**Catalytically active Au-O(OH)$_x$-species stabilized by alkali ions on zeolites and mesoporous oxides**

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We report that the addition of alkali ions (sodium or potassium) to gold on KLT-zelite and mesoporous MCM-41 silica stabilizes mononuclear gold in Au-O(OH)$_x$-(Na or K) ensembles. This single-site gold species is active for the low-temperature (<200°C) water-gas shift (WGS) reaction. Unexpectedly, gold is thus similar to platinum in creating –O linkages with more than eight alkali ions and establishing an active site on various supports. The intrinsic activity of the single-site gold species is the same on irreducible supports as on reducible ceria, iron oxide, and titania supports, apparently all sharing a common, similarly structured gold active site. This finding paves the way for using earth-abundant supports to disperse and stabilize precious metal atoms with alkali additives for the WGS and potentially other fuel-processing reactions.

**SYNTHESIS**

The water-gas shift (WGS) reaction (CO + H$_2$O → CO$_2$ + H$_2$) is an important reaction for hydrogen upgrading during fuel gas processing. Emerging applications in fuel cells require active, nonprophoric, and cost-effective catalysts. Along with a new group of platinum catalysts with atomically dispersed Pt sites to maximize activity and catalytic efficiency (1–3), the lower apparent activation energy $E_a$ for the WGS reaction (~45 kJ/mol) for gold (Au) versus ~75 kJ/mol for platinum (3–5) can be exploited for low-temperature WGS and other reactions (6, 7). Low-temperature activity is important to avoid multiple-treatment units in practical low-temperature proton-exchange membrane (PEM) fuel cell systems, wherein the deleterious CO should be totally removed for stable, long-term operation. The active Au species in the WGS reaction can be enhanced through various catalyst preparation protocols. Gold nanoparticles (Au NPs) that can form during catalyst preparation are spectator species in these chemistries (3, 4, 10), in that most of the Au atoms are not activated by the support. Thus, the approach of “cage encapsulation” of Au NPs in mesoporous supports is not advantageous for the stability of the active (atomically dispersed) Au sites.

**SYNTHESIS**

Other approaches—for example, AuCl vapor produced by sublimation and introduced into various zeolites (44, 45)—may be used to produce active Au(I)–Cl species for ambient-temperature NO reduction to N$_2$O by CO. Mohamed and Ichikawa (16) have shown that the Au(I) species are the main active sites for the WGS reaction at temperatures as low as 50°C. Because these sites are not chloride-free (Au–Cl bonds exist) and have weak chemical binding to the zeolites, the Au(I) sites are easily reduced to inactive Au(0) and form Au NPs upon increasing the temperature to only 100°C (16). Similarly, low stability of gold on zeolites was found by Gates and coworkers (17, 18). Careful anchoring of mononuclear Au(III) complexes from organometallic precursors produced chloride-free single-atom Au(III)–O–NaY catalytic centers that were active for CO oxidation but unstable at 25°C and 790 torr, losing ~75% of their initial activity after 15 min on stream (17). Finally, attempts to ion exchange gold in zeolites have been unsuccessful. Thus, gold ions in zeolites tend to be unstable toward aggregation in realistic reaction gas environments at temperatures above the ambient, an issue already understood for other inert supports such as silica or alumina, minimally interacting with gold (19). Hence, it is difficult to determine if the gold catalysts operate through similarly structured Au-O(OH)$_x$-species on inert supports as in the Au-CoO$_x$, Au-FeO$_x$, and Au-TiO$_2$ systems (20).

To study the nature of the active gold sites on inert supports, it is important to maximize the number of the atomically dispersed gold sites and fully eliminate the formation of Au NPs. Titania is inferior to ceria and iron oxide in that Au NP growth occurs rapidly on its surfaces (21), but with special ultraviolet (UV)–assisted preparation methods, mononuclear Au-O(OH)$_x$-species is pending.

**SYNTHESIS**

Materials and Methods

Supplementary Text

Figs. S1 to S6

Tables S1 to S15

References (32–44)

$^1$H and $^{13}$C NMR Data

$^1$H and $^{13}$C NMR Spectra

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**SUPPLEMENTARY MATERIALS**

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can be stabilized on titania up to 1.2 weight % (wt %), and the cations remain stably anchored and active for the WGS reaction from ~80°C to 250°C (4). Alkali ion addition was investigated in this work as a means to boost further the number of stable mononuclear Au-O(OH)$_x$ species. This was reported as a successful approach to prepare single-site active Pt-O(OH)$_x$ species. From the Au/Al$_2$O$_3$ catalysts and estimated NaOH wash to remove the adsorbed Cl ions.

We show how to use alkali addition to activate and stabilize atomic Au for the WGS reaction even on inert zeolite (KLTL) and mesoporous [Si]MCM-41 silica materials. The WGS activity was measured to be comparable to that of Au on reducible oxide supports, and good stability was found up to 200°C (Table 1). The $E_a$ values measured for the reaction over alkali-stabilized gold on the inert supports are all $45 \pm 5$ kJ/mol, similar to those on the Au-FeO$_x$, Au-FeO$_{0.5}$, and Au-TiO$_2$ systems (20), indicating that the gold active sites are of similar structure on all support types. It is not straightforward to produce the active alkali-stabilized gold centers on the inert supports, as the alkali ions must interact with the gold, not the support.

Notably, the KLTL-zeolites used here have an abundance of potassium ions (16.8 wt %), but gold addition from a typical precursor (e.g., HAuCl$_4$) by incipient wetness impregnation (IWI) or deposition precipitation fails to prepare an active catalyst. However, using IWI of KAu(CN)$_2$ on the KLTL-zeolites-wetted by solid-state impregnation of KOH (Au:K = 1:10) did form an active Au-K/KLTL catalyst after careful heating (details of the preparation methods are described in the supplementary materials (23)). In another preparation, a gold sol formed from HAuCl$_4$ with NaOH (Au:Na = 1:10) at pH ~14 was used to prepare an active Au-Na/[Si]MCM41 catalyst (table S1). For other supports, including a hydrothermally treated alumina in NaOH, see preparation details in the supplementary materials (23). In another preparation, a gold sol formed from HAuCl$_4$ with NaOH (Au:Na = 1:10) at pH ~14 was used to prepare an active Au-Na/[Si]MCM41 catalyst (table S1). For other supports, including a hydrothermally treated alumina in NaOH, see preparation details in the supplementary materials (23).

The preparation protocols show that the requirement for an active catalyst is that the alkali ions are linked to the atomic gold through –O ligands and not merely be present on the support. It has been widely reported that the support plays a crucial role in the WGS reaction, providing facile dissociation of water molecules to supply –OH species to the vicinal gold sites where CO is adsorbed (24), but the active sites were not resolved. These may still involve just the Au-O(OH)$_x$ species attached to the support through –O ligands. We present evidence here for the latter by surrounding the gold atom with a large number of alkali ions (8 to 10) of Na or K ions through –O ligands. The choice of the supporting surface (zeolite, silica, alumina, etc.) is then unimportant for the chemistry.

The lack of sensitivity of $E_a$ for the WGS reaction on the type of support is a strong first indication of a structurally similar gold active site present on all supports. Corroborating this finding, kinetics measurements found that the reaction order for H$_2$O is 0.7 to 0.8 for all the catalysts (with or without alkali) used in this work (fig. S2), demonstrating that the role of water is common on all the gold catalysts. The alkali addition modifies the support properties at higher temperatures; for example, after a...
thermal treatment to 600°C, Amenomiya and co-workers found that alkalized alumina was activated for the WGS reaction above 400°C with $E_A$ of ~80 kJ/mol (25, 26).

CO temperature-programmed reaction (TPR) tests were conducted to titrate the WGS-active hydroxyls on the alkali-stabilized gold sites (up to 350°C) (Table 1, table S2, and fig. S3). The presence of alkali markedly increased the amount of these hydroxyls, and correspondingly the overall WGS activity of the catalyst within the same temperature window. These hydroxyls are regenerable, as shown by consecutive CO-TPR cycles with intermittent rehydration of the catalyst at 25°C (fig. S3). In the absence of gold, the addition of K⁺ only provides trace amounts of dry [O] through the surface transformation of –OK to K₂O (27). With the gold present, as in Au-K/KLTL, gold associated with the potassium shows a large amount of CO₂ formation from active –OH species corresponding to a Au:K atomic ratio of 1:8. This was accompanied by the production of a large amount of H₂ (1/2 of CO₂) from the –OH species (fig. S3). Notably, from the samples with fully dispersed gold (0.25Au-K/KLTL and 0.25Au-Na/[Si]MCM41) and earlier reports (4), we found that the total activity is proportional to the number of the surface –OH species, whereas the activity per gold atom (turnover frequency) is the same for all gold catalysts irrespective of the support (fig. S4). The Au-K/KLTL sample also shows good stability in 100 hour-long operation in a reformate-type gas mixture (fig. S5).

Electron microscopy studies revealed that alkali ion addition markedly increased the dispersion of gold on all the inert supports that we investigated in this work (Table 1, Fig. 1, and figs. S6 to S9). For example, 72% of the gold counted in the images was present as isolated atoms away from each other on the surface of the 0.25Au-Na/[Si]MCM41 sample (Fig. 1 and fig. S6). A minority of subnanometer gold clusters present on the same sample did not have the packed gold atom structure of Au NPs. These species appear to comprise a few atoms of gold anchored close to each other but nonaggregated. The presence of the surrounding alkali atoms could not be determined by imaging because of the low contrast of these light elements. EXAFS analysis under in situ conditions for the working catalysts further confirmed that the gold species were atomically dispersed and associated with alkali ions before and after reaction (table S3 and fig. S10). For both the KLTL-zeolite and [Si]MCM41-supported samples, the Naₓ-Oᵧ linkages to gold effectively reduced the Au-Au coordination number from 11 or 12 to the 3 or 4 range, which means that 100% dispersion of Au had been achieved (19). Although microscopic analysis (transmission electron microscopy or scanning transmission electron microscopy) provides a number-weighted particle distribution, the volume-weighted distribution provided by EXAFS can behave almost linearly for the reaction rate measurements is less than 10%. The $R^2$ for the linear fit is 0.9927.

Along with the EXAFS results showing an enrichment of the Au-O shell for the alkali-containing samples, in situ x-ray absorption near-edge structure spectra (fig. S11) and x-ray photoelectron spectroscopy data (fig. S12) show the cationic nature of the gold species, whereas the alkali-free, catalytically inactive samples contain metallic Au NPs exclusively. The extra K⁺ ions stabilizing the Au-O site in the Au-K/KLTL sample are different from the ion-exchanged K-O-Al sites in the as-received KLTL zeolite,
but are associated with –O (28), –OH, and H₂O in their vicinity (29), as indicated by the K₂p x-ray photoelectron spectra (fig. S12). These results demonstrate the substantial interaction between gold and potassium through oxygen bonding.

We thus propose a cationic gold-centric active site [Au-O(OH)]⁻ species for the WGS reaction that is stabilized by several alkali ions via -O- linkages. To gain further insights, we used density functional theory (DFT) calculations, performed in the framework of ab initio molecular dynamics (30), by using the VASP code (31) (details of the computational methods are described in the supplementary materials). To create candidate structures for the Au-O(OH)ₓNaₙ₊ clusters, we began by inspecting a series of AuNaₙ clusters (x = 1 to 10, without oxygen). Out of these, the AuNa₉ precursor was selected for further studies because of its high stability (9 is the maximum number of Na atoms that can fit in a single shell around Au; beyond 9, additional Na atoms must be accommodated in a second shell around the gold atom; see supplementary materials for details) and because its Na:Au ratio closely matches the experimental facts/environment. To create the cationic gold species detected experimentally and to account for the involvement of oxygen in the active site, electron-withdrawing groups (O/OH) were then added in the form of adsorbed CO and the O/OH groups bound on the threefold “Na₉” sites that surround the gold atom offers the possibility for facilitating COOH formation, a critical intermediate in the WGS reaction (34). An analog of this structure was recently proposed for single gold atoms stabilized on uncapped oxygen and surrounded by Fe(III) cations on Fe₂O₃(111) surfaces (29). Notably, the catalytic activity of Au on iron oxide (35) is similar to that of Au in the alkaline-stabilized structure reported here, as shown in Fig. 3.

In Fig. 3, we scaled the steady-state reaction rates by the amount of gold loading for the atomically dispersed gold catalysts studied here, and for other gold catalysts reported to comprise only atomic gold on other supports e.g., after leaching of gold particles – and cast them in terms of a turnover frequency (TOF) in an Arrhenius plot. In addition to the similar Eₚ values, the close-to-TOF’s over gold catalysts prepared on different supports and from different precursors, and subjected to different treatment methods, is noteworthy. With these findings, we conclude that, being structurally similar as on CeO₂, Fe₂O₃ and TiO₂, single-site cationic Au-O(OH)⁻ species, stabilized by a number of alkali ions in the form of AuOₓ(OH)ₓNaₚ, clusters, may be formed in appreciable amounts on inert supports. These species are highly active for the WGS reaction, the single gold atom maximizing the catalytic efficiency.

**REFERENCES AND NOTES**

23. Supporting materials are available on Science Online.

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**SUPPLEMENTARY MATERIALS**

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Figs. S1 to S13
Tables S1 to S4
References (36–40)

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