The determination of reaction rate.

The reaction mixture containing 100-500 ppm CO, 1.0 vol.% O_2, 0.5 vol.% Ne, 2.3 vol.% H_2O, and helium the balance was fed at a rate of 200 cm^3/min to the initial catalyst. The catalyst volume was 0.25 cm^3, catalyst weight was 0.343 g, GHSV was 48000 h^{-1}.

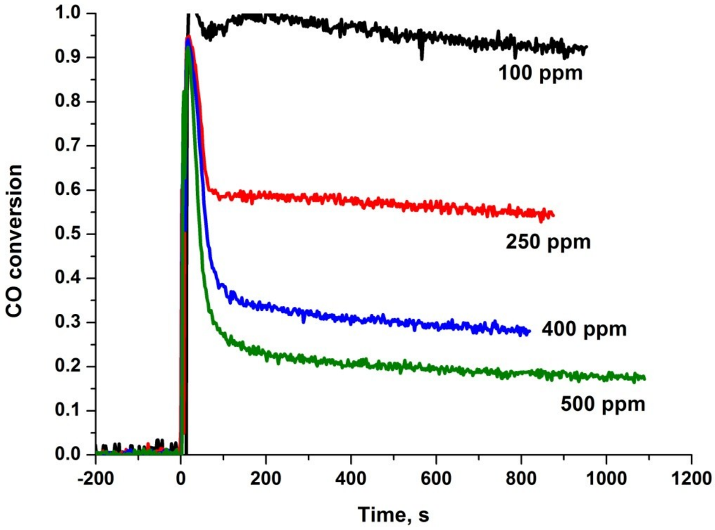

Figure S1. CO conversion vs time measured at 25°C with different inlet CO concentrations.

The specific reaction rate was calculated for CO conversions below 20% using the formula:

$$W[cm^{-2}\cdot s^{-1}] = \frac{C_{CO}\cdot X_{CO}\cdot V_{RM}[M\cdot s^{-1}]\cdot N_A[M^{-1}]}{10000\cdot m[g]\cdot S_{BET}[m^2\cdot g^{-1}]}, \qquad (1)$$

Where C_{CO} is the initial CO content in the reaction mixture (fraction), X_{CO} is the CO conversion, V_{RM} is the reaction mixture rate, m is the catalyst loading, S_{BET} is the specific surface area of the catalyst, and N_A – the Avogadro number.

Specific CO oxidation rate was calculated to be $4.8\cdot 10^{10}$ CO molecules$\cdot$cm$^{-2}\cdot$s^{-1} using X_{CO} = 18% obtained at C_{CO} = 500 ppm (fig.S1).

The estimations of the TOF values using TEM, XPS and FTIR CO adsorbed spectroscopy data.

1). The 1%Pd(DF)/Fe_2O_3 sample after reduction by hydrogen was studied by TEM. The results (presented in detail below) have shown that the mean Pd particle size is 2 nm. The calculations give the dispersity of 71%. Then the palladium surface concentrations is equal to $8*10^{13}$ atom Pd/cm^2 (1wt% Pd, S_{BET} = 50 m^2/g). In this case the TOF value is equal to 0.0006 s^{-1}. This is a lowest estimation of the TOF value for this catalyst.

2) An alternative TOF estimation was obtained from the XPS data, in particular, from Pd concentration in the XPS area of analysis. Note that the true concentration of Pd atoms taking part in CO oxidation reaction can differ from the corresponding value obtained from XPS due to different morphological factors. These factors are surface or interdomain distribution of Pd particles, Pd particles size, possible aggregation of Pd particles etc, and it was considered in the text of manuscript. TOF was estimated for Pd particles size of 2 nm in assumption of its semispherical shape using formula:

$$TOF_{XPS} = \frac{W[cm^{-2}\cdot s^{-1}]}{10^{15}[cm^{-2}]\cdot X_{Pd/Fe}}\left(1-\left(1-\frac{A/2}{r}\right)^3\right)^{-1} \qquad (2)$$

Where, $X_{Pd/Fe}$, corresponding atomic ratio obtained from XPS, A – lattice parameter for Pd metal (3.89 Å), r – particle radius, Å, 10^{15} the typical value of surface atoms concentration on 1 cm^2 of the surface. Obtained TOF value is equal to 0.035 s^{-1}.

3). For a more precise calculation the Langmuir adsorption isotherm was used to estimate the values of CO adsorption at reactions conditions (510 ppm or 0.39 torr CO) from the values of CO adsorption measured at higher pressures, 10-100 torr. This estimation was made for linear and bridged CO adsorption (Fig.S2).

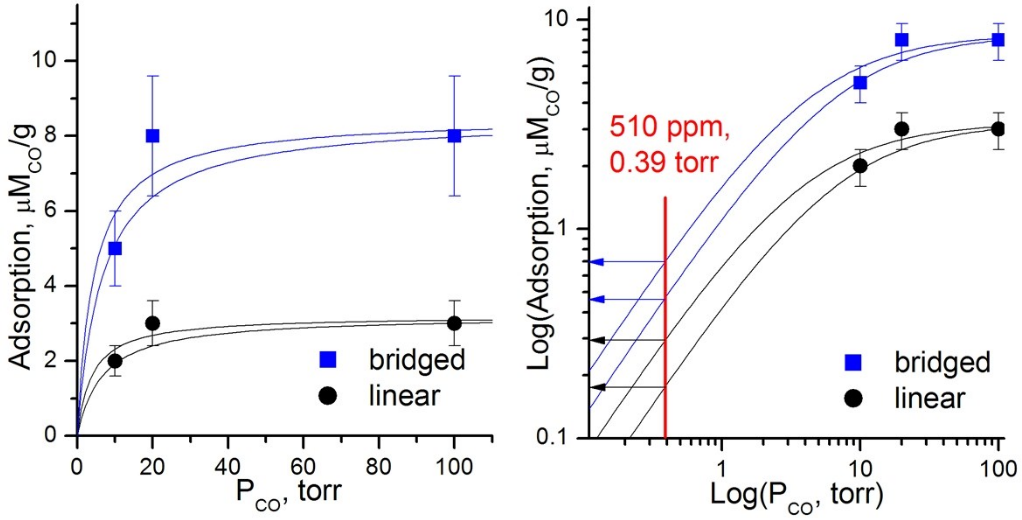

Fig.S2. Values of linear and bridged CO adsorption vs CO pressure obtained for 1%Pd(DF)/Fe_2O_3 catalyst at 25°C.

Estimated values of CO adsorption at 0.39 torr (510 ppm) were then used for TOF calculation according to formula:

$$TOF_{FTIR} = \frac{10000 \cdot W[cm^{-2} \cdot s^{-1}] \cdot S_{BET}[m^2 \cdot g^{-1}]}{10^{-6} \cdot a[\mu M \cdot g^{-1}] \cdot N_A} \quad (1)$$

where, W – the specific CO+O_2 reaction rate, a – the estimated value of CO adsorption, N_A – the Avogadro number.

Calculation of TOF from FTIR considering all bridged and linear adsorbed species gives value (0.050±0.015 s^{-1}) which is close to values obtained from XPS (0.035 s^{-1}).

The TPR-H_2 study.

The 1%Pd(D)/Fe_2O_3 catalyst virtually does not consume hydrogen at the room temperature. We have performed an additional experiment which consisted in temperature-programmed reduction of 1%Pd(D)/Fe_2O_3 with hydrogen and subsequent catalytic testing of the reduced sample.

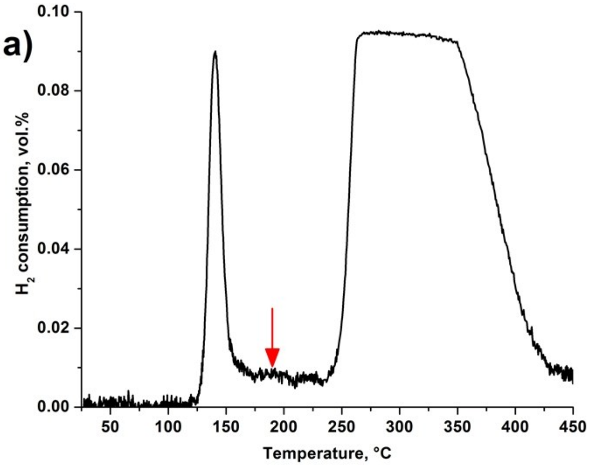

Figure S3. H_2 consumption during TPR-H_2 for 1%Pd(D)/Fe_2O_3 catalyst.

Note that hydrogen consumption virtually was not observed at temperatures below 120°C (fig. S3). The narrow peak of hydrogen consumption was observed at 140°C and was attributed to Pd^{2+} reduction whereas the H_2 consumption in the range of 250-450°C was assigned to Fe_2O_3 reduction. The ratio of H_2/Pd for peak at 140°C was equal to 2.3. As the theoretical value of H_2/PdO is 1, the obtained value of this ratio may indicate that, along with reduction of the Pd^{2+}, the reduction of a portion of DMF has probably occurred.

In order to avoid reduction of Fe_2O_3 we didn't exceed the temperature of 190°C (marked by arrow on fig.S3) during the reduction of the 1%Pd(D)/Fe_2O_3 catalyst prior to its testing in wet CO oxidation reaction.

Investigation of the catalytic activity in CO oxidation

After the reduction with H_2 up to 190°C the 1%Pd(D)/Fe_2O_3 catalyst was cooled in helium. The obtained catalyst designated as 1%Pd(D-H_2)/Fe_2O_3 was tested in CO oxidation at the same conditions as in Manuscript: reaction mixture contained 100 ppm CO, 1.0 vol.% O_2, 0.5 vol.% Ne, and the balance helium; the temperature was 20°C; the reaction mixture rate was 200 cm^3/min; in the presence (2.3 vol.%) and absence of water vapor.

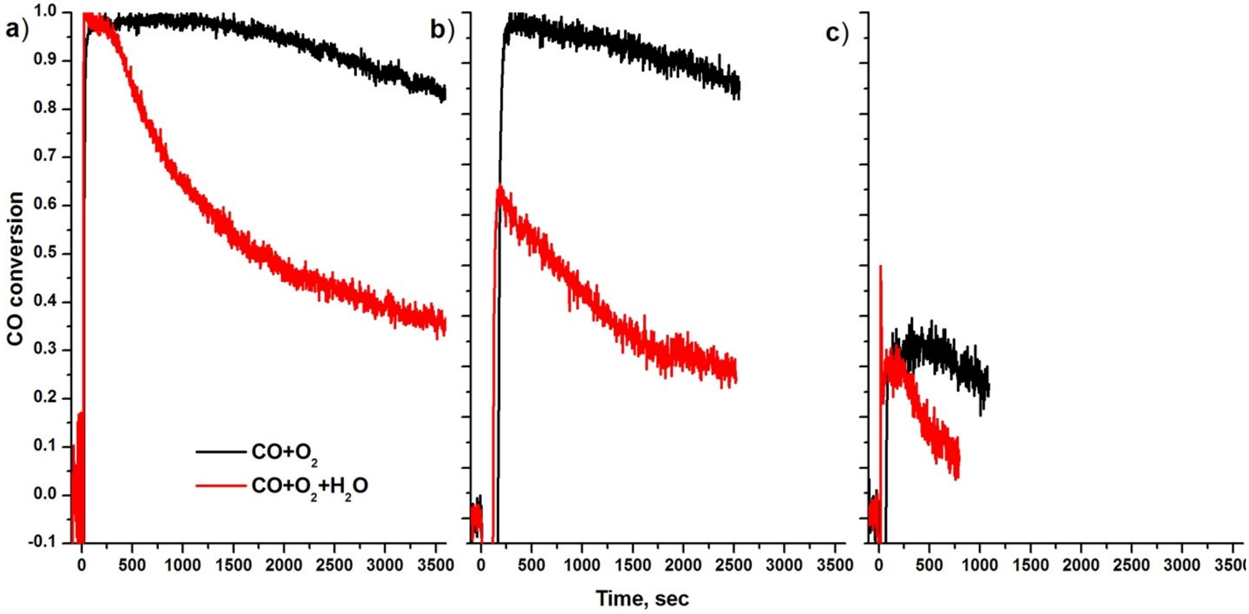

Fig. S4.CO conversion vs. time at 20°C in dry (black curves) and wet (red curves) conditions obtained for 1%Pd(D-H_2)/Fe_2O_3 catalyst (a) and for 1%Pd(T)/Fe_2O_3 (b), 1%Pd(D)/Fe_2O_3 (c) catalysts (from manuscript) for comparison.

Fig. S4a shown that the 1%Pd(D-H_2)/Fe_2O_3 catalyst was characterized by high activity in dry conditions for about 20 minutes, then the conversion was observed to decrease slowly. In wet conditions the 1%Pd(D-H_2)/Fe_2O_3 catalyst deactivates more rapidly. Comparison with initial 1%Pd(D)/Fe_2O_3 (fig. S4c) allow concluding, that reduction with hydrogen at 190°C resulted in formation of reduced palladium species which led to activation of the catalyst after hydrogen pretreatment. However comparison with the 1%Pd(T)/Fe_2O_3 catalyst without DMF-modification (fig. S4b) clearly shown the instability of the obtained 1%Pd(D-H_2)/Fe_2O_3 catalyst due to removal or destruction of hydrophobic DMF-layer. This assumption agree well with the value of H_2 consumed at 1st reduction peak on TPR-H_2 curve (fig. S3) and suggested the reduction of Pd^{2+}-DMF surface complexes.

Thus, reduction with sodium formate allowed us to reduce the Pd^{2+} species without affecting the hydrophobic DMF layer, which leads to active and stable in wet ambient CO oxidation catalysts.

TEM study of the 1%Pd(D-H_2)/Fe_2O_3 catalyst

The representative image for the 1%Pd(D-H_2)/Fe_2O_3 catalyst is shown on Fig. S5. In this case we can easily observe the palladium nanoparticles by conventional TEM. The mean size of these nanoparticles is 2 nm. We expect that the dispersity for the sample reduced by sodium formate is even higher as the treatment with sodium formate occurred at room temperature and reduction with hydrogen required T>140°C. The possibility to investigate the 1%Pd(D-H_2)/Fe_2O_3 easily without contamination also confirms that the hydrogen treatment affects the DMF layer making the sample appropriate for TEM study but inactive in wet CO oxidation.

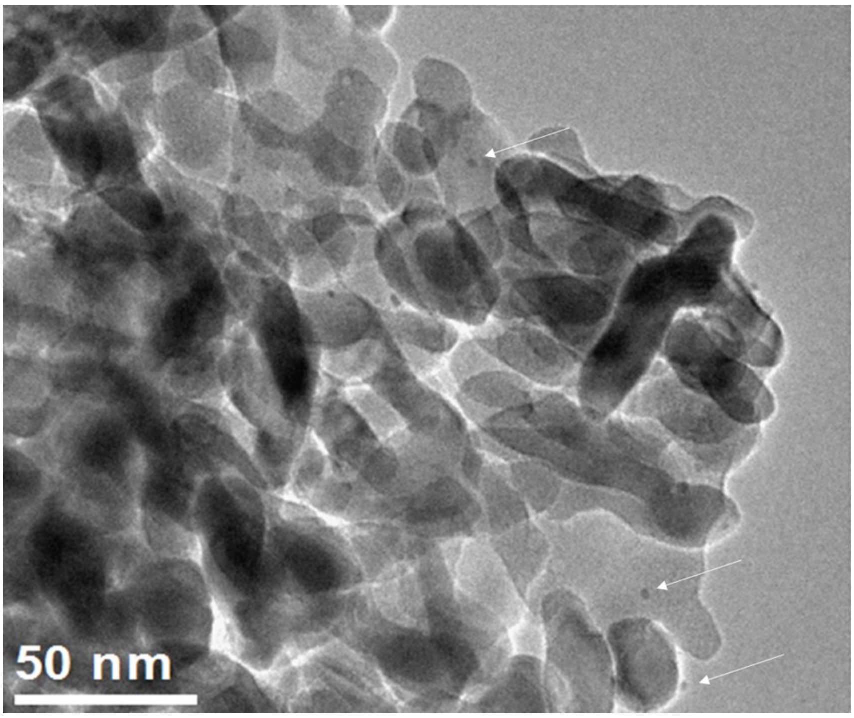

Fig. S5 TEM image for 1%Pd(D-H_2)/Fe_2O_3 catalyst.

As it was mentioned above, the 5 nm Pd particles were observed in 1%Pd(D)/Fe_2O_3 by TEM episodically. Most probably the main part of palladium remains within interdomain boundaries as a fine particles or clusters unobservable by TEM due to DMF-layer presence. This layer strongly restricts the possibilities of TEM to observe such fine Pd particles localized within the support microstructure.