Active Sites for Methanol Partial Oxidation on Nanoporous Gold Catalysts

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ABSTRACT: Nanoporous gold is a complex material comprised of a small amount of silver that is the residual from the dealloying process used in its formation. This material activates dioxygen and selectively self-couples methanol. The dissociative adsorption of O₂ and the subsequent

reaction of methanol with the adsorbed atomic oxygen are critical steps in this selective oxidation. The density of sites for O₂ dissociation was determined to be 0.1% of the total surface (3×10^{12} per cm²) using both transient and steady flow measurements. The activation energy for O₂ dissociation was measured to be 5.0 kcal/mol and is similar in magnitude to that on metallic Ag and much lower than expected for Au surfaces. The area-averaged dissociation probability of O₂ at 423 K is $\sim 1 \times 10^{-7}$, commensurate with the active site density and the activation barrier to dissociation. The reactive oxygen is immobile under reaction conditions. The collisional reaction probability of methanol striking an adsorbed O atom is 10^{-4} - 10^{-5} , which corresponds well with the measured turnover frequency for methanol conversion to form methylformate of ~ 160 s⁻¹ at 423 K. Taken together, these results strongly indicate that Ag is an integral part of the active site for O₂ activation and the subsequent activation of methanol.

KEYWORDS Nanoporous gold catalysts, O₂ activation, methanol, TAP reactor, Selective oxidation.

1. Introduction

The discovery that gold nanoparticles supported on reducible oxides are active catalysts for CO oxidation [1] has stimulated intense interest in gold-based chemistry, including investigations of unsupported, nanoporous gold (np(Ag)Au) catalysts. The np(Ag)Au catalysts are a network of metal ligaments and pores with sizes between 20 – 100 nm. Depending on the pretreatment procedure, they are excellent catalysts for CO oxidation[2,3] and the oxygen-assisted coupling of alcohols[4-7]. When pretreated with ozone and reduced in flowing methanol, np(Ag)Au is highly reactive and selective for oxidation of alcohols, including methanol, remaining active for at least several months under reaction conditions and regenerating readily even after storage in air for extended periods[6,7]. Surprisingly, the ozone treatment renders the np(Ag)Au catalyst inactive for CO oxidation after initial reduction.

Key to the design of Au-based catalysts, including np(Ag)Au, is understanding how atomic O is produced from molecular O₂. Adsorbed *atomic* oxygen is the active site for reaction of alcohols, initiating the catalytic cycles for alcohol coupling[4-8]. The nature and density of reactive centers for O₂ dissociation on np(Ag)Au is still a controversial issue. On one hand, the residual Ag is thought to play a critical role [9-13]. Specifically, silver multi-atom (pairs) sites have been proposed as the active sites for O₂ activation over Au-Ag bimetallic systems including both supported AuAg alloy particles and high Ag-loaded np(Ag)Au catalysts[14-16]. The essential role of Ag in O₂ activation is also supported by the qualitative correlation between the total number of surface Ag atoms and the oxygen storage capacity (OSC) for a series of np(Ag)Au catalysts with different surface Ag contents (16.6 at.% - 30 at.%) [10,11]. On the other hand, others have proposed that low-coordinated Au sites, such as edge, step or kink sites, are the sites for O₂ activation and catalytic activity[3,17,18]. This viewpoint is consistent with transmission

electron microscopy (TEM) studies that reveal a high incidence of step and kink sites on the material, which are stabilized by a high content of residual Ag by suppressing (111) faceting kinetics[19]. However, recent studies with extremely pure np(Ag)Au synthesized from an intermetallic AuZr alloy (bulk residual Zr content $\sim 0.03\%$) was inactive for O_2 activation and exhibited very low activity toward CO oxidation (several orders of magnitude lower than np(Ag)Au), which leads to the conclusion that Ag impurities play a key role in the dissociation of O_2 on np(Ag)Au[20].

Herein, we quantitatively measure the activity for activation of O_2 on an np(Ag)Au catalyst in the form of microspheres that contain ~ 1 at.% of Ag (based on *ex situ* EDS), which ensures a surface concentration of Ag much lower than in previously reported work (above 15 at.%) [10,11,14-16,21]. The np(Ag)Au catalyst used in these studies were treated in ozone to activate them for selective oxidation of methanol[7]. The studies herein indicate that Ag is an integral part of the active site for O_2 activation and subsequent reaction with methanol and that the oxygen atoms do not migrate significantly away from the dissociation site under reaction conditions.

2. Experimental

The np(Ag)Au material used in this study was initially activated at 423 K for one hour by exposing to a flow of 30 g/Nm^3 of ozone in a 50% O_2 /He gas mixture at a total flow rate of 50 mL/min in a separate flow reactor[7]. The ozone treatment was followed by exposure to a reactant stream of methanol and O_2 while ramping the temperature from 323 to 423 K[7]. This procedure affords a catalyst with high selectivity and stable activity for complex selective oxygen-assisted reactions at atmospheric pressure. The activated catalyst was then transferred to

the TAP reactor, stabilized in a flow of reaction mixture (10% methanol + 20% O₂ + He) for 2-3 hours at 423 K, evacuated, and then reduced with 100 methanol pulses (10¹⁴ methanol molecules/pulse) before subsequent O₂ pulses. The catalyst was selected from among several activated batches, all of which yield 100 % selectivity of methyl formate product in the steady state flow reactor with reaction rates of 0.067 - 0.083 mmol/s/g-cat- the typical activity.

Fig. 1. SEM image of the np(Ag)Au catalyst after use in pulse experiments.

The ligament size of the freshly prepared np(Ag)Au sample is ~50 nm, which increased to ~150 nm after use in the pulse experiments (Fig. 1), resulting in a BET surface area of 1.4 m²/g (see Supporting Information (SI) for more details). For simplicity the BET surface area was taken to be 2 m²/g. The bulk composition of residual Ag determined by EDS was ~1 at.% (Fig. S1), and XPS showed that the surface Ag content was 6.1 at.% in the as-prepared np(Ag)Au sample and 6.3 at.% after use (Fig. S2 and Table S1). This Ag content is within the typical range of npAu catalysts we have used for selective oxidation reactions under steady state catalytic conditions [4-7]. Transmission electron microscopy reveals that the nanoporous material is comprised of large single crystal grains, resulting from the recrystallization process that accompanies the leaching of silver from the initial AgAu alloy material [22]. The surface of the filaments consist of highly stepped (111)-oriented single crystal planes due to their curvature. No small particle crystallites are observed in the material either with TEM or SEM (Fig. 1).

The pulse experiments were carried out in a commercial TAP-2 reactor[23]. In a typical pulse response experiment a narrow pulse of reactant gas (ca. 3×10^{15} molecules/pulse) was injected into a packed-bed microreactor using a high-speed, magnetically controlled pulse valve. The microreactor used was a quartz tubular reactor with a length of 38 mm and a diameter of 6.35 mm housing an internal thermocouple. The microreactor sits on top of a high-throughput vacuum chamber (10^{-8} to 10^{-9} Torr) containing a RGA200 mass spectrometer, which was used to detect the effluent from the reactor. The npAu catalyst (27 mg, packing length ~ 3 mm) was sandwiched in a thin-zone configuration in the middle of the microreactor packed among inert quartz particles with diameters between 250 and 300 μm . Pulse sizes were chosen to ensure Knudsen flow throughout the reactor (see Fig. S4).

Dioxygen was deposited on this activated catalyst using a series of microsecond pulses of O_2 to then p(Ag)Au at 423 K [10,11,21,23]. The number of O_2 pulses was varied between 1 and 200 in order to determine both the sticking coefficient and the saturation site density. The methanol pulses were generated from a methanol/Ar mixture (approximately 1:4 ratio), which was prepared in a heated blend tank and maintained at a constant total pressure (~ 2.4 atm).

3. Results and Discussion

The active site density of the np(Ag)Au catalyst for O_2 activation was determined by exposing the catalyst at 423 K sequentially to O_2 and $\text{CH}_3\text{OH}/\text{Ar}$ pulses. The amount of adsorbed O formed following a determined number of calibrated doses of O_2 on np(Ag)Au was measured by titrating with 100 pulses of $\text{CH}_3\text{OH}/\text{Ar}$ at 423 K and measuring the amount of formaldehyde produced by the methanol titration (Fig. 2). (See SI for calibration details.) No formaldehyde was produced upon exposure to methanol pulses on the pristine sample, i.e. without prior exposure to O_2 (Fig.

2). Reaction conditions were chosen such that formaldehyde was the dominant product, CO₂ and methylformate being formed in negligible amounts. In the present work only the O on the np(Ag)Au for selective oxidation of methanol was measured; thus only the sites specifically responsible for oxygen-assisted methanol activation were probed. Note that the amount of adsorbed O was also quantified by measuring the total uptake of O₂ during the exposure to the diluted O₂/Ar pulses (Fig. S5). These experiments combined yield a 1:2 ratio of the O₂ uptake to the total amount of formaldehyde formation due to titration of the active O as expected (1:1 ratio of active atomic oxygen to formaldehyde) (Table S2). The advantage of the methanol titration method is that it provides higher sensitivity per pulse for low oxygen uptake.

Fig. 2. The formaldehyde produced by titration of active adsorbed O at 423 K according to the reaction $\text{CH}_3\text{OH} + \text{O} \rightarrow \text{H}_2\text{CO} + \text{H}_2\text{O}$ with 100% selectivity (see SI). The formaldehyde was detected using the $m/z=30$ signal, which was corrected for methanol fragmentation.

The O₂ uptake decreases rapidly as the O₂ dosage increases and then slowly approaches zero as the active sites saturate [24]. Based on the amount of np(Ag)Au (27 mg), its specific surface area after activation (2 m²/g), and the amount of formaldehyde formed at the saturation point (3.1×10^{15} molecules), the maximum concentration of active adsorbed O was calculated to be

6.2×10^{16} O atoms/m² or 4.4×10^{-3} ML, assuming a surface atomic density of 1.4×10^{19} atoms/m² (see SI for detailed analysis).

Fig. 3. a) The amount of adsorbed oxygen atoms by O_2 dissociation on the np(Ag)Au catalyst at different temperatures (a single pulse of O_2 followed by complete titration with pulses of CH_3OH/Ar at each temperature). b) The Arrhenius plot of O_2 activation on the np(Ag)Au catalyst at different temperatures.

The initial dissociative sticking probability of O_2 on the activated np(Ag)Au catalyst at 423 K was determined to be $\sim 1 \times 10^{-7}$ at 423 K (see SI for the derivation). In these experiments, the flow through the pulsed reactor was in the Knudsen diffusion regime (see SI for details)[23]. Quantitative calibration of the O_2 pulse size and transient pressure pulse response in the reactor allows one to calculate the number of collisions of the O_2 molecules with the surface during each pulse. By measuring the number of adsorbed O atoms resulting from a particular exposure, the fraction of the O_2 molecules that dissociated is determined; the initial dissociation probability is derived by using the points in the initial linear portion of the uptake vs. exposure curve [24].

The measured initial dissociation probability on np(Ag)Au is lower than, but on the same order of magnitude, as Ag single-crystal surfaces, Ag powder, or even supported Ag catalysts (Table

1). In a recent work, by titration with CO pulses the average probability of O₂ dissociation on a np(Ag)Au catalyst with a much higher surface Ag content (18.6 at.%) was measured as 2×10^{-4} at 303 K[21]; three orders of magnitude higher than the lower Ag-content microspheres studied here. This difference strongly suggests that increasing Ag content increases the amount of O₂ dissociation[12,25] and produces adsorbed O that is reactive with gaseous CO.

Table 1

Sticking probability of O₂ and saturation coverage of adsorbed O on metal surfaces.

Metal surfaces	Dissociation probability of O ₂	Saturation coverage of O (ML)
Ag(110)	3×10^{-3} at 300 K[26]	0.5 (294 ~ 475 K)[27]
Ag(111)	$\sim 10^{-6}$ at 490 K[28]	0.38 (294 ~ 475 K)[29]
Ag powder	$\sim 10^{-4}$ at 418 K[30]	~ 0.25 at 418 K[30]
Ag/Alumina catalyst	6×10^{-6} at 415 K[31]	0.38 at 480 K[31]
np(Ag)Au (18.6 Ag at.%)	2×10^{-4} at 303 K[21]	Not available
np(Ag)Au (6.3 Ag at.%)	1×10^{-7} at 423 K [This study]	4.4×10^{-3} at 423 K [This study]

Table 2

Apparent activation energies (E_a) of dissociative adsorption of O₂ on metal surfaces determined by theoretical calculations and by experiments.

Metal surfaces	E_a (kcal/mol)	
	Theoretical	Experimental
Ag(110)	12.7[32]	7.8[28]
Ag(111)	18.0[32]	8.3[28]
Au(111)	42.6[32], 51.4[33]	No Activity[34]
Au(110)	19.1[13]	33.4[35] ^a
Au(211)	25.8[36], 21.5[33]	No Activity[37]
Au(321)	23.1[38]	Not Available
Ag _n Au(110)	11.8[13]	Not Available
np(Ag/Au)	Not Available	5.0 [This study]

^a Activation energy of associative O₂ desorption derived from TPD experiments.

The apparent activation energy for O₂ dissociation, E_a , was measured to be 5.0 ± 0.4 kcal/mol (Fig.3). This activation energy on the np(Ag)Au catalyst is comparable to those reported on Ag single crystal surfaces[28] and is significantly lower than those estimated for single crystal Au surfaces (see Table 2). The apparent activation energy (E_a) for O₂ dissociation was measured by determining the amount of O deposited from a *single* pulse of O₂ on the np(Ag)Au catalyst as a function of temperature in the range of 423 K to 473 K. Measurements were made in both ascending and descending order to check the reproducibility of the results. Experimentally,

neither stepped single crystals nor polycrystalline Au surfaces dissociate molecular oxygen even under high temperature or high pressure conditions[34,37,39]. Theoretical calculations show that on pristine gold surfaces, even at stepped sites, the activation energy exceeds 20 kcal/mol (Table 2)[25,33,36,38]. The activation energy determined here for O₂ dissociation on the np(Ag)Au catalyst is actually even lower than those measured experimentally on clean, single crystal Ag surfaces (Table 2).

Table 3

Selective oxidation products formed from dioxygen and ozonepredosednp(Ag)Au. The amounts of products were obtained from summing the mass spectrometer signal of each product formed from all pulses of methanol until the product yield reached zero. The amounts are scaled for detection sensitivity and expressed in arbitrary units.

Oxygen saturation exposure	Formaldehyde (a.u.)	Methyl formate(a.u.)	Total(a.u.)
Dioxygen	1.21	0.18	1.39
Ozone	56.13	3.81	59.94

The reactivity and density of sites was compared for np(Ag)Au resulting from exposure of the activated catalyst to ozone or to dioxygen exposure, respectively, using an O₃ or O₂ flow (1×10^{-6} torr) through the pristine np(Ag)Au at 423 K for 20 min. The fully oxidized sample, was then reduced with 100 methanol pulses in both cases. Conditions were chosen such that formaldehyde was the dominant oxidation product, as was the case for the experiments described above. The saturation coverage of adsorbed atomic oxygen on the npAu, created by dioxygen dissociation, was not high enough in order to produce detectable amounts of methanol consumption, as would be expected from the low site density reported above. However,

formaldehyde was readily detected (Table 3). In contrast for the first 10 methanol/argon pulses following ozone exposure, only carbon dioxide could be detected, due to complete combustion of methanol. More significantly, after the CO₂ production declined, approximately 30 times more partially oxidized products formed compared to the O₂-dosed surface (Table 3). This observation shows that ozone exposure leads to a higher surface density of sites active for selective oxidation, presumably due to greater enhancement of Ag at the surface, due to segregation of Ag from the bulk of the sample, as verified in separate studies [22].

Under atmospheric pressure flow conditions, methyl formate was detected as the predominant product in the TAP reactor with nearly 100% selectivity (Fig. 5), consistent with previous studies[4,5,7]. Furthermore, the measured rate of conversion was in good agreement with that obtained in the initial activation of the catalyst in a separate reactor (see SI). Work in progress in our laboratory suggests that the different selectivity under pulse reaction (nearly 100% formaldehyde under the conditions studied) and steady flow conditions may be due to the significantly different contact times of the reactants and intermediate species with the catalyst surface in the two cases. This difference would be consistent with the sequential nature of the reactions in the catalytic cycle which requires the formation of formaldehyde in advance of methyl formate[40]. Following previously published procedures[41], we find that 15.7% of the methanol is converted in the reactor (Fig. 5). Combining this number, the specific surface area of the catalyst, the mass of catalyst used, and the reactant flow rate, we estimate the turnover frequency to be 159 s⁻¹ at 423 K (see SI for details). Cutting off the methanol feed under steady flow conditions to expose the catalyst to the O₂-only gas (50 mL/min of 20 vol.% O₂ in N₂) results in a surface concentration of active O of 6.1(±1.5)×10⁻³ ML (see SI), which compares well to the saturation coverage obtained by O₂ pulses under lower pressure conditions (see above). This

result indicates that the achievable surface concentrations of active adsorbed O on the np(Ag)Au catalyst are the same under Knudsenflow pulses of O₂ and steady flow atmospheric conditions.

Fig.5. Flow reaction of methanol oxidation over np(Ag/Au) catalyst in the TAP reactor. Reaction conditions: 423 K, 14 vol.% methanol, 20 vol.%O₂, balance N₂, 50 mL/min.

If all the active sites are assumed to be saturated with adsorbed O during the catalytic reaction at atmospheric pressure, the reaction probability of methanol with an active adsorbed oxygen atom under these conditions can be calculated to be $\sim 1 \times 10^{-5}$ from the kinetic theory of gases (for 14% methanol mole fraction in the reactant mixture at 1 atm and 423 K) (see SI for details). Also, the reaction probability of methanol with the adsorbed O can be determined directly from the pulsed titration experiments, such as those in Fig. 2.

For the reaction of methanol with adsorbed O, $\text{CH}_3\text{OH} + \text{O} \rightarrow \text{H}_2\text{CO} + \text{H}_2\text{O}$, the reaction rate can be expressed as

$$r = -\frac{dC_{O_{ad},t}}{dt} = kC_{\text{CH}_3\text{OH}}C_{O_{ad},t}$$

Titration of the active adsorbed O with methanol pulses produces an exponential decay in the amount of formaldehyde formed with total exposure to the methanol as expected from this relationship (Fig.6). It is easily shown(see SI) that the probability for methanol reacting with a site occupied with O is given by

$$P_{reaction} = kC_{site,total} \sqrt{\frac{2\pi m}{k_B T}} = 1.35 \times 10^{-4}$$

where k is the reaction rate constant determined from the exponential decay with methanol exposure (S) ($k = 7.69 \times 10^8 \text{ cm}^3/\text{mol/s}$), $C_{site,total}$ is the surface atomic density of np(Ag)Au catalyst ($1.4 \times 10^{15} \text{ atoms/cm}^2$), m is the molecular weight of methanol (0.032 g/mol), and T is temperature (423 K). This value of 10^{-4} is somewhat higher than determined from the steady state rate under catalytic conditions ($\sim 10^{-5}$); the fact that the collisional reaction rate is lower under steady flow conditions suggests that the active sites may not be fully saturated in the steady state.

Fig.6. Formaldehyde formation during methanol titration on the oxygen-saturated surface of np(Ag/Au) catalyst at 423 K as a function of integrated methanol exposure.

4. Conclusions

The saturation coverage of active adsorbed atomic oxygen on np(Ag)Au microspheres, and thus the active site density for dioxygen activation, is 4×10^{-3} monolayer (ML), an order of magnitude lower than the average bulk silver concentration of 1 at. %[7,42]. Furthermore, the surface-averaged initial collisional dissociation probability for O_2 is $\sim 1 \times 10^{-7}$ is an order of magnitude lower than on Ag(111) and ~ 4 orders of magnitude lower than for Ag(110). The low dissociation probability can be rationalized by the low density of active sites and the measured activation barrier for O_2 dissociation. The low saturation coverage of adsorbed O at 423 K also suggests that the atomic oxygen generated at the active sites does not migrate onto the general surface and remains associated with the site at which dissociation occurs. Further, the collisional reaction probability of methanol striking an adsorbed oxygen atom measured under Knudsen flow on the np(Ag)Au is 10^{-4} and agrees well with that estimated from the rate of the catalytic reaction under operating conditions.

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Notes

The authors declare no competing financial interests.

Acknowledgments

This work was supported as part of the Integrated Mesoscale Architectures for Sustainable Catalysis, an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences under Award # DE-SC0012573. Support for Dr. Fushimi was provided by the U.S. Department of Energy, under DOE Idaho Operations Office Contract DE-AC07-05ID14517.

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