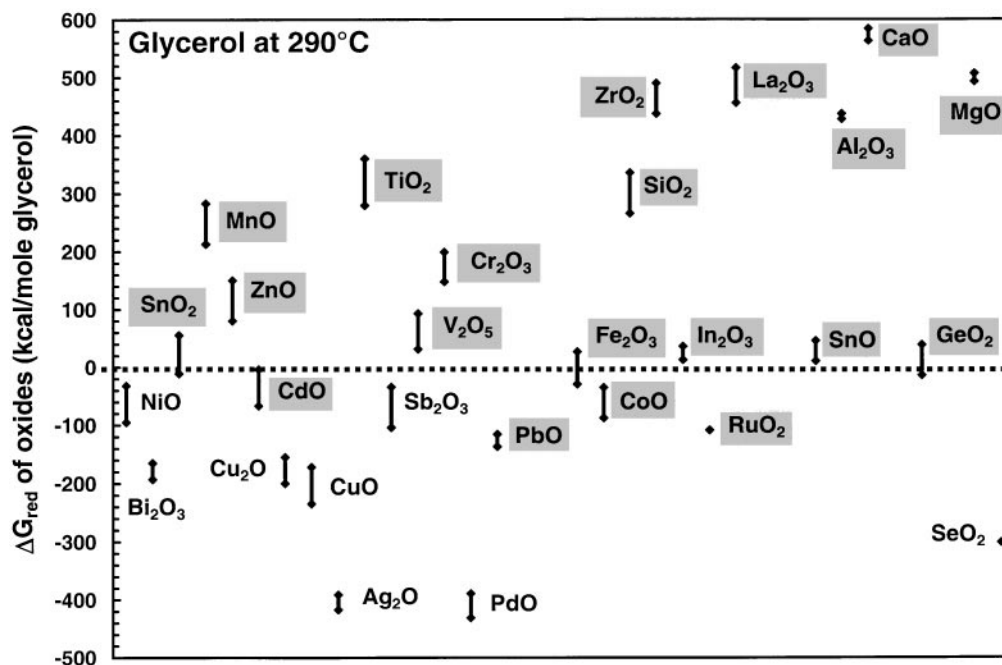


FIG. 4. Calculated ΔG of reduction (ΔG_{red}) by glycerol at 290°C for various oxides assuming a total oxidation of the alcohol and the formation of the metal according to reaction [5]. The shadowed and nonshadowed labels indicate the experimentally nonreduced and reduced oxides, respectively.

Ca, Al, alkaline metals). For unstable hydroxides (Zn, Cu) we evaluated ΔG_{red} at the decomposition (dehydration) temperature. An unexpected prediction of this calculation is the

possible formation of Fe from iron hydroxide $Fe(OH)_3$. Starting from oxides, we already showed that iron is not formed, consistent with the calculation. In order to confirm

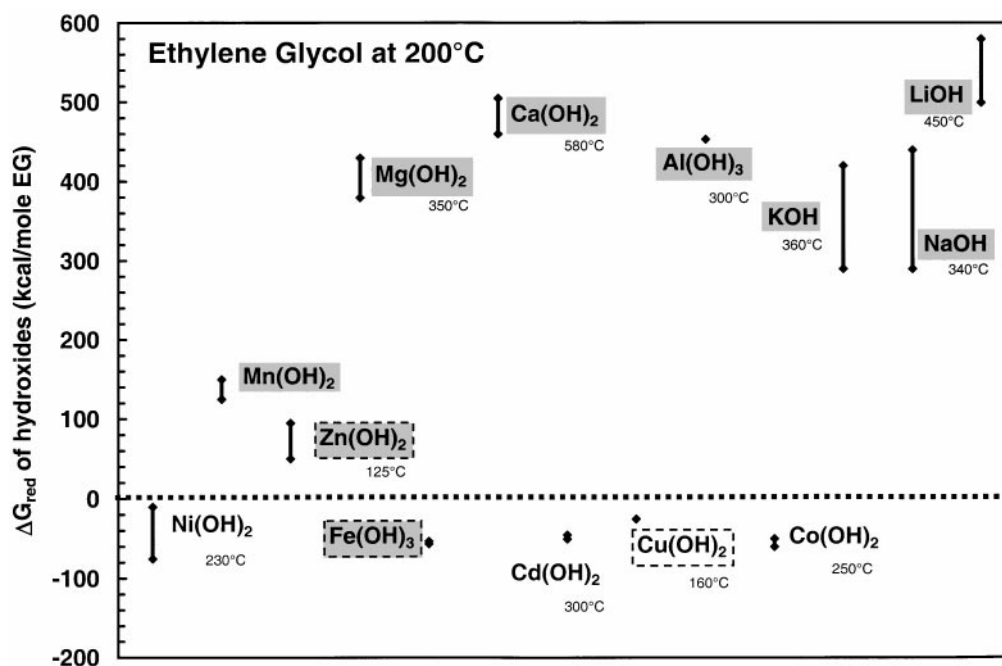


FIG. 5. Calculated ΔG of reduction (ΔG_{red}) by ethylene glycol at 200°C for various hydroxides assuming a total oxidation of the alcohol and the formation of the metal according to reaction [6]. The shadowed and nonshadowed labels indicate experimentally nonreduced and reduced hydroxides, respectively. Dashed frames indicate unstable hydroxides. $Zn(OH)_2$ and $Cu(OH)_2$ dehydrate below 200°C to form ZnO and CuO , respectively. When well documented, the dehydration temperatures are indicated.

this point, we treated in boiling EG freshly prepared powdered Fe^{III} hydroxide. Finally, this resulted in the formation of insoluble Fe-alkoxides without any trace of metallic iron. We observed that small variations in the preparation/aging of this precursor or in the conduction of the reaction in EG resulted in very different final products such as various iron oxides and alkoxides. Due to intrinsic instability, these results are not surprising. Indeed, iron hydroxide is prone to readily transform into stable oxides and/or oxyhydroxides upon soft heating and depending on numerous experimental parameters.

Alloys

Intuitively, one can believe that the formation of any *A-B* alloy by reduction of precursors in polyol medium automatically implies that each precursor could be separately reduced to form the metal. So far, this has been practically demonstrated for systems such as Co-Ni, Ag-Pd, and Au-Pt (9, 11, 12). To obtain such alloys, the preparation conditions must be carefully optimized in order to adjust the kinetics of reduction of both constituents. If observed, the direct formation of an alloy is therefore thermodynamically more favorable than the separate formation of the constituting metals. Following this hypothesis, it would be theoretically possible to prepare a bimetallic alloy starting from two precursors, one *individually* leading to metal and the other not. This is schematically depicted in Fig. 6. Presently, none of our attempts to prepare such alloys in EG have been successful (e.g., Ag-Sn, Ag-Zn, Cu-Zn, Cu-Sn, Cu-Ge).

The addition of a strong reducing agent (e.g., NaBH_4) to an aqueous solution of metallic salts can be used as an alternative route for the preparation of bimetallic alloys (e.g., SnSb) under mild temperature conditions (38). To overcome the apparent impossibility of preparing certain alloys in pure boiling EG, Viau *et al.* (39, 40) recently

showed that Fe-based alloys (Fe-Co, Fe-Ni, and Fe-Co-Ni) can be prepared from Fe^{II} salt-containing highly alkaline EG solution. The proposed mechanism resides in the ability of Fe^{II} to undergo in such hot alkaline medium a disproportionation reaction leading to $\text{Fe}^\circ + \text{Fe}_3\text{O}_4$. Note that here EG is not supposed to play any role in the iron reduction process.

Given the large number of metals that can be prepared in polyol media (Ni, Bi, Cu, Ag, Pd, Pb, Co, Sb, Ir, Os, Pt, Au, Rh, Ru, Se) and the numerous solid solutions and line phases reported in binary systems comprising two of these elements, it is quite surprising that only a few alloys were successfully synthesized (Co-Ni, Ag-Pd, and Au-Pt). Numerous works have been aimed at preparing other alloys (e.g., Co-Cu, Pd-Ni, Pd-Cu) but systematically resulted in biphasic nanocomposite materials (41-45). As suggested in Refs. (42, 44, 45) for Pd-Cu and Pd-Ni systems, the reduction of Cu/Ni species is taking place at the surface of the growing Pd particles, which then act as *in situ* formed nuclei. In such a situation, the formation of bimetallic nanocomposites instead of alloys is therefore a direct consequence of a difference in reduction kinetics.

Actually, a close examination of Figs. 1 and 5 shows very close values of ΔG_{red} for sets of oxides/hydroxides experimentally leading to alloys. This is the case for Co-Ni (from $\text{Ni}(\text{OH})_2 + \text{Co}(\text{OH})_2$) and Ag-Pd (from $\text{Ag}_2\text{O} + \text{PdO}$) prepared in EG. No reliable thermodynamics values for gold and platinum precursors are available, but it is well known that they are highly reducible. Intuitively, this tends to mean that the formation of bimetallic compounds would require that the precursors be reduced at close potential, that is to say, following EG similar oxidation path. Consistently, it has been shown that the degradation products of EG when used to reduce $\text{Ni}(\text{OH})_2$ and $\text{Co}(\text{OH})_2$ are identical, but very different from those detected for the reduction of copper or silver (2, 3, 11, 15). Naturally, such speculation must be carefully confirmed by additional examples, and numerous other binary and multinary systems are being presently explored.

CONCLUSION

The preparation of metallic powders and alloys has been theoretically investigated by simple thermodynamic calculations and basic assumptions. The results of calculations confirmed numerous well-documented experimental observations as well as original reactions. However, depending on the polyol used, a few oxides have never been reduced, although the formation of the metal was found to be thermodynamically feasible. Kinetics and/or solubility limitations of the initial compound and/or the intermediate phases can be invoked to explain these findings. Preliminary investigations show that similar computations can be successfully applied to various other systems such as the

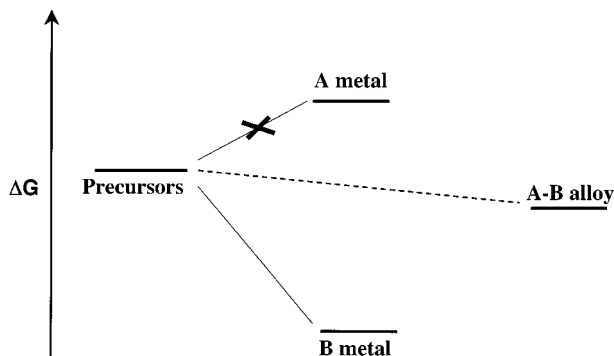


FIG. 6. Schematic representation of the energetically favorable formation of a bimetallic alloy compared to the independent formation of metals from their respective precursors.

preparation of metallic alloys and nitrides from sulfides ($\text{TiS}_2 \rightarrow \text{TiN}$), or the partial reduction of oxides ($\text{MoO}_3 \rightarrow \text{MoO}_2$) in reducing media.

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