***Graphical Abstract**

Water co-catalyzed selective dehydrogenation of methanol to formaldehyde and hydrogen

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Abstract

The non oxidative dehydrogenation of methanol to formaldehyde is considered a promising method to produce formaldehyde and clean hydrogen gas. Although Cu-based catalysts have excellent catalytic activity in the oxidative dehydrogenation of methanol, metallic Cu is commonly believed to be unreactive for the dehydrogenation of methanol in the absence of oxygen adatoms or oxidized copper. Herein we show that metallic Cu can catalyze the dehydrogenation of methanol in the absence of oxygen adatoms by using water as a co-catalyst both under realistic reaction conditions using silica-supported PtCu nanoparticles in a flow reactor system at temperatures below 250 °C, and in ultra-high vacuum using model PtCu(111) catalysts. Adding small amounts of isolated Pt atoms into the Cu surface to form PtCu single atom alloys (SAAs) greatly enhances the dehydrogenation activity of Cu. Under the same reaction conditions, the yields of formaldehyde from PtCu SAA nanoparticles are seven times higher than on the Cu nanoparticles, indicating a significant promotional effect of individual, isolated Pt atoms. Moreover, this study also shows the unexpected role of water in the activation of methanol. Water, a catalyst for methanol dehydrogenation at low temperatures, becomes a

reactant in the methanol steam reforming reactions only at higher temperatures over the same metal catalyst.

Introduction

Formaldehyde (CH_2O) is an important commodity chemical and is extensively used as the starting material for the synthesis of a large number of industrial chemicals such as ethylene glycol, dyes, drugs, and plastics [1]. It is expected that the global formaldehyde production will exceed 52 million tons per year in 2017 [2]. In industry, the majority of formaldehyde is produced by the oxidative dehydrogenation (ODH) of methanol over iron-molybdenum mixed oxide and silver based catalysts [3, 4]. However, in the ODH process a larger fraction of methanol is wasted in the production of by-products such as water, carbon monoxide, dimethyl ether, carbon dioxide and formic acid. Since the main by-product of non-oxidative dehydrogenation of methanol is hydrogen, it is a promising approach for obtaining formaldehyde along with hydrogen, and eliminating other by-products.

It has been reported that methanol can be dehydrogenated to formaldehyde and hydrogen without any catalyst at high temperatures ~ 1173 K [5], but the yield of formaldehyde is less than 20% and the selectivity is less than 43% at the reported conditions. Therefore, an active catalyst is needed to catalyze methanol dehydrogenation more efficiently and selectively at a much lower reaction temperature. The non-oxidative dehydrogenation of methanol to formaldehyde has been extensively studied on bulk and supported transition metal oxides including CuO [6, 7], AgO [8, 9], and ZnO [10, 11]. However, these catalysts have been shown to deactivate after a few hours of reaction, likely as a result of metallic particle formation on the support surface through the reduction of the metal oxide catalytic phase [3, 6-10]. In other words, the reductive environment in the methanol dehydrogenation reaction leads to fast deactivation of oxygen-containing catalysts. Once these catalysts lose their oxygen, they are not active for the non-oxidative dehydrogenation of methanol [12]. Therefore, a different metal particle preparation is in order to investigate methanol dehydrogenation in the absence of any oxygen, which is the subject of this work.

Extensive ultra-high vacuum (UHV) studies on the interaction of methanol with various metal single crystal surfaces generally agree that either oxygen adatoms or metal oxides are required to facilitate the dehydrogenation of methanol to formaldehyde and water [13-21]. Only on a very highly stepped Cu(210) single crystal surface, Chen and Masel observed significant conversion of methanol to formaldehyde in the absence of oxygen [22]. To the best of our knowledge no metallic nanoparticle catalysts have been reported to effectively catalyze the dehydrogenation of methanol at low temperatures. Surprisingly, as we reported in recent UHV work, adsorbed water molecules on the Cu(111) surface can catalyze the dehydrogenation of methanol to formaldehyde in the absence of atomic oxygen and the reaction can be further promoted by isolated Pd atoms in Cu(111) [13]. Furthermore, we hypothesized that the low temperature desorption of H_2 observed on isolated Pd atoms inhibits the high temperature recombinant desorption of methanol from methoxy and H. Using scanning tunneling microscopy (STM), we observed hydrogen bonded methanol-water clusters that can assist in the dehydrogenation of methanol to form methoxy on Cu(111). The methoxy remains on the surface until it further dehydrogenates to formaldehyde at higher temperatures. Using Au (111) surfaces, Mullins and co-workers have demonstrated the exchange of H with either water or methanol and found an increased stability of H adatoms in the presence of water [23, 24]. This water-catalyzed dehydrogenation of methanol opens a new route for the production of formaldehyde and hydrogen in oxygen-free environments using metallic Cu-based catalysts. These findings are also fundamentally important when considering the mechanism involved in the methanol steam reforming reaction that produces CO_2 , and H_2 , where the dehydrogenation of methanol to formaldehyde is the first elementary step [25].

Pt is one of the most widely used transition metal catalysts due to its superior activity for many catalytic reactions. However Pt is very expensive and scarce in nature which imposes major limitations on its practical application in catalysis. One solution is to design catalysts with single

dispersion of Pt atoms necessary to catalyze a target reaction. Recently, development of catalysts with single-atom dispersion of a precious metal which is highly active and selective in the production of targeted products has attracted considerable attention [26-28]. Various “single- site heterogeneous catalysts” containing atomically dispersed active metal species have been reported to be high active for many catalytic reactions [29-34]. For example isolated Pt and Au cations stabilized by -O bonds on various supports supplying vicinal -OH groups have been reported as the active sites for the water-gas shift reaction [29, 30]. Atomically dispersed Au atoms in metallic Ni have been shown to dramatically suppress carbon deposition in the steam reforming of methane [33]. Single Pd and Pt atoms in metallic copper hosts catalyze selective hydrogenation reactions [31, 35].

In the current work we extend the UHV study of water-catalyzed methanol dehydrogenation to supported PtCu SAA nanoparticles; while we also explore the reactivity of PtCu(111) SAA model catalysts. We show here for the first time that metallic Cu nanoparticles can catalyze the non-oxidative dehydrogenation of methanol under realistic reaction conditions by using water as co-catalyst. The addition of small amounts of highly dispersed isolated Pt atoms in Cu greatly promotes the water-catalyzed dehydrogenation rate for model surfaces and supported nanoparticles. Additionally, we compare PtCu and PdCu SAA nanoparticles and show a more pronounced promotional effect for PtCu catalysts.

Experimental

PtCu SAA nanoparticles with various Pt concentrations were synthesized through the galvanic replacement (GR) method and a wet chemistry approach was followed as described in detail in our recent publications [35, 36]. Here, we give a brief overview of the procedure. First, the metallic Cu nanoparticles were prepared and supported on silica. Under nitrogen protection, a 0.1 M solution of ascorbic acid was added to an aqueous solution of $\text{Cu}(\text{NO}_3)_2$ and PVP (200:1

molar ratio of Cu to PVP). The solution of NaBH_4 (0.1 M) was added to the Cu/PVP solution dropwise. The solution turned to an opaque brown suspension after the addition of NaBH_4 . Fumed silica with surface area $200 \text{ m}^2/\text{g}$ was suspended in deionized water under constant stirring and added to the Cu NPs colloidal solution dropwise. Afterwards, the solution was kept under nitrogen protection and constant stirring for 30 min before it was filtered and washed with deionized water several times. The resulting materials were dried in vacuum for 12 h, and calcined in air to 350°C for 4 h. The addition of Pt atoms to Cu nanoparticles was achieved through GR, which was performed in an aqueous solution at 80°C with nitrogen protection and constant stirring. Designed amounts of $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ (Sigma-Aldrich) were added to a suspension of Cu nanoparticles in an aqueous solution containing 2 mM HCl. After 20 min reaction, the obtained material was filtered and washed with deionized water several times at 60°C , and then dried in vacuum at 60°C for 12 h. The Pt loading was confirmed by inductively coupled plasma (ICP) analysis.

X-ray powder diffraction (XRD) patterns were collected on a PANalytical X'Pert Pro instrument using nickel-filtered Cu $K\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). The measurements were taken at 45 kV and 40 mA in a continuous mode. Data was collected for 2θ between 25° and 80° . Aberration-corrected high-angle annular dark-field (HAADF) STEM images of supported PtCu SAA nanoparticles were obtained with a JEOL 2200FS-AC STEM/TEM system at Oak Ridge National Laboratory. EDS imaging was collected with a Bruker-AXS 30 mm^2 silicon-drift detector system, which was operated at 200 kV for all imaging and EDS work.

In-situ Extended X-ray absorption Fine Structure (EXAFS) measurements were performed at beamline 12-BM at Argonne National Laboratory. EXAFS data of PtCu SAAs at the Pt L_3 -edge in fluorescence mode were collected at room temperature. All samples were reduced in H_2 *in situ* prior to the measurements. The EXAFS data of Pt metal foil was also collected in the reference mode for X-ray energy calibration and data alignment. Approximately 10 consecutive scans were

collected for each sample to improve the signal-to-noise ratio. EXAFS data processing and analysis were performed using the IFEFFIT package.

Methanol dehydrogenation activity on silica supported Cu nanoparticles and PtCu SAA nanoparticles was evaluated in a fixed-bed flow reactor tests at atmospheric pressure. Typically 100 mg sample was loaded into a U-shaped quartz reactor between two layers of quartz sand and packed in between two quartz wool plugs. The catalyst was heated in a furnace equipped with a temperature controller. The temperature of the catalyst was measured with a K-type thermocouple reaching the top of the catalyst bed. Prior to testing, the catalysts were first reduced *in-situ* under a flow of H₂ (10% in argon) with a flow rate at 10 mL/min at 300 °C for 60 min. The typical reaction gas composition was 3% methanol and 3% water balanced in He, using a flow rate of 10 mL/min He. The effluent gas was monitored online by a residual gas analyzer (SRS RGA 200). Methanol, formaldehyde, H₂, CO, and CO₂ were monitored by $m/z = 31, 30, 2, 28, \text{ and } 44$ respectively. In addition, in the case of formaldehyde, the contribution from the methanol fragment was subtracted from the original $m/z = 30$ signal prior to further processing.

PtCu SAA model catalysts were probed using temperature programmed desorption/reaction (TPD/R) and scanning tunneling microscopy (STM) experiments in multiple UHV chambers with base pressures $<1 \times 10^{-10}$ mbar. Cu(111) single crystals were cleaned with cycles of Ar⁺ sputtering (1.5 keV, 15 μ A) and annealing to 700 K. The roughened Cu(111) surface was prepared without the final anneal to 700 K. Pt was deposited using a flux monitored EFM 3 electron beam evaporator (Focus GmbH). Pt was deposited at a flux of 0.02 monolayer (ML) min⁻¹ while holding the Cu(111) sample at 380 K. STM images of Cu(111) and PtCu(111) SAA were acquired using a variable-temperature STM (VT-STM) (Omicron NanoTechnology) at room temperature. A low-temperature STM (LT-STM) (Omicron NanoTechnology) was used to image the roughened Cu surface at 5 K due to the high mobility of Cu atoms at step edges.

TPD/R experiments were performed in another chamber where the model catalysts were cooled to 85 K with liquid nitrogen before reactants were deposited. A linear heat ramp of 1 Ks⁻¹ was applied and desorbing species were detected with a quadrupole mass spectrometer. Methanol (Alfa Aesar, ultrapure HPLC grade 99.8%), water (deionized H₂O), and methanol-D (Sigma-Aldrich, 99.5%) were further purified via freeze-pump-thaw cycles prior to deposition via a high precision leak valve. All exposures are quoted in Langmuirs (1 L = 1*10⁻⁶ torr × 1 sec). Pt surface coverages and Cu step densities were quantified by CO (99.99% Airgas) titration after saturating the surface with CO (10 L). CO desorption from Cu terraces occurred at <200 K, Cu step sites at 205 K, and Pt sites at >300 K.

Results and discussion

Inspired by the interesting finding of water-catalyzed methanol dehydrogenation on Cu(111) and Pd/Cu(111) SAA model catalysts [13], we prepared silica supported Cu nanoparticles and PtCu SAA nanoparticle catalysts and examined their catalytic performance for methanol dehydrogenation in the presence of water under realistic reaction conditions. As discussed below, the atomic distribution of Pt atoms on the Cu surface was confirmed by STEM, EDS, and EXAFS analysis.

Fig.1 XRD patterns of as-synthesized silica supported Cu nanoparticles and $\text{Pt}_{0.01}\text{Cu}$ SAA nanoparticles before and after the water-catalyzed methanol dehydrogenation reaction.

Fig. 1 shows the XRD patterns of as-synthesized silica supported Cu nanoparticles (bottom trace), as-synthesized silica supported $\text{Pt}_{0.01}\text{Cu}$ SAA nanoparticles (middle trace), and silica supported $\text{Pt}_{0.01}\text{Cu}$ SAA nanoparticles after the water-catalyzed methanol dehydrogenation reaction (top trace). The XRD pattern of the supported Cu nanoparticles shows metallic Cu diffraction peaks, (111), (200) and (220) [37]. A rather broad peak centered at 37° is also present, which is attributed to the (111) diffraction of Cu_2O [37]. The appearance of a small Cu_2O peak is expected since the Cu_2O phases are thermodynamically more stable than metallic Cu nanoparticles [37, 38]. Prior to reactivity testing, the oxide was removed via reduction in a H_2 atmosphere. XRD patterns of as-synthesized silica-supported $\text{Pt}_{0.01}\text{Cu}$ SAA nanoparticles show no observable difference as compared to Cu nanoparticles, indicating that introduction of small amounts of Pt through GR does not change the lattice structure of the Cu nanoparticles. Moreover, the XRD pattern of supported $\text{Pt}_{0.01}\text{Cu}$ SAA nanoparticles after the reaction is preserved, suggesting that the water-catalyzed methanol dehydrogenation reaction does not alter the lattice

structure of Cu. In all three cases, the average crystallite size of Cu was estimated to be ~ 14 nm as determined by the Scherrer equation.

Fig. 2 ac-HAADF-STEM image of a typical region of the $\text{Pt}_{0.01}\text{Cu}/\text{SiO}_2$ sample. The sample was pre-reduced in H_2 at 350°C . Some of the isolated Pt atoms are highlighted by white circles.

An ac-HAADF-STEM image of the silica-supported $\text{Pt}_{0.01}\text{Cu}$ SAA nanoparticles is shown in Fig. 2. The sample was pre-reduced in H_2 atmosphere at 350°C . The isolated Pt atoms are brighter than the Cu areas in the dark field STEM image. Thus, we can identify the isolated Pt atoms from their higher brightness compared to their surrounding area. The white circles highlight some of the isolated Pt atoms. Therefore the STEM imaging supports the formation of isolated Pt atoms in Cu. In addition, Fig. 3 shows the elemental mapping by energy dispersive X-ray spectroscopy (EDS) of the silica-supported $\text{Pt}_{0.01}\text{Cu}$ SAA nanoparticles and the silica support. The EDS sample was mounted on a carbon-film-coated Be grid. EDS clearly shows that Pt was only distributed on the Cu nanoparticles and not on the silica support by comparing the elemental maps of Pt and Cu.

Fig. 3 (A) Bright-field STEM image of $\text{Pt}_{0.01}\text{Cu}/\text{SiO}_2$ SAA nanoparticles. (B) O, (C) Si, (D) Cu and (E) Pt elemental maps obtained from the same region on the sample. (F) EDS of the sample. (G) EDS spectra obtained from a Cu nanoparticle (region A), and (H) EDS spectra obtained from the silica support (region B). The EDS sample was mounted on a carbon-film-coated Be grid.

Fig. 4 Pt L₃-edge EXAFS data of as-synthesized silica supported Pt_{0.01}Cu SAA nanoparticles. The sample was pre-reduced in-situ with H₂ at 300°C prior to collecting the data at room temperature.

Table 1. Quantitative analyses for Pt-Pt and PtCu contributions to the EXAFS data.

Samples	Shell	CN ^[a]	R (Å) ^[b]	σ^2 (Å ²)
Pt foil	Pt-Pt	12	2.77	0.0054
PtCu/SiO ₂	Pt-Pt	0		
	PtCu	10.6 ± 4.1	2.59 ± 0.01	0.0042

[a] CN, coordination number; [b] R, distance between absorber and backscattered atoms.

EXAFS data of the silica supported Pt_{0.01}Cu SAA nanoparticles are shown in Fig. 4. The sample was pre-reduced in-situ with H₂ at 300 °C for 1h and cooled down to room temperature in a H₂ atmosphere prior to collecting the EXAFS data at the Pt L₃-edge in fluorescence mode at room temperature in a H₂ atmosphere. Further quantitative analysis revealed that there is no Pt-Pt bonding in the silica supported Pt_{0.01}Cu SAA nanoparticles, as shown in Table 1. The EXAFS data therefore clearly confirms the atomic distribution of Pt atoms in the Cu surface agreeing with the STEM characterization of the silica supported PtCu SAA nanoparticles. On the other hand,

the Pt-Cu coordination number (CN) is 10.6 for $\text{Pt}_{0.01}\text{Cu}/\text{SiO}_2$, which is between the CN of the bulk (12) and surface (9), inferring that Pt atoms reside in both the surface and bulk. Though galvanic replacement method exchanges surface atoms, the samples have been pre-reduced in-situ at 300°C prior to the EXAFS measurements. At this temperature the Pt and Cu atoms may have significant mobility to diffuse into the bulk of the nanoparticles. Due to the error in CN measurements, we cannot conclude the absolute distribution of Pt in Cu host based on the EXAFS characterization.

Fig. 5 TPSR of methanol on silica supported $\text{Pt}_{0.01}\text{Cu}$ SAA nanoparticles. Reaction conditions: 100mg catalyst, 13% methanol balanced in He, He flow rate 10mL/min. During the reaction, the gas concentration of H_2 increased from 0.7% to 12%, and the concentration of CO increased from 1% to 7%.

We first examined the dehydrogenation of methanol in the absence of water on the silica-supported Cu nanoparticles and $\text{Pt}_{0.01}\text{Cu}$ SAA nanoparticles. Fig. 5 shows the temperature-programmed surface reaction (TPSR) of methanol on silica supported $\text{Pt}_{0.01}\text{Cu}$ SAA nanoparticles in the absence of water. No formation of formaldehyde was observed up to 400 °C. Above 350 °C, the full decomposition of methanol to H_2 and CO was observed. The change of the H_2 and CO concentrations follows the 2:1 H_2 to CO stoichiometric ratio in the methanol decomposition reaction. Similar TPSR data of methanol on silica-supported Cu nanoparticles were obtained (not shown here). Therefore the TPSR of methanol indicates that both PtCu SAA nanoparticles and

Cu nanoparticles are not active in the dehydrogenation of methanol to formaldehyde in the absence of water.

Fig. 6 TPSR of methanol in the presence of water (water:methanol = 1:1) on silica supported Cu nanoparticles (A) and on silica supported Pt_{0.01}Cu SAA nanoparticles (B). Reaction conditions: 100mg catalyst, 3% methanol and 3% water balanced in He, He flow rate 10mL/min.

Fig. 6 shows the TPSR of methanol on silica supported Cu nanoparticles (A) and on silica supported Pt_{0.01}Cu SAA nanoparticles (B) in the presence of water. In both cases, the water to methanol ratio was kept at 1:1. Clearly, formaldehyde is formed in both cases. The contribution of formaldehyde from the methanol fragment in the mass spectrometer was subtracted from the original $m/z = 30$ signal prior to the product analysis. At 230 °C the yield of formaldehyde on Cu nanoparticles is ~0.5%; while the yield of formaldehyde on Pt_{0.01}Cu SAA nanoparticles at is ~7%. At lower Pt loadings, a lower yield of formaldehyde (3%) was observed for Pt_{0.003}Cu SAA nanoparticles indicating that as expected, a higher concentration of single Pt atoms in Cu increases the conversion (Table 2). The formation of CO and CO₂ at 230 °C is negligible; hence the selectivity to formaldehyde at 230 °C on supported Pt_{0.01}Cu SAA nanoparticles approaches 100%. Higher Pt concentrations such as nanoparticles of Pt_{0.1}Cu, catalyzed the full decomposition of methanol to CO and H₂ under the same reaction conditions (not shown here). This result is

consistent with the formation of Pt clusters or nanoparticles, which are very active for the decomposition of methanol [39].

Table 2. The yield of formaldehyde at 230 °C from various catalysts operating at different water to methanol ratios

Sample	Water to methanol ratio	Reaction conditions	Formaldehyde yield
Cu/SiO ₂	1:1	100mg catalyst, 3% methanol, 3% water, 10mL/min	0.5%
Pt _{0.003} Cu/SiO ₂	1:1	100mg catalyst, 3% methanol, 3% water, 10mL/min	3%
Pt _{0.01} Cu/SiO ₂	1:1	100mg catalyst, 3% methanol, 3% water, 10mL/min	7%
Pt _{0.01} Cu/SiO ₂	1:5	100mg catalyst, 9% methanol, 2% water, 10mL/min	0
Pt _{0.01} Cu/SiO ₂	3:1	100mg catalyst, 3% methanol, 9% water, 10mL/min	1.2%
Pt _{0.01} Cu/SiO ₂	7:1	100mg catalyst, 1% methanol, 7% water, 10mL/min	7%
Pd _{0.01} Cu/SiO ₂	1:1	100mg catalyst, 3% methanol, 3% water, 10mL/min	0.8%

Interestingly, desorption of methanol at higher temperatures was seen in the presence of water but not observed in the absence of water (Fig. 5 and 6). The detection of methanol at 150° C in the presence of water could be due to an increase in methoxy formation facilitated by the methanol-water complex that we previously observed with STM for PdCu(111) [13]. Potentially, at higher temperatures, the increased coverage of methoxy species on the surface could undergo recombination with H atoms to desorb as methanol or further dehydrogenate to formaldehyde. At higher temperatures (>250 °C), the selectivity to formaldehyde decreases due to light off of the methanol steam reforming reaction.

Fig. 7 Stability test of the silica supported $\text{Pt}_{0.01}\text{Cu}$ SAA nanoparticles in the water-catalyzed methanol dehydrogenation at $230\text{ }^{\circ}\text{C}$ (water:methanol = 1:1).

Fig. 7 shows the stability of the silica-supported $\text{Pt}_{0.01}\text{Cu}$ SAA nanoparticle catalyst in the water-catalyzed methanol dehydrogenation reaction at $230\text{ }^{\circ}\text{C}$. The water to methanol ratio was kept at 1:1. The yield of formaldehyde was rather constant at $230\text{ }^{\circ}\text{C}$ up to 16 h, indicating good stability of the silica supported $\text{Pt}_{0.01}\text{Cu}$ SAA nanoparticle catalyst in the reaction. The good stability of PtCu SAAs was also confirmed by UHV studies, as will be discussed below.

Fig. 8 Arrhenius-type plot of the reaction rate over the silica supported $\text{Pt}_{0.01}\text{Cu}$ SAA nanoparticles for the water co-catalyzed methanol dehydrogenation reaction.

Kinetic studies of the water catalyzed methanol dehydrogenation on PtCu SAA nanoparticles were performed by measuring the conversion of methanol at different temperatures under steady-state conditions. Fig. 8 shows an Arrhenius-type plot of the reaction rate on the silica-supported Pt_{0.01}Cu SAA nanoparticles. The water to methanol ratio was kept at 1:1 during the whole measurement. To ensure the apparent activation energy (E_a) was obtained in the kinetically controlled regime, the conversions of methanol were kept below 10%. The apparent activation energy calculated from the Arrhenius plot is 69 ± 7 kJ/mol.

Fig. 9 TPSR of methanol on the silica supported Pt_{0.01}Cu SAA nanoparticles with a water to methanol ratio of 1:5 (A) and with water to methanol ratio of 3:1 (B). Reaction conditions: (A) 100mg catalyst, 9% methanol and 2% water balanced in He, He flow rate 10mL/min; (B) 100mg catalyst, 3% methanol and 9% water balanced in He, He flow rate 10mL/min.

Fig. 9 shows TPSR of methanol on the silica supported Pt_{0.01}Cu SAA nanoparticles with a water to methanol ratio of 1:5 (A) and with water to methanol ratio of 3:1 (B). For the case with a water to methanol ratio of 1:5, there is no detectable formation of formaldehyde; while in the case with water to methanol ratio of 3:1, the yield of formaldehyde at 230 °C is only 1.2%, which is much less than the 7% yield at 1:1 water to methanol ratio, Fig. 6B. As shown in Table 2, the yield of formaldehyde at 230 °C is also close to 7% at 7:1 water to methanol ratio. In these

experiments, several measurements were taken, and the average yield of formaldehyde was used in Table 2. Thus, the best formaldehyde yield for water-catalyzed methanol dehydrogenation over supported Pt_{0.01}Cu SAA nanoparticles is achieved at water to methanol ratio of 1:1, selected for further studies because it minimizes the amount of water for a practical application.

To further investigate the methanol dehydrogenation reaction, we performed TPD/R studies on model surfaces in UHV. Fig. 10 shows the TPD/R traces resulting from the adsorption of methanol-D (CH₃OD) onto Cu(111). In agreement with previously reported desorption of methanol from Cu(111) [22, 40], we observe intact methanol-D (m/z 33) desorbing from Cu(111) terraces at 160 K and from Cu step edges at 200 K. Small amounts of reactively formed formaldehyde (m/z 30) desorbs from Cu(111) surface at 370 K. Small amounts of reactively formed formaldehyde (m/z 30) desorbs from Cu(111) surface at 370 K. The fragmentation pattern of both methanol and formaldehyde includes m/z 30, however, at 370 K, we observe desorption of m/z 30 independent of m/z 33 (methanol-D). Thus we conclude that reactively formed formaldehyde desorbs at higher temperatures. Additionally, water (m/z 18) from the chamber background is also observed desorbing from the surface at 150 K, though the surface coverage of water is small at 0.2:1 water:methanol ratio. Water is known to co-catalyze the dehydrogenation of methanol on Cu in vacuum and will be discussed later [13].

Interestingly, when methanol is adsorbed on a roughened Cu(111) surface (Fig. 10A), the amount of reactively formed formaldehyde desorbing at 370 K increases. An increase in desorption of methanol-D at 200 K indicates that there is an increase in step sites on the roughened copper surface. Using STM, we imaged both a typical Cu(111) (Fig. 10B) and a roughened Cu(111) surface (Fig. 10C). A typical Cu(111) exhibits monoatomic steps separated by large terraces (30 – 100 nm). A roughened surface prepared through Ar⁺ sputtering without annealing, yields a highly stepped surface. Using CO titration, we estimate the concentration of step sites on the roughened Cu(111) surface is 5x that of a typical Cu(111) surface. From this

experiment we conclude that the higher density of Cu step sites increases the conversion of methanol to formaldehyde.

Fig. 10 (A) TPD/R traces for the adsorption of methanol on Cu(111) and a highly roughened Cu(111) surface. Methanol-D (0.6 monolayer (ML)) was adsorbed onto the surfaces (water:methanol = 0.2:1). Desorption traces for reactants water (m/z 18) and methanol (m/z 33) and the product formaldehyde (m/z 30) are shown. STM images of a (B) typical Cu(111) surface and (C) roughened Cu(111) surface.

To investigate if Pt atoms can enhance the reactivity of Cu(111), we prepared PtCu(111) SAAs and probed the methanol dehydrogenation reaction (Fig. 11). We have previously characterized PtCu(111) SAAs and showed that the Pt atoms exist as isolated species dispersed in the Cu terraces at low Pt coverages [41, 42]. In Fig. 11B, the Pt atoms appear in STM images as

single protrusions in the Cu(111) terrace. TPD/R for the adsorption of methanol-D on PtCu(111) SAAs exhibits an increase in formaldehyde desorption (370 K) compared to the Cu(111) surface (Fig. 10A and 11A). Furthermore, the addition of Pt does not change the desorption temperature of methanol or formaldehyde; it only increases the production of formaldehyde. To further investigate the ability of Pt atoms to catalyze the reaction, we increased the concentration of Pt atoms in the Cu surface. Formaldehyde yield increases linearly as a function of Pt coverage in the single atom regime (<0.05 ML Pt), but begins to decrease beyond 0.05 ML Pt where clusters greater than one Pt atom exist in the surface. Additionally, PtCu SAAs exhibit high stability; the percent yield of formaldehyde remains constant at $9\% \pm 1$ for 7 consecutive reaction cycles on the same PtCu SAA surface with 1:1 water to methanol ratio.

Fig. 11 (A) TPD/R traces of methanol on a PtCu SAA. 0.6 ML methanol-D was adsorbed on 0.01 ML PtCu(111) surface (water:methanol = 0.2:1). (B) STM image of PtCu(111) SAA surface where the bright features are Pt atoms substituted into the Cu(111) surface. (C) Formaldehyde percent yield versus Pt concentration for adsorption of 0.6 ML methanol adsorbed onto varying surface coverages of Pt (water:methanol = 0.2:1).

Furthermore, we do not observe reactively formed CO desorbing from PtCu(111) SAA surfaces indicating that PtCu SAAs cannot fully decompose methanol resulting in 100% selectivity to formaldehyde on the Pt-Cu SAA surface. After increasing the coverage of Pt to 0.3 ML, a significant decrease in the amount of reactively formed formaldehyde and unreactive methanol is observed, reducing the selectivity to formaldehyde. This is due to an ensemble effect as at 0.3 ML Pt in Cu(111), our previous STM imaging data showed a heterogeneous atomic surface structure of Pt where linear clusters of Pt atoms were present on the surface [35, 42]. We propose that these larger Pt ensembles are capable of decomposing formaldehyde or methanol since Pt(111) was observed to decompose methanol and formaldehyde [43].

Fig. 12 Formaldehyde yield as a function of the ratio of water to methanol for Cu(111) and PtCu(111) SAA surfaces. Methanol was adsorbed prior to water and the methanol surface coverage was 0.6 ML for each trial.

Table 3. Percent yield of formaldehyde for various coverages of water and methanol

Cu(111)		0.01 ML PtCu(111)	
Water to Methanol ratio	Percent Yield	Water to Methanol ratio	Percent Yield

0.1	1.6 %	0.1	6.9%
0.9	1.8%	0.2	7.2%
2.0	2.0%	0.7	5.9%
4.1	2.9%	2.0	8.0%
12.0	3.7%	4.5	8.1%
23.9	5.6%	13.5	10.7%
		26.1	10.1%

To investigate the role of water in PtCu SAA catalysts, we co-adsorbed water and methanol onto a PtCu(111) SAA surface. Increasing the ratio of water:methanol led to an increase in the percent yield of formaldehyde on both Cu(111) and PtCu(111) SAA (Fig. 12) with PtCu SAAs being more reactive than Cu(111). At maximum formaldehyde conversion, PtCu SAAs are about twice as reactive as Cu(111). We previously reported that water co-catalyzes methanol dehydrogenation on Cu(111) surface [13]. Combining STM with TPD/R, we demonstrated that excess water is needed to convert methanol to formaldehyde on a Cu(111) surface. Since both water and methanol form hydrogen bonded clusters, the co-adsorption of methanol [44-46] and water [47, 48] results in methanol-water networks that assist in the dehydrogenation of methanol to methoxy.

Through our surface science studies, we investigated the active sites for the dehydrogenation of methanol. Although Cu(111) terraces are incapable of converting methanol to formaldehyde [13], we demonstrate that we can dramatically increase the reactivity of Cu through producing additional active sites and utilizing the co-catalyst water. First, increasing the step density on a Cu(111) surface doubles the conversion of methanol to formaldehyde in agreement with previous studies that demonstrate the formation of methoxy on Cu steps [13, 49]. Furthermore, addition of 0.01 ML isolated Pt atoms increases conversion to formaldehyde by 2 - 4 times depending on

surface coverage of water (Table 3). Both Cu steps and PtCu SAA catalyze the reaction via a similar mechanism. With our TPD/R studies, we elucidate the mechanism for dehydrogenation of methanol on PtCu SAA surfaces. In order to identify desorption peaks for O-H versus C-H activation, we adsorbed methanol-D (CH_3OD) (Fig. 11A). Intuitively, one would expect at low temperatures to observe the exclusive desorption of m/z 4 (D_2) from the initial O-D bond scission, however, we observe desorption of m/z 2 (H_2) and 3 (HD) at 250 K preceded by m/z 19 (HDO) at 160 K. Since at < 100 K methanol is initially dehydrogenated to methoxy on Cu steps, the D adatoms isotopically exchange with H_2O as previously reported by Mullins and co-workers on Au (111) [23, 24] or isotopic exchange occurs between H_2O and CH_3OD , because excess water co-catalyzes the reaction on Cu surfaces. Due to the competition between methoxy formation and methanol desorption, we hypothesize that isolated Pt atoms increase the formation of methoxy on the surface. The methoxy is then converted to formaldehyde at higher temperatures. The high temperature desorption of H_2 (m/z 2) that coincides with formaldehyde desorption, supports C-H activation as the rate limiting step to the formation of formaldehyde. This rate limiting step agrees with a previous report that C-H bond scission occurs at 430 K on Cu(111) [50]. Furthermore, the overall process is reaction rate limited since formaldehyde desorption occurs from Cu surfaces < 200 K [15, 51, 52].

As discussed above, the water-catalyzed methanol dehydrogenation to formaldehyde on Cu surfaces was clearly observed both under realistic reaction conditions (Fig. 6) and UHV conditions (Fig. 10). Although water-catalyzed dehydrogenation of methanol has been observed on the Cu(111) surface under UHV conditions [12], it is the first time that this reaction has been observed under realistic reaction conditions. The promotion effect of water can be explained by the co-operative interactions of water and methanol facilitating the dehydrogenation of methanol to methoxy, thereby, increasing the formation of methoxy species. Methoxy can further dehydrogenate to formaldehyde by the activation of C-H bond. Additionally, as observed in Fig.

6, the stabilized methoxy can also undergo recombination with H atoms to desorb as methanol at higher temperature, which is kinetically more favorable in the absence of water. In the presence of water, however, stabilization of H atoms by water clusters increases the reaction barrier of recombination of methoxy and H therefore allows the dehydrogenation of methoxy to formaldehyde via the C-H bond activation. Furthermore, we demonstrate that the catalytic activity of Cu surface originates from under-coordinated Cu atoms. Although the Cu(111) surface is active in the presence of water, the reactivity of Cu surface can be dramatically increased by increasing the step density of the Cu(111) surface.

Adding individual, isolated Pt atoms to Cu surface also significantly promotes the reactivity of Cu in water-catalyzed methanol dehydrogenation. In TPSR measurements in the flow reactor, the yield of formaldehyde on silica-supported Pt_{0.01}Cu SAA nanoparticles is 7 times larger than on supported Cu nanoparticles (Fig. 6). In UHV conditions, depending on the concentration of water, the conversion of formaldehyde is 2 – 6 times higher than on Cu(111) at comparable water concentrations (Fig. 12). Therefore, our data under both realistic reaction conditions and UHV supports the dramatic increase of formation of formaldehyde by addition of single Pt atoms in Cu. We attribute this promotional effect to an increase in methoxy formation on PtCu SAAs. As we previously demonstrated, isolated Pt atoms reduce the desorption temperature for H₂ [35, 42], thereby facilitating the dehydrogenation of methanol to methoxy and increasing the surface coverage of methoxy, as well as allowing more conversion of methoxy to formaldehyde.

In a previous publication, we demonstrated that single Pd atoms in the Cu surface promote the water catalyzed methanol dehydrogenation [13]. In the current study, we found that the promotional effect of Pt is much more pronounced than Pd. Under UHV conditions, at low water to methanol ratio (<1) the formaldehyde yield on dCu(111) is almost the same as on Cu(111) [13]; while the yield on PtCu(111) is 2 - 4 times larger than on Cu(111) at the same water to methanol ratio. TPSR measurements in Table 2 also show that under reaction conditions the formaldehyde

yield on Pd_{0.01}Cu SAAs is approximately 0.8% at 1:1 water to methanol ratio which is much lower than on Pt_{0.01}Cu SAAs. We also performed tests with other Pd concentrations (Pd_{0.003}Cu and Pd_{0.05}Cu) and observed that the yield of formaldehyde from these samples was similar to Cu. We propose that the increased reactivity for PtCu SAA can be rationalized based on Brønsted-Evans-Polyani (BEP) relationship in terms of the adsorption strength of descriptor molecules affecting the reactivity [53-56]. For SAAs, PtCu SAAs bind key descriptor molecules stronger than PdCu SAAs and via the BEP would be expected to exhibit lower activation energies. We observed CO desorbing at a higher temperature from PtCu(111) SAAs (350 K) [35], than PdCu(111) SAAs (270 K) [55], despite similar desorption temperatures observed for Pd(111) and Pt(111) surfaces (450 K) [57, 58]. Additionally, Fu *et al.* predict that PtCu SAAs exhibit stronger binding of H atoms and a lower barrier for H₂ activation consistent with the BEP relationship [59]. Due to the stronger binding of these molecules to PtCu SAAs, we propose that isolated Pt atoms are more reactive than Pd atoms, thereby enhancing the methanol activation to methoxy.

Furthermore, on PtCu(111) SAAs, a high conversion of methanol to formaldehyde is observed at rather low water to methanol ratios (<1); while under reaction conditions at 1 bar, a slightly different trend is observed with the maximum formaldehyde yield at 1:1 water to methanol ratio (Table 2). Moreover at intermediate water to methanol ratio (3:1), the yield of formaldehyde decreases followed by an increase again at 7:1 water to methanol ratio. Obviously the relationship between formaldehyde yield and water:methanol ratio on PtCu SAAs is much more complicated than on Cu and it is hard to quantify the surface coverage of different species under catalytic operating conditions compared to the UHV TPR setup. The drop in formaldehyde yields at intermediate water coverages may be due to the interactions between water and methanol. As reported for Au(111), the cluster size and structure of water strongly influences the bonding of H atoms [23, 24]. With increasing water coverage, the competitive adsorption of water and methanol may decrease the amount of methoxy formed on the surface, and therefore

decrease the formaldehyde yields. On the other hand, the bonding of hydrogen atoms with water clusters is strongly influenced by water cluster size and structure [23], which is determined by water coverage [48]. Therefore the stabilizing effect of H atoms by water molecules could be significantly influenced by water coverage on the PtCu SAA surfaces, resulting in the observed variation of formaldehyde yields.

Conclusions

In this work we demonstrate that PtCu single atom alloys are active for the non oxidative dehydrogenation of methanol to formaldehyde and hydrogen in the presence of water. Although Cu itself is also active, addition of single Pt atoms in the Cu surface significantly improves the reactivity where the yield of formaldehyde is strongly dependent on the water to methanol ratio. The promotional effect of water is attributed to the stabilization of H atoms by water clusters that facilitate the dehydrogenation of methanol to methoxy, which can be further dehydrogenated to formaldehyde. Furthermore, PtCu SAAs exhibit both high selectivity and stability in the water-catalyzed methanol dehydrogenation. The selectivities to formaldehyde on PtCu SAA nanoparticle catalysts and on PtCu(111) SAA model catalysts are both nearly 100%. PtCu SAA catalysts also exhibit very good stability in the flow reactor tests and under UHV conditions. The findings of this work are a new manifestation of the utility of combining UHV surface science and high-pressure reactor experiments in exploring reaction mechanisms and guiding realistic catalyst designs.

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