Section S1. Force-field parameters used in the MD simulations

The molecular species in the electrolyte were described using established classical force fields. Water molecules were modeled using the TIP4P model, while methanol and sulfuric acid molecules were parameterized using the General AMBER Force Field (GAFF2). Atomic partial charges for the molecular species were assigned using the Gasteiger method.

The FePt electrode atoms were modeled using Lennard–Jones parameters derived from the Universal Force Field (UFF). Cross interactions between different atom types were computed using the Lorentz–Berthelot combining rules. The Lennard–Jones parameters used in the simulations correspond to the values implemented in the GROMACS topology.

Since GAFF2 is a publicly available and widely used force field, its full parameter set is not reproduced here. Instead, this Supporting Information provides the specific molecular components, atom types, partial charges, and nonstandard electrode parameters used in the present work, which are the key information required for reproducibility. Details as shown in Table S1.

Table S1. Summary of force-field models and key nonbonded parameters used in the MD simulations

Species	**Force field**	**Charge method**	**σ (nm)**	**ε (kJ mol^{-1})**
Water	TIP4P	model default	…	…
Methanol	GAFF2	Gasteiger	…	…
Sulfuric acid	GAFF2	Gasteiger	…	...
Fe (electrode)	UFF	neutral	0.2594	0.0543
Pt (electrode)	UFF	neutral	0.2453	0.3347

Section S2. Determination of adsorption time

The adsorption time of molecules near the electrode surface was analyzed using a trajectory-based algorithm implemented with the MDAnalysis toolkit. The analysis was performed using the simulation topology (.tpr) and trajectory (.xtc) files.

For each molecular species of interest, molecules were first identified according to their residue name in the topology file. Each residue was treated as an individual molecule. For every trajectory frame, the center-of-mass (COM) position of each molecule was calculated.

Adsorption was determined based on the distance of the molecular COM from the electrode surface along the surface-normal (z) direction. A threshold position z_0 was defined to distinguish molecules located inside the near-surface region. Depending on the chosen condition, a molecule was considered to be in the adsorption region when its COM satisfied the criterion ($z_{COM}<z_0$). For each frame, the adsorption state of every molecule was therefore represented by a binary variable: if the molecule satisfied the adsorption criterion, and 0 otherwise. By scanning the trajectory sequentially, a time series of adsorption states was constructed for each molecule. Consecutive frames with state value 1 were interpreted as a continuous adsorption event. The duration of an adsorption event was calculated as the number of consecutive frames satisfying the adsorption condition multiplied by the time interval between frames.

To avoid counting short thermal fluctuations as adsorption events, a minimum-length criterion was applied. Only sequences containing at least five consecutive adsorption frames were considered valid adsorption events. Shorter sequences were discarded. For each molecule, the following quantities were then calculated:

1. The total adsorption time (sum of all valid adsorption events),
2. The number of adsorption events, and
3. The average adsorption lifetime, defined as the total adsorption time divided by the number of events.

Finally, adsorption lifetimes obtained for all molecules were collected and used

to construct probability density distributions of adsorption time. Histograms of the adsorption lifetimes were calculated and used to analyze the statistical behavior of molecular adsorption near the electrode surface.

Section S3. Density distribution analysis of CO

To further characterize the interfacial behavior of CO during the methanol oxidation process, we analyzed the density distribution of CO molecules along the surface-normal z direction. The simulation settings are the same as those described in the main text, with a molecular ratio of CO: H_2SO_4: H_2O = 2000:1000:30000. The density profiles were obtained from the MD trajectories by averaging the number density of each species as a function of the distance from the FePt surface.

This analysis complements the adsorption-time statistics discussed in the main text. While the adsorption-time analysis describes how long CO molecules remain near the surface, the density distribution reveals where these molecules preferentially reside within the interfacial region.

As shown in Fig. S1, CO exhibits a pronounced density enhancement near the electrode surface, indicating strong interfacial accumulation. This behavior is consistent with the relatively long adsorption times of CO and supports the interpretation that CO can persist near the surface and contribute to poisoning during the MOR process. Compared with methanol under the same conditions, the CO density profile shows a broader interfacial peak, suggesting that CO is more strongly localized near the electrode and forms a thicker adsorption layer.

In the methanol system, methanol and water molecules exhibit nearly synchronous increases at similar distances from the surface (0.6--1.0 nm), with comparable growth rates. In contrast, H_2SO_4 increases more gradually, particularly in the 0.6--0.8 nm region, and rises more noticeably only between 0.8 and 1.0 nm. For the CO system, CO shows a much steeper increase near the surface (0.6--0.9 nm) than either H_2SO_4 or H_2O, whereas the latter two species remain low in the 0.6--0.8 nm region and increase only slightly before rising more rapidly beyond 1.0 nm.

These results suggest that methanol and water have comparable probabilities of approaching the surface, which is favorable for the formation of CO and OH intermediates and their subsequent conversion to CO_2. However, the much higher interfacial density of CO compared with water indicates that CO binds much more strongly to Pt sites. As a result, water access to the Pt surface is

hindered, suppressing OH* formation and thereby preventing the oxidation of CO* to CO_2, ultimately leading to CO poisoning.

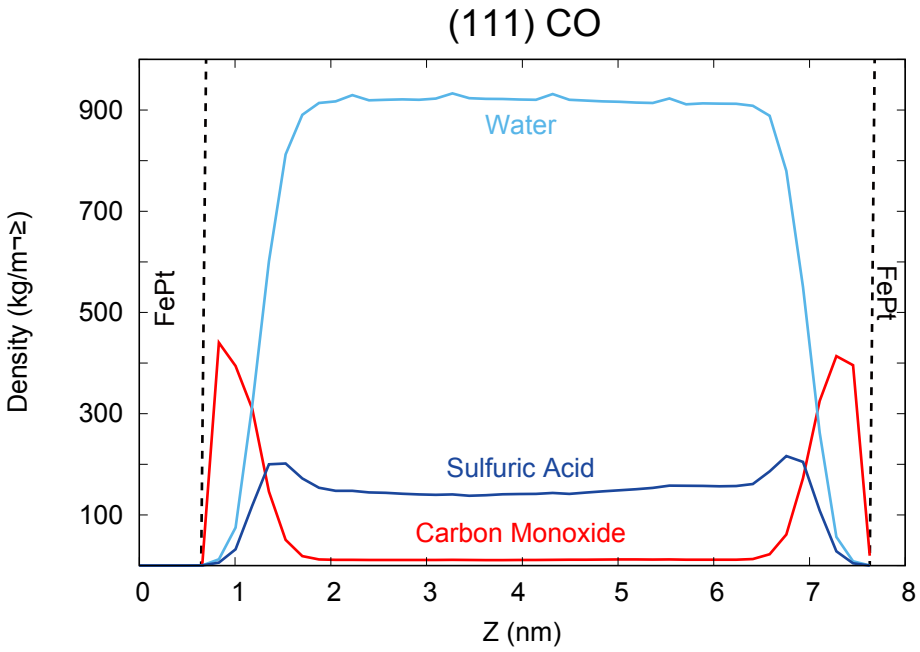

Figure S1: Density distributions of carbon monoxide, sulfuric acid, and water along the Axis-Z for FePt (111) surface.