

## Low-Temperature Formation of Nitrous Oxide from Dinitrogen, Mediated by Supported Tungsten Nanoclusters

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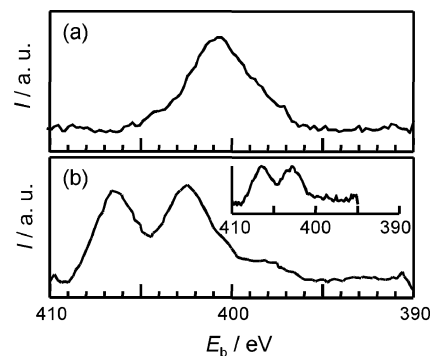
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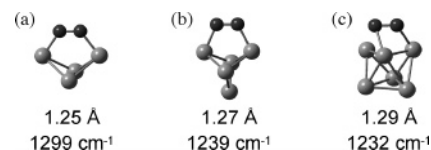
It is now realized that metal clusters have unique catalytic properties that do not exist for bulk surfaces of corresponding metals. This is well illustrated by gold clusters: they catalyze various chemical reactions while the bulk gold is almost inert.<sup>1</sup> In nature, nanoclusters, which usually contain a few atoms of transition-metal elements, can be found at the reaction centers of metalloenzymes. The enzymes catalyze difficult chemical reactions under mild conditions, for which the clusters are known to play key roles.<sup>2</sup> This leads us to expect that, if nanoclusters of a few transition-metal atoms are prepared and supported on a surface, they may also mediate chemical reactions under mild conditions. The present study explores such a possibility by focusing on a reaction of dinitrogen ( $N_2$ ) on tungsten nanoclusters ( $W_n$ ) supported on a graphite surface. We show that the tungsten nanoclusters can activate and mediate reaction of almost inert  $N_2$  in molecular form to yield  $N_2O$  at a temperature as low as 140 K, which has never been observed on metal surfaces.

In the present study, size-selected, supported  $W_n$  ( $n = 2-6$ ) clusters were prepared and exposed to  $N_2$ , and adsorption/reaction of  $N_2$  on the clusters was investigated by X-ray photoelectron spectroscopy (XPS) and thermal desorption spectroscopy (TDS) in ultrahigh vacuum. Figure 1a shows an XPS spectrum for the N 1s binding energy (BE) region, for exposure of  $W_5$  supported on an  $Ar^+$  bombarded graphite (highly oriented pyrolytic graphite, HOPG) surface,<sup>3</sup> to  $N_2$  at 140 K. As seen in the figure, we observed a single peak located at  $\sim 400.0$  eV, which was absent for a bare HOPG surface exposed to the gas and was assigned to a molecular adsorption of  $N_2$ .<sup>4</sup> The spectrum totally differs from that for molecular  $N_2$  adsorption on a bulk polycrystalline tungsten surface at the same temperature,<sup>4</sup> which has a satellite line (unscreened state) in addition to the main line (screened state). The dual-peak structure originates from the interaction of the  $2\pi^*$  antibonding orbital of  $N_2$  with the 5d orbital of W.<sup>5</sup> The absence of the satellite line in the  $N_2$  XPS spectrum on  $W_5$  indicates that such an  $N_2$ -W interaction is absent or not feasible for the  $N_2/W_5$  system. This suggests that  $N_2$  is adsorbed on  $W_5$  taking a highly tilted or a side-on geometry,<sup>6,7</sup> which was also inferred from the fact that the adsorption state on  $W_5$  is a molecular precursor to the dissociation state of  $N_2$ .<sup>4</sup>

To obtain insight into the nature of the adsorbed  $N_2$ , we performed density functional theory (DFT) calculations of the side-on adsorption states on an isolated  $W_n$ . The optimized geometry calculated for the side-on adsorption state on  $W_5$  is shown in Figure 2b. In this configuration, the N-N bond is elongated to 1.27 Å (cf. the calculated value for free  $N_2 = 1.10$  Å),<sup>8</sup> and the vibrational frequency of the N-N stretching mode is greatly reduced to 1239



**Figure 1.** N 1s X-ray photoelectron spectra measured at 140 K. (a) For exposure of  $W_5$  to  $N_2$ . The peak at  $\sim 400.0$  eV is assigned to a molecular adsorption state of  $N_2$ , which is a precursor to dissociation (see ref 4). (b) For exposure to  $N_2$  with  $\sim 10$  ppm  $H_2O$ . The spectrum quite resembles the one obtained for exposure to  $N_2O$  shown in the inset in terms of the overall shape and the peak energy positions.



**Figure 2.** Optimized geometries for side-on  $N_2$  adsorption on (a)  $W_4$ , (b)  $W_5$ , and (c)  $W_6$  as determined by DFT calculations. Light gray and dark gray spheres denote W and N atoms, respectively. The values below each cluster are the length of the N-N bond and the frequency of the N-N stretching vibration.

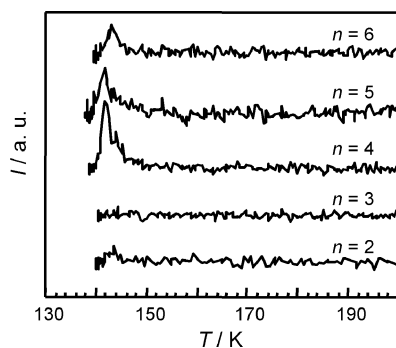
$cm^{-1}$  ( $2445$   $cm^{-1}$  for free  $N_2$ ).<sup>8</sup> This indicates that  $N_2$  is activated in the adsorption state.

When water was mixed in the  $N_2$  gas ( $\sim 10$  ppm), on the other hand, we observed a completely different XPS spectrum: two peaks with almost equal intensity at  $\sim 402.6$  and  $\sim 406.6$  eV showed up (Figure 1b). It turned out the XPS spectrum was quite similar to that of the  $N_2O$  molecule adsorbed on a W surface.<sup>9</sup> That the species was indeed  $N_2O$  was evidenced by comparing the spectrum with an XPS spectrum obtained for  $N_2O$ , intentionally fed to  $W_5$  (see the inset of Figure 1b). We further confirmed this by TDS using  $^{15}N_2$ . The TDS spectrum, shown at the second line from the top of Figure 3, is for exposure of  $W_5$  to the wet  $^{15}N_2$  at 140 K. In the TDS measurement, in addition to  $^{15}N_2$ , desorption of a species with a mass of  $m/e = 46$  was observed with a distinct peak at 143 K, as seen in the figure. For the combination of  $^{15}N_2$  and  $H_2^{16}O$ ,  $^{15}N_2^{16}O$  is the only molecular species having the mass of 46 amu.

The observation that only the wet  $N_2$ , not dry one, yields  $N_2O$  indicates that  $N_2O$  forms by the reaction of  $N_2$  with  $H_2O$ .<sup>10</sup> For nitrogen in  $N_2O$ , there are two possible sources, that is, the  $N_2$  molecule itself or the N atom resulting from dissociation of  $N_2$ . As

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**Figure 3.** Thermal desorption of a species with a mass number of 46 from  $W_n$  exposed to wet  $^{15}\text{N}_2$  at 140 K. For  $W_5$ , a desorption peak is observed at 143 K. With the ingredients of  $^{15}\text{N}_2$  and  $\text{H}_2^{16}\text{O}$ ,  $^{15}\text{N}_2^{16}\text{O}$  is the only possible product with the mass number of 46. For  $W_n$  ( $n = 2-6$ ), the desorption peak was observed for  $n \geq 4$ .

mentioned above, a single peak located at  $\sim 400.0$  eV in the XPS spectrum (Figure 1a) is due to a molecular adsorption state of  $\text{N}_2$ .<sup>7</sup> On the other hand, a peak at  $\sim 397.6$  eV, a fingerprint for N atom adsorption,<sup>9</sup> is absent in the XPS spectrum, indicating that  $\text{N}_2$  does not dissociate on the nanocluster at 140 K. Since  $\text{N}_2\text{O}$  forms also at 140 K in the presence of water, it is not likely that the N atom is the source of nitrogen in the  $\text{N}_2\text{O}$  formation. We therefore conclude that  $\text{N}_2$  in molecular form is involved in the  $\text{N}_2\text{O}$  formation.

The present observation of  $\text{N}_2\text{O}$  formation involving  $\text{N}_2$  on  $W_5$  suggests that the  $\text{N}_2$  molecule, possibly taking the adsorption geometry shown in Figure 2, is indeed an activated species and responsible for the reaction. Then the question is if a  $\text{N}_2$  activation and the reaction are unique for  $W_5$  or is it feasible for W clusters with other sizes. To answer the question, we investigated the cluster size dependence of the  $\text{N}_2\text{O}$  formation/desorption also for  $W_n$  ( $n = 2-4, 6$ ).<sup>3</sup> It was found, as shown in Figure 3, that  $W_4$  and  $W_6$  give  $\text{N}_2\text{O}$  desorption peaks with substantial intensity,<sup>11</sup> but  $W_2$  and  $W_3$  do not. When these clusters were exposed to  $\text{N}_2\text{O}$  gas, on the other hand, we observed desorption of  $\text{N}_2\text{O}$  from all the cluster species. These observations indicate that the formation of the activated  $\text{N}_2$  and the subsequent reaction are cluster size dependent: they are feasible for  $W_4$ ,  $W_5$ , and  $W_6$  but not for the smaller clusters  $W_2$  and  $W_3$ .

To elucidate whether adsorption states similar to that for  $W_5$  in Figure 2b are responsible for activating  $\text{N}_2$  on  $W_4$  or  $W_6$ ,  $\text{N}_2$  adsorption geometries for  $W_4$  and  $W_6$  and also for  $W_2$  and  $W_3$  were examined by the DFT calculation. The result was that the side-on adsorption geometry, similar to the one for  $W_5$ , is a stable one also for  $W_4$  (Figure 2a) and  $W_6$  (Figure 2c) but not for  $W_2$  and  $W_3$ . These results further suggest that  $\text{N}_2$  is activated in the side-on adsorption geometry also on  $W_4$  and  $W_6$  and the adsorption state is responsible for the  $\text{N}_2\text{O}$  formation.

For  $\text{N}_2$  adsorption on small gas-phase  $W_n$ , molecular adsorption is favored,<sup>12-14</sup> and the molecular state seems to act as a precursor to dissociation.<sup>12</sup> It was also shown for anionic clusters ( $W_n^-$ ) that adsorption energies of  $\text{N}_2$  for  $W_2^-$  and  $W_3^-$  are very small compared to those for larger species.<sup>14</sup> These findings are in line with the size-dependent properties of supported  $W_n$  revealed in the present study.

For  $\text{N}_2$  on tungsten surfaces, the most stable, dissociative adsorption and a weakly bound molecular adsorption with end-on

geometry at low temperature are commonly seen.<sup>5</sup> Another type of molecular adsorption, which possibly has a side-on geometry, is also known for the (111) and the (100) surface.<sup>5</sup> For the (100) surface, the N–N stretching vibrational frequency is as low as  $1452\text{ cm}^{-1}$ ,<sup>15</sup> suggesting that the  $\text{N}_2$  molecule is activated. The present study indicates that  $\text{N}_2\text{O}$  formation from such  $\text{N}_2$  molecules on the bulk surfaces may be possible, although no experimental studies to explore the point have been reported.

In summary, we have shown that supported tungsten nanoclusters can mediate the formation of  $\text{N}_2\text{O}$  from  $\text{N}_2$  at 140 K, in which  $\text{N}_2$  without dissociation is involved in the reaction. The DFT calculation has shown that  $W_n$  ( $n = 4-6$ ) activates  $\text{N}_2$  in molecular form, and this should be the key that enables the nanoclusters to mediate such a low-temperature reaction.

**Acknowledgment.** This work was supported by the “Support of Young Researchers with a Term” program of the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan.

**Supporting Information Available:** Details of deposition and fixation of nanoclusters on a graphite surface, TDS measurements, DFT calculation, and so on. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA071860J