REGULAR ARTICLE

Elucidation of the oxidation-reduction reactions in the synthesis of Co-based nanoparticles through polyol process using 1, 2-butanediol (BEG): a theoretical study

KHOULOU MRAD^{a,b,c}, NOURA KHEMIRI^a, FRÉDÉRIC SCHOENSTEIN^b,
SILVANA MERCONE^b, MHAMED BEN MESSAOUDA^a, MANEF ABDERRABBA^a and
SABRI MESSAOUDI^{a,c,*}

^aLMMA, IPEST, University of Carthage, Route Sidi Bou Said, B.P. 51, 2075 La Marsa, Tunis, Tunisia

^bLSPM, CNRS UPR 3407, University Paris 13, 99 Avenue J.-B. Clément, 93430 Villetaneuse, France

^cFSB, Faculty of Science of Bizerte, University of Carthage, 7021 Zarzouna, Bizerte, Tunisia

E-mail: sabri_messaoudi@yahoo.fr

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Abstract. The role of BEG 1,2-butanediol as a reducing agent in Co-based nanoparticle synthesis in the polyol process has not been well-detailed yet. So, we focused on the determination of the main active species derived from 1,2-butanediol (BEG) in Co-based nanoparticle synthesis and their reducing abilities through density functional theory (DFT) calculations. In the reaction medium, BEG is deprotonated by the hydroxyl ions introduced in the solution then oxidized by the metal ions. The progression of reduction and dissociation reactions of metal ions is relatively related to the reducing ability of polyols. Three species which are: dianion, monoanion and neutral molecule of BEG were considered in our investigation. The highest occupied orbital energy was estimated for the different configurations. Considering the experimental and theoretical studies, the monoanion state was suggested as the most active form. A comparative study was carried out between three polyols: BEG, PEG (1, 2-propanediol) and EG (Ethylen glycol), which are the most used solvents in Co-based nanoparticle synthesis. We showed that the highest occupied orbital energy of BEG monoanion state is relatively high compared to PEG and EG ones. Thus, BEG could reduce metal ions more easily by giving its electrons and its use can make the reaction kinetics faster.

Keywords. Co-based nanoparticles; polyols; BEG; oxidation; density functional calculations; active species; reducing ability.

1. Introduction

The synthesis of inorganic nanowires has been the focus of scientific studies for decades, thanks to their tremendous applications in electronics, magnetism and sensors.¹ It has been shown that one-dimensional (1D) nanostructures such as wires, rods, belts and tubes of metallic and alloy materials have significantly different physical properties from their bulk counterparts due to size confinement.² Various strategies have been used to generate nano-sized metallic materials, some techniques are based on the vapor phase, while others are based on the liquid phase. Chemical methods in solution have been considered to be more versatile and adequate to synthesize these nanowires. Among them, two methods have been widely used to prepare metallic

nanoparticles: organometallic pathway and polyol process.¹ The organometallic approach includes the use of organometallic complexes as sources of metal atoms in a non-polar solvent such as hydrogen gas and also as a reducing agent. Several advantages like well-controlled size distributions, chemical composition and shape have been achieved. Nevertheless, this method is less used due to the sensitivity of the reaction that demands an inert atmosphere for the metal precursor manipulation.³ On the other hand, the synthesis in polyol medium has been mainly used for the synthesis of transition metals and their alloys. It has been used the first time for the preparation of submicronic and micron particles of 3d element (Fe, Ni, Co).⁴ Then it has been developed with Ung in 2007⁵ and Saumare in 2009⁶ for the synthesis of one-dimensional particles of CoNi and Co. In a previous study, secondary reducing agents like hydrazine and

*For correspondence

noble metals like Pt and Ru have been used.⁷ Furthermore, the preparation of Fe nanoparticles in the polyol solvent has been considered difficult, only disproportionation iron (II) hydroxide has been observed previously.⁸ Then, the role of polyol has been limited to prevent undesirable oxidation reactions. In a recent study, Josephus *et al.*,⁹ showed that the reduction of iron (II) is possible through the polyol process. The size and the oxide fraction of Fe nanoparticles are influenced by the variation of the nature of polyol and the magnetic properties depended on the reduction ability of polyols. They supposed that conversely the reaction mechanism in the polyol is by reducing and not through disproportionation.⁹ In the case of less easily reducible metals like silver,¹⁰ nickel and copper,^{11,12} the formation of nanoparticles is possible by a reduction in polyol medium.

The potential of the polyol process lies in reduction ability, polarity and the high boiling points of organic solvent.¹³ In order to exploit the potential of this method, an understanding of the reaction schemes including the reduction of metal ions in polyol medium and the oxidation of this polyol in the presence of sodium hydroxide is crucial. Actually, polyols are well-known as polar protic solvents and as very weak acids because their basic forms are stabilized by the inducing effect of their two alcohol functions. Thus, it is interesting to study the influence of the polyol choice on the reaction kinetics and the growth mechanisms. Several hypotheses could be formulated to evaluate this influence, such as the differences in the reducing properties of these polyols.

The use of sodium hydroxide NaOH could further enhance the reaction kinetics by facilitating the oxidation acceleration of polyols and the formation of acetaldehyde as discussed earlier.^{9,12,13} The excess of OH⁻ could reduce the reduction potential and the growth rate.^{9,13} The sodium hydroxide is used to adjust the solubility of the solid intermediate phase, to accurately control the metallic concentration and to promote the reaction by oxidizing the polyol.⁶

In the literature, some studies have been devoted to explain the oxidation reaction in ethylene glycol EG.^{11,12,14} Only one study has been reported by Matsumoto *et al.*, to determine the active species of ethylene glycol (EG) through theoretical and experimental studies. They detailed the reduction and the dissolution of Cobalt ions in the polyol process using EG. Since EG is the most used polyol for the synthesis of transitions as well as noble metals,¹² the authors showed through theoretical estimations that the monoanion state is the true active species to form a reducible complex during the reaction. Although the energy levels of dianion state have been found to be very high, the probability to find

the dianion in the solution is very low. For ethylene glycol, the energy orbital is significantly high. When the reaction is heated close to the boiling point of EG, the energy increases by 2.12 eV and the EG becomes highly reactive. EG was studied experimentally and theoretically.¹⁵ The neutral 1, 2-butanediol was also studied with DFT calculations and IR spectroscopy.¹⁶

For the most used polyols to synthesize metal and alloy nanoparticles, ethylene glycol (EG) and diethylene glycol, only isotropic Co₈₀Ni₂₀ particles have been synthesized.¹⁷ Furthermore, all the experiments have been undertaken in the 1,2-propanediol (PEG) for the formation of well-individualized cobalt based nanoparticles of Co₈₀Ni₂₀ and Co have not been driven to obtain well-isolated wires, but to obtain only urchin-like morphologies.¹⁸ The use of 1,2-butanediol (BEG) instead of PEG under normal experimental conditions allowed the formation of well-isolated nanowires of Co₈₀Ni₂₀.^{18,19} The preparation of pure Cobalt nanorods in an organic solvent as BEG, with controlled size, shape and structure was possible. It depends on three parameters: the nature of the cobalt carboxylate, the temperature ramp, and the basicity of the medium.⁶ Therefore, regardless of the other experimental conditions, the reaction kinetics can be enhanced by varying the nature of polyols.⁹

Since the assessment of the reduction ability of various polyols at a boiling point are often obtained empirically⁶ it is absolutely not enough to understand the reaction mechanism of the dissolution of metal precursors, complexation with a polyol, and the reduction of cobalt metallic cations to form metallic particles. Molecular orbital calculations have been proposed as a solution to elucidate the oxidation reaction of polyol through the identification of the active species of EG.¹²

In this work, we report a theoretical calculation of orbital molecular energy of the active species derived from BEG. We also perform a comparative theoretical study of the most used polyols to synthesize cobalt-based nanoparticles such as EG, PEG and BEG. The identification of the active species and their electronic structures will open the way to understand the reduction/oxidation scheme reaction between metal ions and polyol, and to have high-quality control over the physical properties of metal particles.

2. Theoretical calculation

The reaction kinetics can be enhanced by proper choice of polyols.⁹ Since the experimental evaluation of the oxidation reaction of polyol at boiling point was difficult, molecular

Figure 1. Energy diagram showing the electrons transfer between polyol and metal salt.

orbital calculations were carried out in our work to elucidate the oxidation and the reduction ability of polyol in milder reaction conditions.⁹ The reduction of metallic complex is done by electron transfer from polyol to metal compound. Indeed, the electron transfer depends on the relative levels of molecular orbital of both metal and polyol. The transfer is carrying out from the HOMO (Highest Occupied Molecular Orbital) of polyol to the LUMO (Lowest Unoccupied Molecular Orbital) of metal salts as appearing in Figure 1. The progress of the reaction is related to the difference between these levels. The smaller the difference is, the easier the transfer is. The orbital energy calculations give an idea about the ability of the polyol to donate electrons. Then, to estimate the reduction ability of polyol, an experimental parameter effect like the temperature is taken into account by considering the conformational changes in the polyol.¹² In our work, we consider only the HOMO energy value of polyol and we fix the orbital energy of metal salt.

The optimization of the structures (conformers) and the calculation of orbital energies were carried out using density functional calculations as implemented in the Gaussian 09 software.²⁰ B3LYP/6-31G(d)^{20,21} method was used for geometry optimization and orbital energy calculations. For the study of HOMO orbitals of polyols, this level of calculations is satisfactory.¹² It allows us to compare our results to the previous study.¹² Our goal is to evaluate the reduction ability of BEG by density functional calculations. In DFT calculations, all internal coordinates were optimized by the use of Berny algorithm and all the convergence conditions, the maximum force component, root-mean-square force, maximum displacement component, and root-mean-square displacement was verified.

3. Results and Discussion

3.1 Models for the species derived from BEG

For the synthesis of metallic nanoparticles using BEG, many reactions of the polyol could be considered with

different components in the medium. Consequently, we have estimated many electronic states of BEG dianion (1) monoanion (2) (2') and neutral (3), the monoanion presents two species because the hydrogen can be removed from O1 or O4. We will study its reduction ability compared to PEG and EG. The rotational dihedral angles of possible BEG-derived species are noted in Figure 2.

3.2 Determination of the active species derived from 1,2-butanediol (BEG)

In this study, we will determine the active species derived from BEG estimated by HOMO energy calculation. These active species are considered as crucial components for the formation of the intermediate phase. This phase presents the rate-determining step for the growth of the metal nanoparticle. We will compare the reduction ability of BEG to the two other polyols PEG and EG, which are considered the most used for the synthesis of cobalt-based nanoparticles.

The theoretical estimation for the three electronic states of BEG, dianion, monoanion and neutral will be discussed in detail by evaluating the self-consistent field energies obtained by varying the dihedral angles in Figure 2 for each active species and the HOMO orbital energy calculated from the most stable conformational isomers.

3.2a Dianion derived from BEG: The dianion is characterized by two negative electric charges gained from the removal of two hydrogens from the two hydroxyl groups in BEG.

The relative DFT energies and the HOMO orbital energies of each conformation for the dianion state were obtained by varying the dihedral angle O-C-C-O, the structures with minimum and maximum energies (starting with letter A) are shown in Figure 3a and b. The most stable conformational isomer is (A2) (+180°) in which the relative DFT energies go through a minimum and it is registered when the two oxygen atoms have the largest distance between them. The relative energies of conformations (A6) and (A4) are 5.02 kcal/mol and 3.13 kcal/mol higher than conformation (A2). The fingerprints of HOMO energies of each conformation for dianion species are in Figure 3. This figure shows that the highest HOMO orbital energy is obtained from stable conformer (A2).

3.2b Monoanion derived from BEG theoretical estimation: Monoanion is a state with a single negative charge where one of the hydrogen atoms is removed from the

Figure 2. The rotational dihedral angles of possible BEG-derived species in the reaction medium.

Figure 3. (a) Characteristic conformers of the dianion state derived from BEG and the DFT relative energies curves obtained by varying the rotational angle: 1-2-3-4 (O-C-C-O) (b) The fingerprint of HOMO energies of each conformation derived from BEG dianion species.

two hydroxyl groups in BEG molecule. For the BEG, two types of monoanions will be obtained from the

motion of one hydrogen of the two hydroxyls as shown in Figure 2b which are (2) and (2'). Our calculations show that (2) is more stable than (2'). We will focus our study in the monoanion type (2) because of its more important abundance.

The two dimensional DFT energy curve obtained by varying the two dihedral angles: angle 1: O-C-C-O and angle 2: H-O-C-C of the BEG monoanion type (2) and the characteristic conformers are illustrated in Figure 4a. The conformational analysis reveals that the most stable conformers given from the DFT energy curve were determined to B1 (0 (angle 1), 5 (angle 2)). Also, five other stable, B2 (−40, 25), B3 (30, −10), B4 (155, −5), B5 (170, 45) and B6 (60, −35) are localized in the DFT energy curve, with relative energies 0.62 kcal/mol, 1.25 kcal/mol, 13.17 kcal/mol, 12.5 kcal/mol et 5.02 kcal/mol higher than B1 respectively.

For the most stable conformer B1, the negatively charged oxygen of the anion state is in front of the hydrogen in the hydroxyl group, then electrostatic attraction could contribute to the formation of hydrogen bond and the stability of the conformer. In the other stable conformers such as B2, B3, B6, the oxygen and the hydrogen positions are shifted and moved away from each other, so the stabilization of the conformer is decreasing with the angle. On the other hand, in the case of B4 and B5 conformers, the oxygen in the anion state and the hydrogen of hydroxyl group are in opposite direction and far away from each other, which leads to destabilizing the conformer and the formation of a hydrogen bond is impossible.

Figure 4. (a) DFT Energy curve (a.u) and the most stable conformers of monoanion derived from BEG (b) the fingerprint of HOMO energies of each conformation for monoanion species.

The HOMO energies of these conformers are plotted in a 1D coordinate axis fingerprint as illustrated in Figure 4b. In other words, the fingerprint is specific to the monoanion derived from the BEG. The energy difference between B1, which possesses the lowest energy, and second lowest HOMO energy conformer B2 (0.02479 a.u.) is 0.16 eV.

3.2c Neutral derived from BEG: For the neutral state of BEG with the two hydroxyl groups, three angles will be considered, rotational angle 1: 1-2-3-4, rotational angle 2: 5-1-2-3 and rotational angle 3: 2-3-4-10. The DFT relative energy curve obtained by rotating the dihedral angle 1 (O-C-C-O) of the neutral BEG shows three stable conformers C, D and E as shown in Figure 5a. The C conformer has minimum energy and then the D and E conformers stabilized at an energy level of 5.64 kcal/mol and 2.51 kcal higher than the C conformer respectively.

In the case of (C), the two hydroxyl groups face each other and the ethyl group is far from the hydroxyl group in the asymmetric carbon, which ensures the formation of hydrogen bond stabilizing the conformer. On the other hand, the hydroxyl groups in (D) are far away from each

other, and the formation of hydrogen bond that contributes to the stability of the conformers is not realized. Otherwise, in the (E) the two hydroxyl groups face each other but the ethyl group is close to the hydroxyl group in the asymmetric carbon that leads to destabilizing the conformer and the formation of hydrogen bond would be difficult.

We are interested only in the most stable conformer (C) by rotating the two dihedral angles: H-O-C-C (rotational angle 2: 5-1-2-3) and H-O-C-C (rotational angle 3: 2-3-4-9), at the same time fixing the dihedral angle O-C-C-O (rotational angle 1: 1-2-3-4). The calculation of the relative energy (DFT) and the orbital energy HOMO were achieved and illustrated in Figure 5b and c. When (C) is taken as the starting structure, four stable conformers are identified from the two-dimensional DFT energy curve obtained by rotating the two dihedral angles: angle two and angle three as shown in Figure 5b. The most stable conformers are C1 (-160, -65), C2 (-70, 35), C3 (-145, 180) and C4 (-160, -85). The HOMO orbital energy of C1 is the maximum among the other HOMO energies. The most stable structure is in agreement with the neutral 1, 2-butanediol determined by Lopes Jesus *et al.*¹⁶

The fingerprint of the HOMO orbital energies of conformers got from the DFT energy curve is illustrated in Figure 5c. The range of HOMO energies values are dispersed compared to the monoanion state.

3.3 Comparative study

The HOMO energies of the neutral, monoanion and dianion states of BEG are illustrated in Figure 6. To show the reduction ability of BEG, we have also calculated the HOMO orbital energies of the most stable conformers of PEG and EG at the same level of theory. The structure of calculated EG is in agreement with the structure found by Abdelmoulahi *et al.*¹⁵ The results of each polyol are collected in the same fingerprint Figure 6. The orbital energy levels for each polyol increase in the order: neutral, monoanion and dianion and the value of HOMO orbital energies for neutral states are very narrow and lower compared to monoanion and dianion states. Actually, the higher value for HOMO energies represent the easiness of polyol to donate electrons. Also, the reaction rate could be further increased especially with the introduction of sodium hydroxide. As mentioned earlier,¹² considering the mass conservation for matter entering and leaving the system (the sodium hydroxide/the polyol), the amount of sodium hydroxide allow us to presume that there is low chance to get dianion in the solution. The acidic properties of BEG are similar to EG. If we suppose that we have the same

Figure 5. (a) DFT energy curve of BEG molecule rotated around O-C-C-O and the stable conformers (b) DFT Energy curve obtained by rotating the two angles rotational angle 2: 5-1-2-3 and H-O-C-C (rotational angle 3: 2-3-4-10) and the most stable conformers of neutral states derived from BEG (c) the fingerprint of HOMO energies of each conformation for neutral species.

concentration of BEG and NaOH, fewer BEG would be deprotonated. Thus, it can't be possible to have dianions in the reaction. On the other hand, if we suppose the absence of sodium hydroxide in the solution, the neutral state will be present. This state is less reactive. In the experimental conditions, and as we have discussed, only neutral and monoanion are abundant.

The formation of the monoanion states will be promptly activated through the introduction of the

Figure 6. HOMO energies of the neutral, monoanion and dianion states of each polyol: BEG, PEG and EG.

sodium hydroxide. The fingerprint in Figure 6 shows that only the orbital energies level of BEG monoanion state is relatively high compared to PEG and EG. At milder reaction conditions such as low temperature and $[OH^-]$ concentration, the reduction reactivity between BEG monoanions is extremely high compared to the two other polyols. Moreover, heating the solution could increase the energy level more by 0.16 eV (Figure 6) and then the BEG becomes more reactive. The orbital energy of the monoanion state of 1,2-butanediol (BEG) is higher than their neutral states and also than the two other polyols. Hence, the theoretical calculations show that the monoanion state of BEG behave as the true active species under normal experimental conditions.

This study shows that through orbital energy calculations BEG could donate electrons more easily to metals orbitals than PEG and EG in their monoanions states. The reaction kinetics of BEG monoanions states is faster than PEG and EG in the solutions. The reduction rate in BEG is higher than the other polyol and the concentration of the metallic ions increase in the solution. This fast rate contributes to the formation of more products containing different metals.

4. Conclusions

The orbital energy calculations were used to determine the more active species of BEG. The reaction rate can be enhanced by accelerating the oxidation of the polyol in the presence of the sodium hydroxide and also by selecting a highly reducing polyol. For the first time, the HOMO was calculated for different species of BEG in order to show its oxidation properties and to compare it to other polyols. Based on our orbital molecular calculations and the experimental conditions, the monoanion states derived from 1,2-butanediol have been identified

to be the more active species. The quantum comparative study between BEG, PEG and EG shows that the BEG possesses the relatively higher occupied orbital for the active species. These results help us to suggest that the rate of the reaction is faster with BEG and it could contribute to progress the dissolution and the reduction of metallic ions. Slow reaction kinetics like for PEG and EG would contribute to the decrease of the concentration of ions in the solution. On the other hand, the oxidation of BEG helps to reduce faster metallic ions. The reaction kinetics are faster and the concentration of metallic ions are increased in the solution which could influence the growth and nucleation rates of the metal formation and the final physical properties of the nanoparticles.

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