Size dependent catalysis with CTAB-stabilized gold nanoparticles†

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CTAB-stabilized gold nanoparticles were synthesized by applying the seeding-growth approach in order to gain information about the size dependence of the catalytic reduction of p-nitrophenol to p-aminophenol with sodium borohydride. Five different colloidal solutions of stabilized gold nanoparticles have been characterized by TEM, AFM, UV-Vis, SAXS, and DLS for their particle size distributions. Gold nanoparticles (mean sizes: 3.5, 10, 13, 28, 56 nm diameter) were tested for their catalytic efficiency. Kinetic data were acquired by UV-Vis spectroscopy at different temperatures between 25 and 45 °C. By studying the p-nitrophenol to p-aminophenol reaction kinetics we determined the nanoparticle size which is needed to gain the fastest conversion under ambient conditions in the liquid phase. Unexpectedly, CTAB-stabilized gold nanoparticles with a diameter of 13 nm are most efficient.

Introduction

Size dependent effects of metal clusters have been studied for a long time and are of utmost importance in the gas phase, at surfaces, in colloidal systems and in theory because clusters of a few atoms change dramatically their electronic properties and structure with an increasing number of atoms. Therefore mass selected clusters were utilized to gain information about their electronic and catalytic properties in the gas phase. In addition the photographic process, discovered 170 years ago, was examined in detail with mass selected cluster methods by Wöste et al. in the 1980s. Especially theoretical investigations of small mixed silver–gold systems were used to gain detailed information on the photographic processes taking place in the nanoscopic size regime. Also the non-metal to metal transition was an unsolved problem in those days.

Another advantage of gas phase clusters is the absence of any undesired effects due to a ligand sphere or surface support interactions which affects the desired properties of the cluster. For catalytic purposes the activation mechanism of small molecules (e.g. CH₄, CO, NO) was in the focus of several research groups. Nowadays these findings are used as standard references for more complex systems. Also noble metal clusters with reduced dimensions are of great interest because of their unusually high activity in catalysis with respect to the inactive bulk material. One recent example from the Bernhardt group emphasizes the importance of detailed size dependent studies for catalytic applications for very small clusters with only two gold atoms. Besides the gas phase cluster catalysis investigations another large field of heterogeneous catalysis can be found in the supported metal cluster catalysis research area. The support can be either an oxide or an innocent metal. It turned out in most cases that there is an interference of the metal cluster with the support. Size dependence was also of interest for these systems. Nowadays, supported gold nanoparticles have been extensively studied during the recent years because of their catalytic activity. For heterogeneous catalysis involving gold nanoparticles deposited on metal oxides, size-sensitive catalysis is reported for CO oxidation, propylene oxidation and selective hydrogenation. It has been found by Masatake Haruta that the dependence upon the size of gold nanoparticles on oxide substrates is remarkably strong. Thus this system was tested under a very controlled environment for the oxidation of CO to CO₂.

Catalytic size effects for colloidal nanoparticles at the transition point from heterogeneous to homogenous catalysis are in the focus of on-going research because of the tunability of size, shape, and stabilizer. It is generally accepted that chemistry changes with size. In particular colloidal gold nanoparticles were used to test their catalytic capability in redox reactions like CO oxidation and hydrogenation of various compounds.

Thus there is strong interest in gaining information about the active site of the catalyst, the intermediate structure and the rate determining factor. Therefore gold nanoparticles with well-defined properties (size, shape, polydispersity, and surface chemistry) were used to explore its catalytic performance.

The reduction of p-nitrophenol to p-aminophenol by sodium borohydride in the presence of gold nanoparticles is a standard
system to test the catalytic capability of nanoparticles. Hence, there is a strong interest in gaining more information about the underlying mechanism of the reaction. A first mechanistic insight was provided by Fritz Haber in the late 1890s using electrochemical methods. Generally speaking, the nitro to amino conversion process itself has industrial relevance i.e. for aniline and paracetamol production.

Gold nanoparticles in colloidal solutions so far were used several times to investigate their catalytic capabilities. Moreover, size regime dependent catalysis by gold nanoparticles for the reduction of eosin was reported by the group of Sau. Since colloidal catalysis is influenced by many factors like shape, ligand sphere, material of the nanoparticles and pH value one of the most commonly investigated is the influence of the size of nanoparticles on catalysis.

Size in different phases (gas, surface, colloidal solutions) is straightforward to measure either by mass spectrometry, scanning tunnelling microscopy or scattering of visible light (DLS) or X-rays (WAXS, SAXS, XRD). But the question is if the size per se is the only decisive parameter for catalytic activity.

For example in colloidal nanoparticles the ligand sphere affects strongly the catalytic activity as was found for palladium nanoparticles. The complex intimate interaction between ligand, pH-value and nanoparticle (its size, shape, and surface morphology) covers the activity of gold nanoparticles in the reaction.

Thus we were encouraged to unravel the size dependence in colloidal solutions with CTAB stabilized gold nanoparticles.

**Experimental methods**

**Synthesis of gold nanoparticles**

The gold nanoparticles were synthesized according to Jana et al. with minor changes in order to improve the reproducibility. Each synthesis has been performed at least five times.

**Materials.** Trisodium citrate (Roth), HAuCl₄·3H₂O (Roth), ascorbic acid (Aldrich), NaBH₄·3H₂O (Merck), and cetyltrimethyl-ammonium bromide (CTAB) (Fluka) were used as received. Deionized water was used for all solution preparations. All glassware was cleaned with aqua regia prior to usage. Every glassware was cleaned using “piranha” solution (30 vol% aqueous hydrogenperoxide solution and sulfuric acid (1 : 1)) prior to the functionalization for 4 h at 80 °C. The samples were rinsed with water and stored under ethanol till usage. Prior to the functionalization with 3-mercaptoptriethoxysilane reaction the substrates were dried in a nitrogen stream. The modification was carried out by dipping the glass slides into a 3 weight% solution of 3-mercaptotriethoxysilane in toluene for 20 min at 60 °C. The thiol-capped glass slides were washed with toluene, toluene/acetone (1 : 1), acetone, acetone/ethanol (1 : 1) and ethanol and stored in ethanol until usage. The thiol-capped glass slides were immersed in the solutions of the different nanoparticle sets (seeds, A, B, C, D) for 20 min prior to AFM characterization.

**Preparation of 3.1 ± 0.7 nm gold seeds.** 10 mL aqueous solution containing 2.5 × 10⁻⁴ M HAuCl₄ is mixed with 10 mL aqueous solution containing 2.5 × 10⁻⁴ M trisodium citrate (citrate serves only as a capping agent). Next, 0.3 mL of ice-cold, freshly prepared 0.1 M NaBH₄ solution was added to the solution while stirring. The solution turned orange-red immediately after adding NaBH₄, indicating gold nanoparticle formation. The particles in this solution were used as seeds within 2 h after preparation.

**Preparation of growth solution.** 3 g of solid cetyltrimethyl-ammonium bromide (0.08 M final concentration) was weighed out in a graduated flask. Next, 100 mL aqueous solution of 2.5 × 10⁻⁴ M HAuCl₄ was added to the mixture, and it was heated to about 45 °C until the solution turned to a clear amber colour. The solution was cooled down to room temperature and used as a stock growth solution. Slowly forming crystals of CTAB were re-dissolved by gentle heating prior to usage.

**Seeding growth.** Four sets of 10 mL snap-cap vials were labelled A, B, C, and D. In set A, 7.5 mL of growth solution was mixed with 0.05 mL of freshly prepared 0.1 M ascorbic acid solution. Next, 5 mL of seed solution was added while stirring. Stirring was continued for 10 min after the solution turned wine red. Particles prepared this way were spherical with a diameter of 10.4 ± 0.1 nm.

Similarly, 9 mL of growth solution and 0.05 mL of 0.1 M ascorbic acid solution were mixed as set B, and 1.0 mL of seed solution was added rapidly while vigorously stirring. Stirring was continued for 10 min. The solution’s final colour was deep red. Particles prepared this way were spherical with a diameter of 12.9 ± 0.1 nm. 30 min after preparation these particles were used as seeds in set C.

In the same way as it was done for set B the nanoparticles in the sets C and D were prepared. 9 mL of growth solution was mixed with 0.05 mL of 0.1 M ascorbic acid solution, and 1.0 mL from set B or set C was added while vigorously stirring, respectively. Stirring was continued for 10 min. The final colour of the solution was reddish brown. Particles prepared in this way were spherical with a diameter of 28.1 ± 0.7 nm and 56.4 ± 1.4 nm respectively. This solution was used as seeds in set D 30 min after preparation.

The solutions A, B, C, and D were stable for more than six months due to the presence of CTAB as a particle stabilizer. Each solution (sets A–D) contained 2.5 × 10⁻⁴ M gold (atoms).

**Thiol-capped substrate preparation**

All microscopy slides were cleaned using “piranha” solution (30 vol% aqueous hydrogenperoxide solution and sulfuric acid (1 : 1)) prior to the functionalization for 4 h at 80 °C. The samples were rinsed with water and stored under ethanol till usage. Prior to the functionalization with 3-mercaptoptriethoxysilane reaction the substrates were dried in a nitrogen stream. The modification was carried out by dipping the glass slides into a 3 weight% solution of 3-mercaptoptriethoxysilane in toluene for 20 min at 60 °C. The thiol-capped glass slides were washed with toluene, toluene/acetone (1 : 1), acetone, acetone/ethanol (1 : 1) and ethanol and stored in ethanol until usage. The thiol-capped glass slides were immersed in the solutions of the different nanoparticle sets (seeds, A, B, C, D) for 20 min prior to AFM characterization.

**Size characterization**

**TEM.** Transmission Electron Microscopy grids were prepared by placing 1 μL of the particle solution on a carbon-coated copper grid and subsequent drying at room temperature. Transmission electron microscopy (TEM) images were acquired with a TEM/STEM JEOL 2200 FS. TEM images were from different parts of the grid and with different magnifications. Approximately 50 particles were counted and measured for size distribution using ImageJ software.

**AFM.** Thiol capped glass slides were functionalized with the gold nanoparticles of sets A, B, C, D or seed particles by placing the substrate into an aqueous solution of the selected...
gold nanoparticles for 20 min. After that the glass slides were washed with MilliQ (18 MΩ water) water and dried with N₂.

Results and discussion

Size selected gold nanoparticles have been synthesized reproducibly by the seeding growth approach. The size range between 3.5 and 56 nm (diameter) has been covered by five different colloidal solutions of gold nanoparticles as schematically shown in Fig. 1. This experimental procedure is based on a method previously reported by Jana et al.35

As shown in Fig. 1, the sizes of individual gold nanoparticles vary, but the total concentration of gold (in terms of atoms) in each tested gold nanoparticle solution is kept constant to a value of 2.5 × 10⁻⁴ M gold. This is a necessary basis for comparing catalytic efficiencies of the different size sets. Another important basis for comparing size-dependent catalytic effects is the precise and reliable determination of the actual size and size distribution of the most active nanoparticles. Accordingly, this result and discussion section has been divided into three parts: Size characterization, Catalytic model reaction, and Size dependent catalysis.

Size characterization

All five gold nanoparticle size distributions have been determined by transmission electron microscopy (TEM) (see Fig. 2), atomic force microscopy (AFM), small angle X-ray scattering (SAXS) (see Fig. 3) and dynamic light scattering (DLS) (see also Table 1).

Catalytic reaction

A standard catalytic test reaction was carried out in 4.5 mL PS-disposable cuvettes. 2 mL aqueous solution of 0.1 mM p-nitrophenol was mixed with 1 mL of 0.1 M sodium borohydride solution. The reaction was started with the addition of 50 µL (sets A to D) and 100 µL (seeds), respectively, of the nanoparticles. The reaction was magnetically stirred vigorously to avoid diffusion limitation. Immediately after catalyst addition, time dependent absorption spectra were collected at 5 s intervals for at least 30 min at temperatures between 25 and 40 °C. The background subtraction was done with deionized water as the reference. All spectra were corrected with the average value around 800 nm due to interferences during the catalytic reaction caused by the evolving gas bubbles (hydrogen release).
assessments of colloidal particles. We have seen notable differences (see Table 1).

The decrease of the polydispersity with increasing size is due to the seeding growth process, which is an example of a self-focusing phenomenon of agitation versus diffusion. Therefore, the position and width of the plasmon band maxima remain almost un-shifted.

Moreover the band width of the plasmon absorption band correlates with the decreasing size distribution measured by SAXS and TEM. The plasmon absorption band width for the seed particles is two-times broader than for the gold nanoparticles in set C.

In addition to TEM, SAXS, and UV-Vis we used AFM and DLS. The latter one is widely used in colloidal chemistry for size characterization purposes. Both methods show a reasonable comparability to the TEM and SAXS results. AFM slightly overestimates the mean size for gold nanoparticles in sets A and B. However, the polydispersity observed by AFM measurements is in line with the polydispersity extracted from TEM images (see Table 1). It is most likely that the increased mean size is caused by the thiol-functionalized glass slides. Also for the DLS results we see a similar trend. The DLS data for the solutions of seeds, sets A and B, are slightly smaller than the results obtained by SAXS measurements.

To conclude, the combination of AFM, DLS, TEM, and SAXS for the characterization of colloidal particles forms a strong basis for further catalytic investigations.

### Catalytic model reaction

The catalytic model reaction of p-nitrophenol to p-aminophenol by sodium borohydride with gold nanoparticles was investigated using a standard UV-Vis setup. A stirred solution is of special importance while following spectroscopically the reaction process. Without stirring, only the diffusion rate of gold nanoparticles in the UV-Vis cuvette is detected. This experimental phenomenon of agitation versus diffusion is often underestimated in the literature.

An initially clear solution of p-nitrophenol turns rapidly greenish-yellow upon adding sodium borohydride. An absorption band centred at approximately 400 nm evolves in the UV-Vis spectra and indicates the formation of p-nitrophenolate ions (see also Fig. 4). The intensity of the absorption band correlates with the concentration of the p-nitrophenolate. After the addition of gold nanoparticles, a typical induction period of about 60 to 90 seconds can be observed depending on the size of the gold nanoparticles. The induction time can be assigned to diffusion processes as reported by Ballauff et al. They proposed a Langmuir–Hinshelwood type of mechanism.

### Table 1

<table>
<thead>
<tr>
<th>Method</th>
<th>TEM/nm</th>
<th>SAXS/nm</th>
<th>AFM/nm</th>
<th>DLS/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seeds</td>
<td>3.1 ± 0.7</td>
<td>3.4 ± 0.1</td>
<td>2.6 ± 0.4</td>
<td>3.0 ± 0.8</td>
</tr>
<tr>
<td>Set A</td>
<td>9.3 ± 2.3</td>
<td>10.4 ± 0.1</td>
<td>12.0 ± 1.9</td>
<td>10.1 ± 1.9</td>
</tr>
<tr>
<td>Set B</td>
<td>12.9 ± 0.1</td>
<td>14.1 ± 2.1</td>
<td>12.3 ± 0.9</td>
<td></td>
</tr>
<tr>
<td>Set C</td>
<td>29.1 ± 1.1</td>
<td>28.1 ± 0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Set D</td>
<td>56.4 ± 1.7</td>
<td></td>
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</table>

The results of all four size determination methods are in good agreement for the size and their polydispersity.

TEM, as the common method for nanoparticle characterization, is sometimes affected by post preparation artefacts and local probing and it is cumbersome to make quantitative statements on the particle statistics. However, reliable information on the size and shape of individual nanoparticles is accessible routinely. Fig. 2(i) displays a single spherically shaped gold nanoparticle from set A with an average diameter of 9.3 nm (Fig. 2(iii)). In addition, we quantified the size distribution for the gold nanoparticle seeds to be 3.1 nm (not shown here). The particle size distribution for set C is shown in Fig. 2(iv) with an average size of 29.1 nm. Fig. 2(ii) displays three selected nearly spherically shaped particles of set C. All nanoparticle sets exhibit a narrow size polydispersity. The decrease of the polydispersity with increasing size is due to the seed growth process, which is an example of a self-focusing formation of gold nanoparticles (see also Table 1). This effect of self-focusing was clearly confirmed by applying all four size determination methods.

Further, we have used SAXS as an orthogonal method. While TEM is ex situ and local SAXS is integral and can be applied in situ. It has been shown that SAXS is a robust and readymade method for very reliable and quick evaluations and assessments of colloidal particles. The SAXS data as seen in Fig. 3 provide information on the size and their distribution simultaneously for colloidal particles.

Therefore statements on the whole analysed solution are straightforward. Only for the size distribution (its polydispersity) we have seen notable differences (see Table 1).
UV-Vis absorption spectra of the gold nanoparticle sets A to D and the seed particles.

During typical time intervals of 10 to 60 minutes the intensity of the absorption band decreases almost completely. The rate of the intensity decline (see Fig. 5) depends significantly on the size of the gold nanoparticles. In the course of the reaction a weak, new band around 280 nm evolves. We take this as an indication for the formation of p-aminophenolate. As a catalytic blank system for reference purposes we mix p-nitrophenol with sodium borohydride without the addition of gold nanoparticles. This solution remains unchanged even for many weeks. With the applied excess of sodium borohydride with respect to p-nitrophenol (typically 1000 : 1) this system can be handled under pseudo first order conditions (see Fig. 5). With all this knowledge in mind, the size versus rate dependence can now be examined quantitatively (see Fig. 6).

Size dependent catalysis

There is a huge interest in the literature on the field of size dependent catalysis. Especially gold nanoparticles are very suitable for this kind of investigations. Therefore we have studied the size dependence with the as-synthesized gold nanoparticles.

Fig. 5 shows the dependence of the catalytic reduction signal ratio upon the size of the different gold nanoparticle sets at room temperature. Every nanoparticle set has been synthesized three times and then the catalytic test reaction was repeated ten times for each nanoparticle set to ensure reproducibility. To ensure a quantitative comparison between different sets, the total amount of gold (in terms of mols [12.5 nmol]) has been kept constant for all tested systems and reactions. The least active nanoparticles are, as expected, those of set D with a diameter of 56 nm, which are the largest particles investigated in this study. The value (1.0 ± 0.1 × 10⁻⁴ s⁻¹) of the rate constant of set D is highly reproducible and is in the range of previous literature data. Surprisingly, the nanoparticles with the size of 10 to 13 nm (sets A and B) (2.4 ± 0.1 × 10⁻³ s⁻¹ and 6.1 ± 0.1 × 10⁻³) are much more active for the investigated reaction than the nanoparticle seeds with a diameter of 3.5 nm (1.2 ± 0.1 × 10⁻³ s⁻¹). Gold nanoparticles of sets A and B are on average four times more active than the seed particles. Taking into account a lower amount of particles per volume in set B, with respect to set A and with respect to the seed solution, this effect is very remarkable. Particularly in view of the fact that the increasing size of the gold nanoparticles in the series (seed, set A, set B) is accompanied by a decrease of the catalyst’s surface area (see Fig. 6). To the best of our knowledge, it is observed for the first time that intermediate sizes (13 nm) show the highest activity for the p-nitrophenol to p-aminophenol test reaction. For the reduction of p-nitrophenol to p-aminophenol polymer supported gold nanoparticles were investigated in the size range of 8 to 55 nm. A clear trend has been reported that smaller particles are more active. Our results are in a clear contradiction to these observations. A size dependence was also found for supported gold nanoparticles for CO oxidation. The optimum value is in the range of 2 to 3 nm.

Temperature dependent studies

Moreover, we have carried out the reaction at five different temperatures from 25 °C to 45 °C for activation energy measurements. The p-nitrophenol to p-aminophenol test reaction catalysed by seed particles exhibits activation energies of 48 ± 2 kJ per mole, the nanoparticles in set A 53 ± 3 kJ per mole and the nanoparticles in set B 50 ± 2 kJ per mole. It seems that there is no obvious correlation between the size of the gold nanoparticles and the activation energy for the reduction of p-nitrophenol to p-aminophenol. The apparent activation energies for the same reaction carried out with different...
gold nanoparticles (various shapes, different supports) range from 30 to 58 kJ per mole. In each case, the mechanisms and details of the catalytic reactions are under discussion in the literature.\textsuperscript{31,43}

Catalytic model

In this section, we discuss a model for explaining the observed catalytic size effect. Three factors will be highlighted (size of the molecule, size of the nanoparticle and partial charging of the molecule metal complex).

A first, probably too simplistic ansatz would be to compare the size of the gold nanoparticle with the size of the reacting molecule while considering the adsorption and desorption energies of the \(p\)-nitro- and \(p\)-amino-phenol. Unfortunately, there are neither experimental nor theoretical data available for this specific reaction. Therefore, nitrobenzene might serve as a suitable basis for further discussions. It is also a flat molecule with a similar size as compared to \(p\)-nitrophenol. Moreover, all relevant functional sites are provided by this molecule. It shows the adhesive properties of the phenyllic group. The nitro group serves as the reaction centre. Indeed, experimental studies of adsorption energies and geometries of nitrobenzene on gold (111) show that the preferred adsorption geometry is a “flat lying” nitrobenzene molecule on the surface.\textsuperscript{45} Thus, a minimal surface area provided by gold is required to adsorb \(p\)-nitrophenol. A rough estimate predicts that at least 6 gold atoms are needed for one molecule to adsorb.\textsuperscript{46}

Highly advanced theoretical calculations (DFT with Grimme corrections) for the model system nitrobenzene on gold (111) clearly show that the adsorption geometry of the nitro group onto the metallic surface critically depends on the van-der-Waals correction terms.\textsuperscript{46} Therefore we safely assume that \(p\)-nitrophenol also lies in a flat, parallel orientation on the surface. A plane parallel configuration requires a larger surface area for adsorption. \(p\)-Nitrophenol is at least five times bigger than CO and therefore needs more space at the particle. Hence, the increased optimum for the highest catalytic activity (3 nm for CO oxidation and 13 nm for \(p\)-nitrophenol reduction) can be explained by a convergence of the increasing surface area verse size of the molecule (Fig. 7).

Smaller nanoparticles, for example seed particles, are too small for an efficient adsorption of \(p\)-nitrophenol and the reaction rate is therefore significantly smaller.

A third important factor is the charge transfer during the reduction process. It was shown that the charge transfer between the bulk metallic surface and the N-atom of the nitro group amounts to 0.44 eV.\textsuperscript{46} It is obvious that this charge transfer has dramatic effects on the rate of the catalytic reaction. It must also be considered that the ionization potentials of colloidal gold change with size. The difference between the gold atom ionization potential (9.2 eV) and the gold bulk work function (4.2 eV) is extremely large. In the relevant size region from 10 to 28 nm this change is less dramatic and has been calculated to be 0.15 eV.\textsuperscript{1,48} Thus the charge transfer in the adsorption complex seems to be more important than changes in the ionization potential of the gold nanoparticles which may play a minor role.

![Graph showing calculated surface area of different sized gold nanoparticles](https://example.com/graph.png)

**Fig. 7** Calculated surface area of different sized gold nanoparticles (total amount of gold 12.5 nmol). For this plot in Fig. 6 the SAXS radii (see Table 1) were used to calculate the surface area. The calculation is based on the total amount of gold (12.5 nmol for each set and the seeds) and the density of gold (19.32 g cm\(^{-3}\)).\textsuperscript{47}

Summary

Summarizing, it has been shown that the activity of CTAB-stabilized gold nanoparticles is neither very efficient for the smallest nanoparticles (3.5 nm) nor for the larger ones (28 and 56 nm). Instead, it turned out that CTAB-stabilized gold nanoparticles of an intermediate size (13 nm) are the most active ones in the series of tested systems for the catalytic reduction of \(p\)-nitrophenol to \(p\)-aminophenol. The reaction rate with 6 \(\times\) \(10^{-3}\) s\(^{-1}\) is 60 times higher than the rate of the biggest gold nanoparticles (1 \(\times\) \(10^{-4}\) s\(^{-1}\)) and a factor of 3 to 6 higher than for smaller gold nanoparticles. In order to gain energetic insight into the mechanism, the activation energies of the catalytic reduction have been determined to be in the range of 42–53 kJ per mole. These energies are in good agreement to the values reported by Ballauff et al.\textsuperscript{31} For the same reaction, \(p\)-nitrophenol to \(p\)-aminophenol on supported gold nanoparticles,\textsuperscript{43} a similar activation energy of 38 kJ per mole has been observed.

A first hint into the details and molecular aspects of the reaction mechanism is provided by advanced DFT calculations (including Grimme corrections). It was observed that the molecule to metal adsorption process is accompanied by a significant charge-transfer from the surface to the N-atom of the nitro group. This charge-transfer phenomenon plays a crucial role in enhancing the catalytic efficiency.

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References