

Synthesis Characterization and Catalytic Oxidation Studies of Nanosized Cobalt Oxide Copper Oxide and Their Composites

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ABSTRACT

Due to industrialization, the VOCs are contaminating both air and water bodies which are a cause of concern due to their health hazards. In the recent year use of noble metal catalyst to destroy VOCs on site has gained importance. However their cost deters their use. We have developed low cost transition metal oxide catalysts such as CuO, Co₃O₄ and their composites (Co₃O₄/CuO) to be used as oxidation catalysts for VOCs. The processes used have been Hydrothermal (HT), Sol-Gel Auto combustion (SGA), Chemical Combustion (CC) Thermal Decomposition (TD), for the production of high surface area, and enhanced catalytic activity of nano structural catalysts (in the range of 16 nm to 71 nm). The synthesized catalysts were studied for the relative oxidation of formaldehyde by aqueous potassium dichromate and respective catalyst, at moderate temperatures (20-40oC). Co₃O₄ being best has been used to catalyze the oxidation of oxalic acid and benzaldehyde by air/oxygen at moderate temperatures (25o -65oC) and (60oC) respectively. As no reagents were employed for the oxidation of oxalic acid and benzaldehyde, the heterogeneous nature, reusability and recoverability of Co₃O₄ catalyst makes the process a truly Green Technology at lower costs.

Keywords – Oxidation, Nanosized

INTRODUCTION

Nanoscience

Nanomaterials are classified as materials ranging in size from about 1-100 nanometers with at least one outer dimension. Nanoscience is defined as the analysis of all kinds of nanostructures involving the properties and processes that exist on this scale. At the leading edge of nanoscience and nanotechnology are materials with this distinctive dimension. Around 40 years ago, the idea of non-materials was introduced, but lately it has become popular. For hundreds of years, Nan materials have already been developed and used by humans. The stunning ruby red colour of

certain glass, for example, is due to gold nanoparticles embedded in the matrix of glass. The physiochemical properties of nanoparticles containing materials are very different from those of bulk materials, due to the extremely small size and large surface volume ratio of nanoparticles [El-Sayed 2001]. Nanomaterials can be non-crystalline, polycrystalline or single crystalline and can be manufactured using a number of techniques.

The surface-edged and corner atoms typically become chemically reactive and catalytically active at the nanoscale stage, thus leading to a high chemical potential. High surface area, for example, is a significant factor for heterogeneous catalytic reactions due to increased interactions between reactive molecules and active catalyst surface sites [Yoon et al. 2005]. Compared to bulk material, the properties of the products change unexpectedly at the nanoscale and have therefore found various applications in the fields of electronics, photonics, information storage, chemical sensing and imaging, environmental remediation, drug delivery, biological labelling and catalysis. It has been found that non-material properties are dependent on size and shape. Gold (Au), Silver (Ag) nanocrystals of different shapes, for example, show unique optical scattering responses while a single scattering peak was observed for highly symmetrical spherical particles, due to highly localized charged polarization, multiple scattering peaks were observed for anisotropic shapes such as rods, triangular prisms, and cubes. This leads to an increased interest in nonmaterial synthesis with established morphology.

Different types of nanostructures have been developed so far and are being applied in various areas. Easy metallic materials, for example ceramic materials and more complex structures. The first and significant step is the synthesis of nanostructures because the material's output depends on it as it greatly influences the properties and applications. These methods should, at the same time, be simple, economical and eco-friendly. Non-material synthesis is roughly divided into two parts: the top-down and the bottom-up method.

OBJECTIVE

1. To synthesized catalysts were studied for the relative oxidation of formaldehyde by aqueous potassium dichromate and respective catalyst, at moderate temperatures (20-40°C)

Top-down approach

This kind of approach involves the breaking down of large material pieces in order to generate the desired smaller nonmaterial from them.

Bottom-up

This kind of approach involves assembling single atoms and /or molecules so as to build larger nanostructures from them. A diagram representing the top-down and bottom-up approach is shown below in the Figure 1.1:

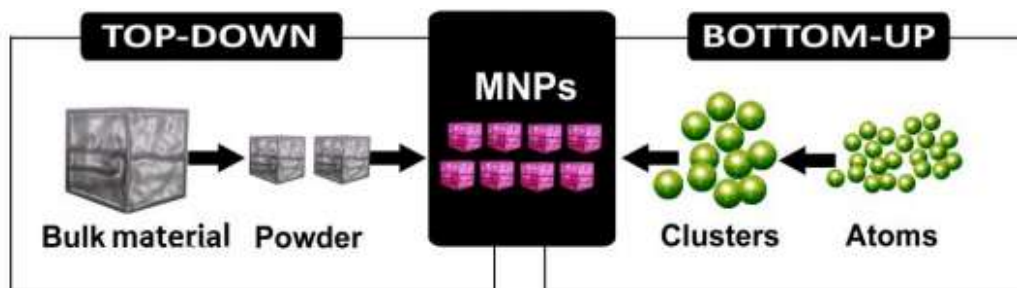


FIGURE 1.1: Top-down and Bottom-up approach

In order to obtain materials with desired physical and chemical properties, the preparation of non-materials across different paths has become an important part of research and development. Different methods are used to synthesise non-materials, depending on the nature of the work, such as hydrothermal solvothermal method solution phase synthesis [Gou and Murphy 2003], sol-gel method wet chemical reduction microwave technique, etc. In order to study the properties, conventional techniques should be merged with those explicitly designed to investigate nanoscale material structures, such as scattering and transmission electron microscopy (SEM and TEM). Classical (IR spectroscopy, Raman vibrational spectroscopy, classical magnetic activity tests) and electron microscopy (SEM and TEM), among others, are now considered to be important instruments for the study of nanomaterial properties. The scale and form of non-materials are of more significant interest. 3D architectures of Nan particles nanorods nanobelts nanocomposites etc.

Metal Oxide

Due to its unique properties and applications, metal oxide and mixed metal oxides are considered to be one of the most significant non-materials from different prepared nanostructures. The specific characteristics of non-materials depend on the size, shape, chemical composition, structure of the crystals and surface chemistry, and researchers have become the primary focus of regulated morphology synthesis of non-materials. The dramatic shift in the properties of non-materials from the bulk material has made them applicable in many fields such as catalysis, energy storage, optoelectronics, sensing, magnetic resonance imaging (MRI), biomedicine, etc. Synthetic methods have been needed to achieve non-material metal oxide. These synthetic methods are categorised by two large categories: the top-down approach and the bottom-up approach. The top-down approach involves the production of large amounts of nano crystals followed by crushing and pulverization, but it is difficult to obtain size control and uniformity by this process, while the bottom-up approach involves the synthesis of uniform and regulated particle size by chemical nucleation and growth by this method in bulk solution, but only subgram amounts are

The bottom-up approach has an advantage over the top-down approach as it provides precise control over the size and shape of the crystallite, making the bottom-up approach a powerful tool for producing new multi-component materials and devices. Capping agents are also used to control crystal growth by reducing crystal surface energy. To regulate the form of nanocrystals, the selective bonding between surfactants and the different crystallographic faces has been found. The resulting nanocrystals of oxide consist of an inorganic core coated with a layer of

organic surfactant molecules. Organic capping results in the passivation of electronics and chemicals and thus avoids uncontrolled growth and agglomeration.

A deep understanding of the actions of growth involves the synthesis of inorganic nanocrystals. In the bottom up synthesis by the Ostwald ripening mechanism, the behaviour of the growth process of nuclei was represented. According to this process, the growth of larger particles occurs at the expense of smaller particles, powered by the reduction of surface energy. Ostwald ripening is used to clarify the development of thermodynamically stable nanocrystals with nearly spherical morphologies. The reaction medium is one of the important variables in solution-based methods. Water can be regarded as a strong competitor because of its environmentally friendly existence from various organic reagents (Toluene, Diphenyl Ether, Oleic acid, etc.) used in solution-based processes, and is also one of the most abundant tools. Many metal chlorides and nitrates are soluble in water, so aqueous-based routes can be used to synthesise high-yield non-materials. There is therefore a high need to develop methods for the synthesis of nanocrystals which, under mild conditions, are low-cost, environmentally friendly and have the potential for the production of regulated metal oxides and mixed metal oxides on a large scale. Thus, synthesis is the first step in the analysis of any non-material metal oxide. Methods for the synthesis of metal oxide-containing non-materials are narrowly divided into two components: transformation of liquid solid and gas solid.

Liquid solid transformations:

It is generally the broadest category used to control morphological characteristics and usually follows a bottom up approaches. The different methods used to synthesize metal oxide nonmaterial's under this transformation are as under:

Co-precipitation method

This method includes dissolving a salt precursor (chloride, nitrate etc.) in water (or other solvent) to precipitate the oxo – hydroxide with the help of a base. Control of size and chemical homogeneity seems to be difficult to achieve in most of the cases but the use of surfactants, son chemical methods and high – gravity reactive precipitation are considered as noble and viable alternatives in optimizing the resulting characteristics [Suslick et al. 1991; Chen et al. 2000].

Sol-gel methods

This process involves the preparation by precursor hydrolysis of metal oxides, normally alcoholic alcohols in alcoholic solution, resulting in corresponding oxo-hydroxides. Condensation of molecules happens, leading to the polymerization of hydroxyl species and the formation of a thick porous gel. Condensation is accompanied by drying and calcinating to acquire ultrafine porous oxides [Interrante and Hampden Smith 1997].

METAL OXIDES SURFACES

Cobalt Oxide

Cobalt oxide generally exists in three forms as shown below:

CoO

CoO (cobalt monoxide) consists of two interpenetrating fcc sublattices of Co^{2+} and O^{2-} with rocksalt structure (NaCl structure)-These two sub lattices are transferred half of their length along the diagonal body. As shown in Figure1.1, each ion therefore has six of the other ions as its nearest neighbors. There are four Co^{2+} and four O^{2-} ions in each cubic unit cell (not the primitive unit cell). 4.260 Å [Weißmantel and Hamann 1995] is the lattice constant of CoO.

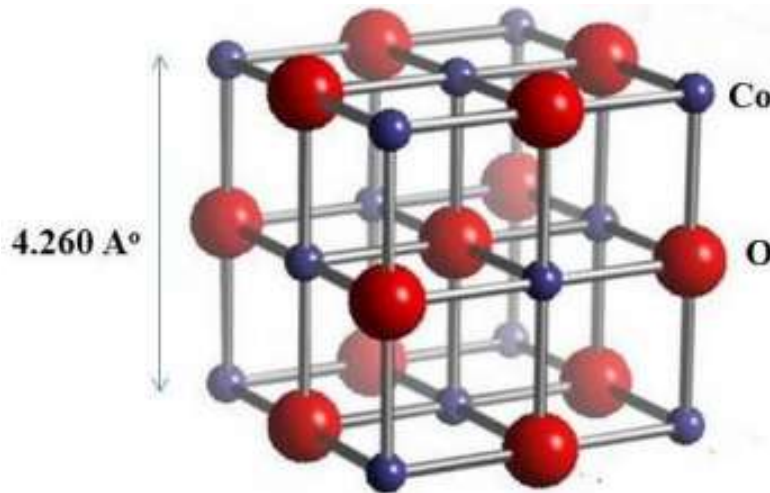


FIGURE1.1: Unit cell of CoO

Co₃O₄

with Co and O atoms in a stoichiometric relationship of Co:O=1:1 is not the only binary oxide phase that forms under readily attainable oxygen partial pressures. Under common ambient conditions, the thermodynamically favored form of the cobalt oxide often is the normal spinel structure Co_3O_4 (Figure 1.2) with a lattice constant $a_0 = 8.080\text{Å}$

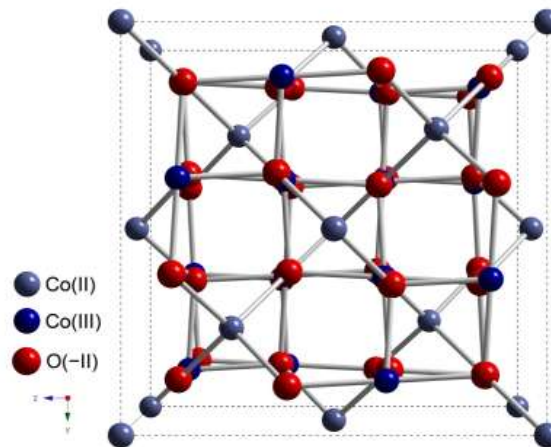
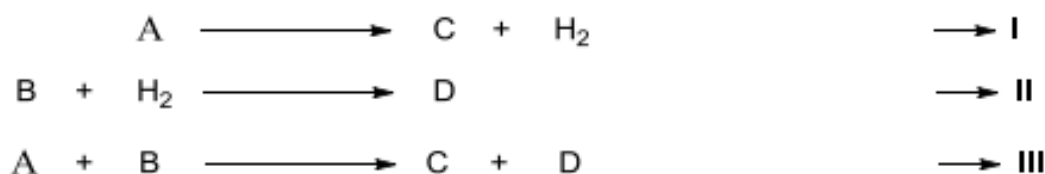


FIGURE 1.2 Unit cell of Co_3O_4 with normal spinel structure

Despite the simple stoichiometry of $\text{Co}:\text{O} = 3:4$, Co_3O_4 with the normal spinel structure is considerably more complicated than CoO with the rocksalt structure. Unlike CoO , there are two kinds of Co ions in Co_3O_4 , tetrahedrally coordinated Co^{2+} (II) and octahedral coordinated Co^{3+} (III). The number of Co^{2+} and Co^{3+} have a ratio of 1:2 ($\text{Co}^{2+}\text{Co}_2^{3+}\text{O}_4^{2-}$). The distance of $\text{Co}-\text{O}$ is 1.929 Å and 1.916 Å for the tetrahedral and the octahedral sites respectively, compared to 2.130 Å in CoO . The unit cell of Co_3O_4 has 8 Co^{2+} , 16 Co^{3+} and 32 O^{2-} ions, which gives a very large unit cell with a total of 56 atoms [Kittel et al. 1993; Kleber 1963]

Catalysis

Catalysis plays a major role in the fields of physics, chemistry and biology. It is fundamentally necessary in the field of chemistry, where at least one of the steps involves catalysts in most chemical processes. The use of catalysts is not restricted only to the scale of the laboratory. Most of the production processes involve/use catalysts in order to get the goods. In the United States, between 1930 and 1980, 60 percent of the 63 major products and 90 percent of the 34 process developments included catalysis, justifying the importance of catalysts in the fuel and chemical industries. Catalytic reactions are preferred because of the reduced quantity of catalysts, unlike other reactions in which all reactants are consumed and more side products are produced. Before 1900, however, only pure components were used as catalysts; multicomponent catalysts were only studied after 1900 and are now widely used in industry. In order to meet the increasing economic and environmental demands, efforts are being made to synthesise new catalysts. In recent years, environmentally friendly catalysts have gained more prominence. Of considerable importance is the production of good active catalysts with a special focus on eco-friendly catalytic materials. Furthermore, cost-effective use of the catalyst is also an important factor. In order to reduce the cost of production in all possible ways, efforts are also being made in this direction. For example, in Scheme 1.1(a) below, reaction I requires dehydrogenation and reaction II is the reaction of hydrogenation.



SCHEME 1.1 (a): General scheme of individual and coupling reactions

In the above scheme, reaction I is generally an endothermic equilibrium process and follows Le-Chatlier's principle whereas reaction II is an exothermic process. When the reactions are performed, the hydrogen released in reaction I will be consumed in reaction II enhancing conversion in reaction I due to Le-Chatlier's principle. Hence no external source for hydrogen is required. Furthermore, the hydrogen produced during reaction I is far more reactive than the molecular hydrogen in gaseous phase [Pramod et al. 2014]. A catalyst is a substance which provides an alternate route of reaction where the activation energy is lower, without actually taking part in the reaction and the process is called catalysis. The working of the catalyst is diagrammatically shown below in Figure 1.3. Catalysts alter the rate of reaction without affecting the chemical equilibrium associated with the reaction.

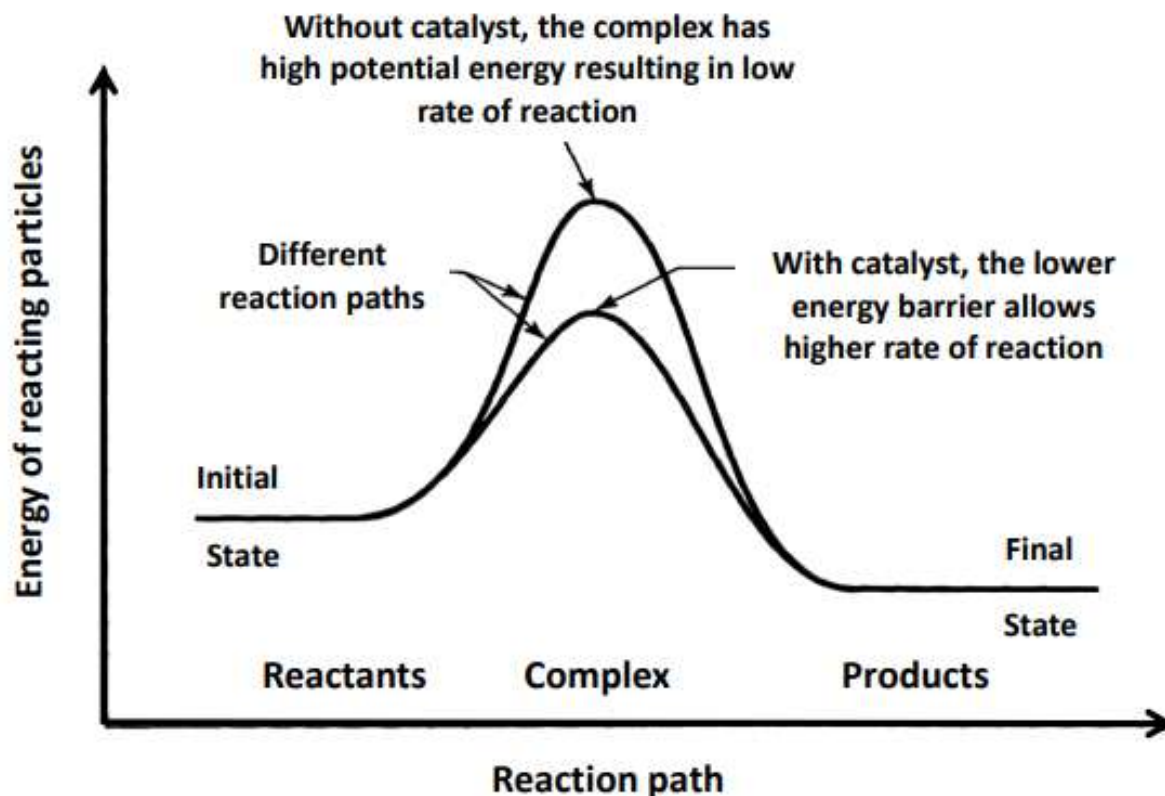


FIGURE 1.3: Role of catalyst

Chemicals and related industries synthesize/manufacture products that need to be recognized and sustained by our modern communities. Many of the chemical and biological modifications involve the use of a product creation catalyst. A catalyst helps to lower the energy barrier and thus allows better product creation control and selectivity. The selection of the correct catalyst and reactor has a significant impact on the process's viability and economics. A catalytic reactor must perform many functions, such as allowing chemical reactions to occur by bringing reactants into intimate contact with active catalyst sites, providing adequate temperature and pressure conditions for sufficient time and enabling products to be safely extracted from the catalyst surface. The requirements of the system should be met, but without sacrificing security, the environment and the economy. A combination of several factors is required for improved technology, such as improved chemistry (thermodynamics, catalysis), improved solvents (supercritical media, ionic liquids), improved atomic quality, water prevention (leaves no waste to be treated) and improved engineering (fluid dynamics, heat mixing and mass transfer), new methods of process intensification, particulate reaction energy

The number of combinations of metal-metal oxides showed significant activity in the oxidation of CO by O₂. Because of the excellent stability, reactivity and activity of Pt/CeO₂, most CO oxidation studies are carried out. Excellent redox behavior (Ce⁴⁺/Ce³⁺), large amount/concentration of oxygen vacancies, substantial oxygen mobility, and high oxygen storage capacity are also observed to assist Pt/CeO₂ in cyclical conditions to act as an effective catalyst for CO oxidation. In terms of nanostructures, faces exposing CeO₂ nanowires and

nanorods (100) and (110) are much more active than CeO₂ nanoparticles with (111) exposed surface for CO oxidation [Zhou et al. 2005]. It is difficult to completely oxidise soot in the case of soot oxidation, because full soot oxidation occurs only after 800°C, which is a difficult task to accomplish under practical reaction conditions. Studies have shown that a better idea for soot oxidation is heterogeneous catalytic oxidation, as molecular oxygen is transferred from the catalyst to soot. Therefore, heterogeneous catalysts such as CeO₂, showing transition/variation in oxidation states (Ce⁴⁺/Ce³⁺), show exceptional soot oxidation activity [Setiabudi et al. 2004; Krishna et al. 2007]. Doping with alkali, transition and noble metals is done in order to increase the amount of reactive oxygen on the surface of CeO₂. Studies have shown, however, that nanocrystalline structures perform better than bulk structures, i.e. nanocrystalline CeO₂ stabilises O₂ as an active superoxide and peroxide species, while CeO₂ bulk stabilises molecular O₂ [Guzman et al. 2005].

CO is also a challenge for the electro-oxidation of alcohols in DAFC (Direct Alcohol Fuel Cells) devices known for their practical applications in transportation and portable devices due to their higher electron density, liquid fuel use (methanol and ethanol), low operating costs and compact design [Carrette et al. 2001, Lamy et al. 2002; Song et al. 2007; Cameron et al. 1987]. CO is produced as an intermediate and during long hours [Lamy et al. 2001], it further poisons the surface of the catalyst. It has been found that metal oxides allow the activation of water at lower potencies. In addition, metal oxides are highly oxophilic, thus helping to lower the potential for electro oxidation of CO to CO₂ in the adsorption of species such as OH [Cuesta 2011]. In combination with carbon, various metal oxide catalysts such as WO₃, RuO₂, CeO₂, MgO, ZrO₂, MoO₃, MoO₂, Nb₂O₅, V₂O₅ and TiO₂ have been identified in this line as promising catalysts for the reduction of CO poisoning. In the waste treatment of farm waste, catalysts also play an important role. Lignocellulose production worldwide is around 1.8 trillion tonnes [Fan et al. 2012], whereas annual crop waste in the form of lignocellulose in India alone is approx. 624 million [Pandey et al. 2009] tonnes. Cellulose (β -1, 4-D-glucose-linked polymer; 40-50 per cent), hemicellulose (C₅ and C₆ sugar co-polymer; 25-30 per cent) and lignin (phenyl-propane macromolecular network; 15-20 per cent) are major components of crop waste [Drummond and Drummond 1996]. The synthesis of significant platform chemicals such as sugars (xylose and arabinose) and furans (furfural and 5-hydroxymethyl fural, HMF) from carbohydrates using solid acid catalysts is one of the best possible ways to treat agricultural waste.

In the rubber/elastomeric industry, catalysts are also used. The major rubber/elastomeric applications are in the production of the tyre/automotive industry. The supply from the rubber industry alone was not sufficient due to the increasing growth rate of the automotive industry. Consequently, requirements for elastomers have been steadily increasing. In synthesising rubber that acts as an alternative to natural rubber, Catalyst plays an important role. The source material for synthetic elastomer production is considered to be conjugated dienes, namely 1,3 butadiene and isoprene. There was no method available before 1954 for the production of polymers with a high degree of structural regularity from conjugated dienes. Butadiene polymerization was carried out using sodium metal, but due to the inferior low temperature resistance [Kennedy 1968] attributed to the presence of different isomeric units in the polymer chain, it did not achieve success. However, it was only after the synthesis of conjugate dienes with the Ziegler-Natta (Z-N) catalyst by stereo specific polymerization that butadiene and isoprene gained commercial interest [Srivastava et al. 2014].

CONCLUSION

At low boiling points, i.e., volatile organic compounds (VOCs), including hydrocarbons, alcohols, aldehydes and ketones, are easily volatile. The presence of these low boiling and readily volatile organic compounds in the air has been the subject of concern as this influence the air quality. In particular, air quality is impaired in their neighbourhood workplaces and habitats. Oil refineries, product storage and distribution sites, pharmaceutical industries, production and formulation units of insecticides, paint and rubber industries, etc. are sensitive sites. Due to spillage or washing of the floor and the cleaning of equipment, these VOCs often contaminate surface water. In recent years, processes have been produced to oxidise VOCs into non-toxic products (CO₂ and H₂O) by their oxidation using noble metal catalysts. For the reaction conditions so far established, which render the processes uneconomical, higher temperatures and noble metal catalysts are required.

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