Catalytic Effect of Pd Clusters in the Poly(N-vinyl-2-pyrrolidone) Combustion

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Abstract

Pd(0) is able to catalyze oxygen-involving reactions because of its capability to convert molecular oxygen to the very reactive atomic form. Consequently, the embedding of a little amount of Pd(0) clusters in polymeric phases can be technologically exploited to enhance the incineration kinetic of these polymers. The effect of nanostructuration on the Pd(0) catalytic activity in the polymer incineration reaction has been studied using poly(N-vinyl-2-pyrrolidone) (Mw = 10,000 g mol−1) as polymeric model system. A change in the PVP incineration kinetic mechanism with significant increase in the reaction rate was experimentally found. The kinetic of the Pd(0)-catalyzed combustion has been studied by isothermal thermogravimetric analysis. After a short induction time, the combustion in presence of Pd(0) clusters shifted to a zero-order kinetic from a second-order kinetic control, which is operative in pure PVP combustion reaction. In addition, the activation energy resulted much lowered compared to the pure PVP incineration case (from 300 to 260 kJ/mol).

Keywords: Heterogeneous catalysis, Palladium, Combustion, Poly(N-vinyl-2-pyrrolidone), Thermogravimetry

Background

On a nanoscopic scale, noble metals show abnormally increased catalytic properties, known as “super-catalytic effect” [1, 2]. Not only the number of catalytic sites increases with the decreasing of the crystal diameter, due to the surface/volume ratio increase (the surface/volume ratio for a spherical particle is 3/R), but also the catalytic site nature (that is, Lewis’ acidity) is strongly affected [1]. In particular, Lewis’ acidity of catalytic sites increases with size decreasing because the relative abundance of different catalytic sites changes. According to theoretical models, like for example the “cubic model” [3], the distribution of the different site types (i.e., basal plane, edge, and corner sites) in a noble metal crystal is revolutionized by decreasing the crystal diameter [1]. In fact, in some micron powders, crystal basal planes are the most abundant, while edge and/or corner sites prevail in a nanoscopic crystal system [2]. Owing to the lower coordination number of these sites, a different catalytic activity follows. Moreover, as the activity also, selectivity and specificity of catalytic sites are modified [4, 5].

Polymer incineration is a technologically relevant chemical process, which involves oxygen and takes place at relatively high temperatures [6, 7]. PVP is a common polymer, industrially exploited in several fields (cosmetics, biomedical, as excipient in drugs, etc.), and hence, it was selected as the “model polymer” to be studied. In addition, the PVP incineration is technologically relevant in ceramic sintering [8], ceramic sensor fabrication [8, 9], battery electrode fabrication [6], waste destruction [10, 11], solid propellant development [12, 13], etc.

Here, we have found that the PVP incineration process can benefit of the presence of a nano-sized noble metal catalyst, probably because it is able to quantitatively convert molecular oxygen (O2) to the more aggressive oxygen atoms (O·) [14, 15]. All types of noble metal/PVP combinations can be easily synthesized, in a high homogeneous form, by using the very common polyol process technique [16–22]. In this study, Pd has been selected as a catalytic metal since it can be achieved in an extremely small size by this simple reaction scheme [21, 22].

Polymer incineration can be readily studied by using thermogravimetric analysis (TGA) [7]. In particular, isothermal TGA tests, performed at temperatures higher than the PVP ignition temperature, have been used for this kinetic analysis. The isothermal TGA tests were
performed at four different temperatures slightly above 370 °C, which corresponds to the onset degradation temperature in a dynamic TGA thermogram. Temperatures higher than 440 °C were not investigated because the reaction rate resulted too high for a satisfactory TGA monitoring. In order to establish the involved combustion mechanism, (i) the reaction order, (ii) kinetic constant, (iii) and activation energy values have been valuated from the isothermal TGA data of pure PVP and nano-Pd/PVP combustions.

Experimental

Samples were prepared according to a literature method [22]. In particular, poly(N-vinyl-2-pyrrolidone) (PVP, Aldrich, Mw = 10,000 g mol⁻¹) was dissolved in dry ethylene glycol (EG, Aldrich, 99.8%), and the solution was placed in a thermostatic bath at 90 °C in air, up to complete dissolution. In a typical preparation, 24 g of PVP powder were dissolved into 70 ml of EG. Separately, a smaller volume (10 ml) of a concentrated solution of potassium tetrachloropalladate(II) (K₂PdCl₄, Aldrich, 99.99%) in EG (0.35% by weight of salt) was prepared, and it was rapidly injected into the vigorously stirred hot PVP/EG solution. The PVP concentration in EG was 30 mM and the Pd(II):PVP molar ratio was 1:10. After heating for 120 min, the solution was cast into a large amount of acetone to flocculate the nano-Pd/PVP system. The product was dried in air and stored at room temperature in a desiccator. A second type of nano-Pd/PVP samples was also prepared by dispersing a commercial micrometer-sized Pd(0) powder (Pd, Aldrich, particles size < 1 μm, 99.9%) in PVP having the same molecular weight. The dispersion concentration was similar to that used for the nano-sized Pd in PVP samples (0.3% by weight).

The morphology of Pd clusters was investigated in a PVP-embedded form by using transmission electron microscopy (TEM, FEI Tecnai G2 Spirit twin apparatus) operated at 120 kV, and after the combustion process, the residual product was imaged by using scanning electron microscopy (SEM, FEI QUANTA 200 FEG apparatus).

According to the literature [23, 24], the combustion properties of pure poly(N-vinyl-2-pyrrolidone) (PVP) and nano-Pd/PVP samples were investigated by thermogravimetric analysis (TGA, Q5000, TA Instruments) in oxidative atmosphere (fluxing air) at standard pressure conditions. The combustion process was investigated by burning PVP and nano-Pd/PVP samples in both dynamic (from room temperature to 600 °C, at a heating rate of 10 °C min⁻¹) and isothermal conditions, under fluxing air (25 ml min⁻¹). The temperature of TGA isothermal tests was taken above the ignition temperature (onset) determined by the TGA dynamic scan. Isothermal data were recorded for all samples up to a complete weight loss.

Results and Discussion

A representative TEM micrograph of nano-Pd/PVP samples is shown in Fig. 1a. Contact-free Pd clusters, having a size of 2.8 ± 0.2 nm (see Fig. 1b), appear to be uniformly dispersed into the PVP matrix.

The SEM micrograph shown in Fig. 2 evidences as, in presence of the Pd(0) catalyst, the PVP combustion resulted complete. In fact, the combustion product consisted of only aggregated Pd clusters, without traces of any organic residue. In particular, this nano-Pd/PVP sample was burned in a thermogravimetric balance, under dynamic conditions (i.e., from room temperature to 600 °C, at a heating rate of 10 °C min⁻¹), using fluxing air (25 ml min⁻¹). The continuous metallic framework has been generated by the sintering of adjacent Pd(0) clusters after the PVP removal.

The combustion processes for pure PVP and nano-Pd/PVP samples were studied by dynamic and isothermal thermogravimetric analysis (TGA). Dynamic TGA allowed
to determine at which temperature the combustion starts (i.e., the ignition temperature) and ends, and it provided general information regarding reaction kinetics and other parameters that characterize the combustion behavior. A comparative analysis of the TGA (weight loss ratio) and DTG (weight loss rate) curves is presented in Fig. 3 for pure PVP and nano-Pd/PVP samples. The shape of the curves indicates that the major weight loss occurs between 400 and 500 °C. Pure PVP and nano-Pd/PVP samples differ in reactivity as clearly exhibited by the deviations in peak decomposition rate and by the trend of the weight loss curve of nano-Pd/PVP which on the whole is faster compared to that of pure PVP. In fact, the presence of a very small amount of Pd catalyst affects the polymer thermal degradation both before and after ignition (see Fig. 3a). Further, a residual weight loss of ca. 0.3%, due to the Pd catalyst content, is clearly visible in the nano-Pd/PVP TGA. The DTG curves of pure PVP and nano-Pd/PVP samples exhibit a maximum decomposition rate at ca. 420 °C (see Fig. 3b). In addition, the nano-Pd/PVP curve displays a second peak which is visibly anticipated compared to the pure PVP (470 °C instead of 540 °C).

TGA isothermal analysis was used to study the combustion kinetic of the PVP catalyzed by Pd(0). Figure 4 shows the isothermal weight loss fraction, $X(t)$, as a function of time during the combustion process for pure PVP and nano-Pd/PVP samples at temperatures slightly above the ignition temperature. The weight loss fraction is defined as $X(t) = w(t)/w_0$, where $w_0$ and $w(t)$ refer to the initial weight and weight at time $t$, respectively. Isothermal thermogravimetric analysis was carried out at four different temperatures: 400, 420, 430, and 440 °C.

Two combustion stages are visible in the thermograms (see Fig. 4): in the first stage, a similar weight loss behavior, characterized by perfect curves that overlap, is found for both pure PVP and nano-Pd/PVP samples. This stage tends to become shorter with temperature increasing. In the second stage, the nano-Pd/PVP weight loss curve decreases very rapidly and then level off to become asymptotic to the residual Pd content. These two stages are linked together through a short time interval in which the weight loss keeps almost constant.

Such behavior can probably be ascribed to the time needed to saturate the Pd surface by molecular oxygen [9]. Pd catalyst is able to quantitatively convert the low-reactive molecular oxygen (O$_2$) to a very reactive atomic oxygen species. Therefore, in the first stage, common to both PVP and nano-Pd/PVP combustion, only the molecular oxygen plays the dominant role in the reaction while atomic oxygen plays a major role in the second stage of nano-Pd/PVP combustion.

The weight loss curve of pure PVP reaches its asymptotic value only after a very long time, and according to the applied regression analysis, it follows a second-order kinetic behavior. Differently, the nano-Pd/PVP curves quickly drop to their asymptotic values (see Fig. 4) following a linear behavior, thus suggesting a zero-order kinetic control for this second stage of combustion. In particular, a correlation factor of $R^2 = 0.98$ was found for...
all curves. The estimated values of kinetic constants both in presence and absence of the Pd(0) catalyst are given in Table 1 for each combustion temperature.

In order to determine the activation energy for the fast stage of the nano-Pd/PVP combustion process, the 
\[ k = A \exp(-E_a/RT) \]

Arrhenius equation has been used to fit the kinetic constants at different temperatures. The constant \( A \) is the frequency factor, \( E_a \) is the activation energy, and \( R \) is the gas constant. The Arrhenius plot (\( \ln(k) \) vs. \( 1/T \)) is given in Fig. 5. The solid line is the linear fit of the experimental kinetic constants, and its slope depends on the activation energy \( (E_a) \). The calculated pre-exponential factor \( A \), was \( 1.7 \times 10^{19} \) min\(^{-1}\) (\( \ln(A) = 44.3 \)), and the activation energy \( (E_a) \) was ca. 260 kJ/mol. For comparison, Fig. 5 shows also the Arrhenius plot of the kinetic constants for pure PVP combustion. The calculated pre-exponential factor \( A \) was \( 7.7 \times 10^{21} \) min\(^{-1}\) (\( \ln(A) = 50.4 \)), and the activation energy \( (E_a) \) was ca. 300 kJ/mol, determined from the slope of the linear fit to the kinetic constants (black dots) of the PVP combustion.

According to Fig. 5 and to the data shown in Table 1, the presence of the palladium catalyst has the global effect of lowering the activation energy of the polymer

**Table 1** Kinetic constants of pure PVP and nano-Pd/PVP combustion at different temperatures

| Temperature (°C) | \( k \) (min\(^{-1}\)) for nano-Pd/PVP combustion | \( k \) (min\(^{-1}\)) for pure PVP combustion |
|------------------|-----------------------------------------------|------------------------------------------|
| 400              | 0.113                                         | 0.041                                    |
| 420              | 0.409                                         | 0.152                                    |
| 430              | 0.711                                         | 0.324                                    |
| 440              | 1.632                                         | 0.886                                    |
combustion, allowing the reaction to speed up (higher kinetic constant values).

The knowledge of the activation energy, $E_a$, helps to develop hypothesis on the reaction mechanism. In fact, by comparing $E_a$ with the tabulated values of bond energies, one can determine which is the rate-limiting step in the combustion reaction under investigation. The calculated activation energy, $E_a = 260$ kJ/mol, is about one half the molecular oxygen double bond energy ($498.36 \pm 0.17$ kJ/mol) [25]. Since the single-bond energy of oxygen is quite close to the measured activation energy, it can be concluded that atomic oxygen formation ($O_2 \rightarrow 2O$) takes place on the palladium cluster surface and it is the rate-limiting step of the nano-Pd/PVP combustion. In fact, under fluxing oxygen condition (constant oxygen concentration), the kinetic order of this elementary process is just like zero. Other elementary processes involved in the catalyzed combustion mechanism, which can be schematically indicated as $PVP + O \rightarrow$ gaseous products, should take place on a time scale much faster than the atomic oxygen formation step.

The nanostructuration of the palladium phase plays an important role in this catalytic combustion process. In fact, the embedding of a micronic Pd(0) powder in the PVP phase, using the same amount of the synthesized nano-Pd/PVP samples (0.3% by weight), does not affect the reaction kinetic (see Fig. 6). In such figure, the weight loss fraction of the pure PVP, of the Pd/PVP sample prepared by using a micronic powder, and of the synthesized nano-Pd/PVP sample are compared. Comparisons are at temperatures of 420 °C (Fig. 6a) and 440 °C (Fig. 6b), respectively. The enhanced catalytic effect of nano-sized Pd compared to the micrometric Pd powder is visually evident. The catalytic activity of the nano-sized Pd increases; thanks to its high specific surface and enhanced catalytic site reactivity.

As a consequence of such a kinetic mechanism (atomic oxygen formation as a rate-limiting step), an effect of the nano-sized Pd catalyst on other polymer combustion could be expected too. Therefore, nano-sized Pd catalyst could be industrially exploited in polymer incineration.

Conclusions
In this paper, we have investigated the catalytic effect of palladium clusters in the PVP incineration reaction. PVP was selected as the “model polymer” to study the incineration in presence of a catalytic amount (0.3% by weight) of nano-sized Pd(0) clusters (diameter of ca. 2.8 nm). We have found that the polymer incineration performed in presence of nano-sized Pd clusters is promoted by the oxygen atom action, which are more reactive than the molecular form. After a short induction time, it was shown that the presence of nanoscopic Pd(0) catalyst determined an almost instantaneous combustion of the PVP. The isothermal TGA data of the nano-Pd/PVP combustion reaction have been elaborated in order to determine the combustion mechanism, the kinetic constants, the reaction order, and the activation energy. According to the kinetic analysis, a reaction
mechanism involving the catalytic formation of atomic oxygen as a zero-order rate-limiting step has been proposed. Nano-sized Pd clusters have shown to exhibit a super-catalytic effect compared to micrometric Pd powder in the PVP incineration. This catalytic effect of nano-sized Pd could be of interest for the incineration of other polymers.

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Authors’ Contributions
LS with GC and S De N conceived the experimental design. LS contributed to the fabrication and to the characterization of the samples. LS wrote part of the paper. GC and S De N participated to the development of the theoretical analysis and helped to draft the manuscript. All authors have read and approved the final manuscript.

Authors’ Information
LS (Dr.) is an industrial chemist, coming from the University of Naples “Federico II,” Italy. She received her degree in 2005 and her Ph.D. in Physics at the University of Trento in 2017. Her background is based on the knowledge of polymeric materials (thermoplastic and thermosetting polymers), nanostructured materials, and different types of composites of the materials investigated. Her research experiences started during her thesis work done on the “study of the relationship between structure and mechanical properties of polymeric materials” which was consolidated both during her Ph.D. research activity concerned to the “Synthesis and characterization of nanostructured materials (and their polymeric composites) for hydrogen storage applications” and during her work as a research fellow at the National Research Council (CNR) of Naples since 2007. GC (Dr.) is a senior researcher at the CNR at the Institute CNR-IPC. He presents present research interests are in the field of advanced functional materials based on polymer-embedded inorganic nanostructures. In particular, his activity concerns the development of new chemical routes for the controlled synthesis of metal and semiconductor clusters in polymeric matrices, the fabrication of devices based on properties of nanoscopic objects (e.g., luminescence of quantum dots and tunable surface plasmon absorption of nano-sized noble metal alloys), and the investigation of mechanisms involved in atomic and molecular cluster formation in polymeric media (nucleation, growth, aggregation, etc.) by optical and luminescence spectroscopy. He has also authored 180 research articles published in international journals, 10 patents, and many conference papers. He is the editor of two Wiley books devoted to metal-polymer nanocomposites, and he is a member of the editorial board of different scientific journals. S De N received his BSc degree in physics from the University of Naples “Federico II,” Italy, in 1982. From 1983 to 1987, he was a system analyst at “Electronica” (Rome) and “Alenia” (Naples). He has been a staff researcher at the National Institute of Optics (CNR-INO). Currently, he is a senior researcher at the “SirPerConducting and other INnovative materials and devices institute” (CNR-SPIN). He has been a scientific coordinator of the research project “Imaging techniques for studying and analyzing microstructured materials” of the Department of Physical Sciences and Technologies of Matter Technologies of CNR. He has been a coordinator of the research unit in the framework of the CNR-FIRB 2001 Italian national program, “Photonic microdevices in lithium niobate.” He has contributed to about 300 technical papers in peer-reviewed international journals, book chapters, conference papers, and several patents. His research interests include the development of quantum methodologies to the description of coherent phenomena in many body systems, quantum tomography, theoretical modeling for studying dynamical effects in mesoscopic systems, transport properties in nanostructured polymeric materials and biological media, and optical and electron beam propagation in nonlinear media and plasma.

Competing Interests
The authors declare that they have no competing interests.
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