Electronic Supplementary Information (ESI)

# Dehydrogenation inhibition: a novel route for catalyst anti-deactivation enhancement in methanol to propylene reaction

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## Preparation of Au/ZSM-5 catalysts

For the preparation of Au/ZSM-5 catalysts with nanoscaled gold particles, the routine deposition-precipitation (DP) method was employed. Typical procedures were described in the literature . Usually, 500 ml of deionized water were mixed with a solution of $HAuCl_4$ containing certain amount of gold. The resulting solution was heated under an oil bath of 75 $^oC$ with stirring for 1 h followed by dropwise addition of ammonia until the pH value was adjusted to 10.00 at room temperature. Then the solution was mixed with 5 g of zeolite HZSM-5 and kept stirring for 1 h and subsequently underwent filtration and washing by deionized water for at least 3 times until no chloride ion was detected. Finally the as-prepared Au/ZSM-5 samples were calcined at 550 $^oC$ for 6 h with a heating rate of 2 $^oC$ $min^{-1}$ under air. The obtained product was designated as Au/ZSM-5(X), where X=0.5, 1.0 or 2.0 indicates the gold loading (wt%).

## Computational details

All calculations were carried out using the Gaussian package. Geometry optimizations were carried out at the B3LYP level of theory. H, C, O, were represented by the 6-31+G(d) basis set while Au by LANL2DZ basis set. Model compounds were designed to be derivatives of naphthalene while gold atom as well as AuOH are employed tosimulate the adsorbed gold species on zeolite ZSM-5.

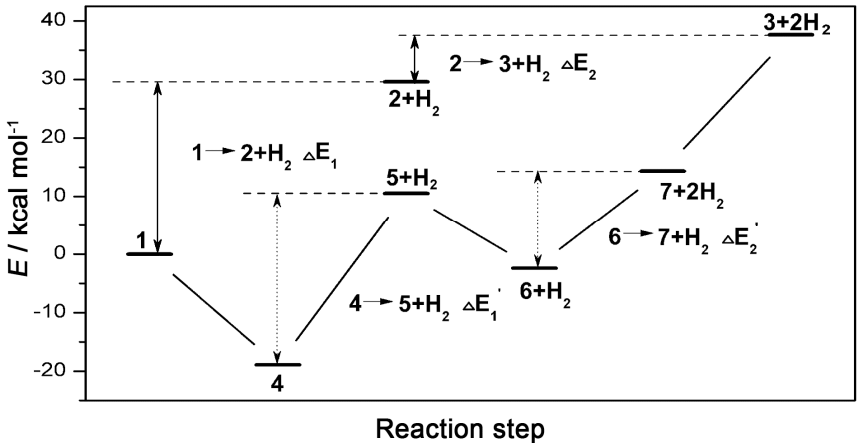


**Fig.S1** Simulated energy change of dehydrogenation reaction with and without gold

In search for the role of gold in the dehydrogenation reaction, DFT calculations have been taken to reveal the insight of this process. For similarity, a precursor of naphthalene (compound **1,** *cf.* scheme 1) was set as the model compound involved in the dehydrogenation process and AuOH was used to imitate the adsorbed nanoparticle of gold. The effect of gold on the dehydrogenation of **1** stepwise to **2** and **3** is investigated (Fig. S1). As for the case without gold, the energy rise for the two dehydrogenation steps ($\Delta E_1$ and $\Delta E_2$) is 29.6 and 8.0 kcal/mol respectively which is compensated by the exothermicity of the hydrogen capture reaction. After the introduction of gold, compound **1** is firstly forced to coordinate with gold and form **4,** due to a distinctive stabilization energy of 18.9 kcal/mol that is high enough to alter the following reaction pathway entirely. Subsequent dehydrogenation energy from **4** to **5** ($\Delta E_1$') nearly remains only with a slight decline of 0.2 kcal/mol as compared to that in the absence of gold. Then gold switches to the newly formed C=C double bond for higher stabilization energy forming complex **6**, followed by the second dehydrogenation step with the energy rise from **6** to **7** ($\Delta E_2$') of 16.8 kcal/mol which is more than doubled in comparison with the one $\Delta E_2$. Arising from the significant stabilization toward intermediates, gold uplifts the dehydrogenation energy of both steps, especially the second one. Therefore, the dehydrogenation reaction is decelerated and less amount of coke is formed within certain period of reaction. With this simple DFT calculation, it clearly justifies the presence this dehydrogenation inhibition effect on gold particles.

**Table S1** $NH_3$-TPD data of Au/ZSM-5 catalysts

| Sample | Temperature at maximum/ $^oC$ | | Acid quantity (mmol/g) | |
|---|---|---|---|---|
| ZSM-5 | 150 | 314 | 0.049 | 0.075 |
| Au/ZSM-5(0.5) | 152 | 322 | 0.051 | 0.078 |
| Au/ZSM-5(1.0) | 152 | 318 | 0.052 | 0.083 |
| Au/ZSM-5(2.0) | 153 | 321 | 0.053 | 0.078 |

**Catalytic performance test**

The MTP reaction was carried out at 460 $^{o}$C in an auto-sampled fixed-bed microreactor under atmospheric pressure. The catalyst load was 0.5 g and the WHSV for methanol was 1.25 $h^{-1}$ with a feed of methanol solution (n(MeOH):n($H_2O$) = 1:5). The total products were analyzed by an on-line thermo trace gas chromatograph equipped with a Flame Ionization Detector (FID) and a 50 m CP-ParaPLOT Q capillary column. Both methanol and DME are regarded as reactants for calculation. The mass balance is above 95%.

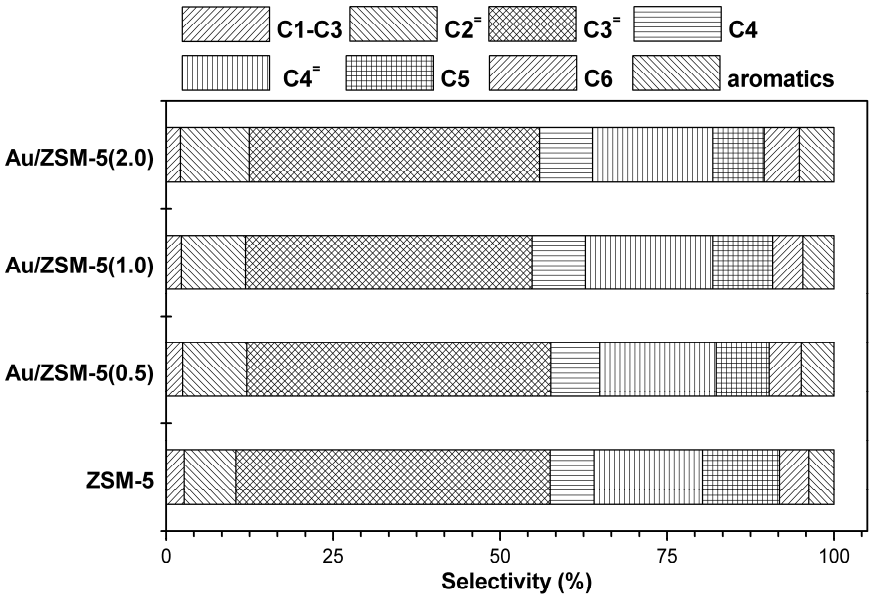


**Fig. S2** Initial product selectivity of MTP reaction over ZSM-5, Au/ZSM-5(0.5), Au/ZSM-5(1.0) and Au/ZSM-5(2.0), reaction conditions: WHSV=1.25 $h^{-1}$, T=733 K, n($CH_3OH$):n($H_2O$)=1:5, $P_{total}$=1 atm