Supplementary Information

Title: Surface plasmon-enhanced zeolite catalysis under light irradiation and its correlation with molecular polarity of reactants

Xingguang Zhang,^a Aijun Du,^a Huaiyong Zhu,^a Jianfeng Jia^b, Jun Wang^c and Xuebin Ke^{*a}

^a School of Chemistry, Physics and Mechanic Engineering, Queensland University of Technology. Brisbane, QLD 4101, Australia. Fax: +61 731381804; Tel:+ 61 731389197; E-mail: <u>x.ke@qut.edu.au</u>
^b School of Materials and Chemical Engineering, Shanxi Normal University, Linfen, Shanxi Province, China.
^c State Key Laboratory of materials-oriented Chemical Engineering, College of Chemistry and Chemical Engineering, Nanjing University of Technology, Nanjing, China.

Section 1: Experimental Section

Synthesis of zeolite NaY. All chemicals used were purchased from Sigma-Aldrich without further treatment. The zeolite NaY was prepared by the method reported in literature,^[s1] and the organic templates were removed by calcinating the samples at 550°C for 5 hours. Thus-obtained samples were ion-exchanged at 90°C for 3 h for each run (three times in total) under continuous stirring with the 0.1 mol/L sodium chloride (NaCl) aqueous solution to remove the sodium defects on the zeolite surfaces. After each run of ion-exchange, the samples were washed thoroughly with deionised water and then calcinations were conducted at 400°C for 3 hours.

Preparation of Au/NaY catalysts. Typically, 1.25 g of NaY was dispersed into 50 mL of 3.8×10^{-3} mol/L aqueous solution of chloroauric acid (HAuCl₄). Then 0.125 g of poly(vinyl alcohol) (PVA) was dispersed in 10 mL of deionised water, and was added into the mixture of zeolite and HAuCl₄ solution under stirring for 0.5 h. To this suspension, 0.5 mL of 0.38 mol/L aqueous solution of tetrakis-(hydroxymethyl)phosphonium chloride (THPC, the reducing agent) was added dropwise, followed by adding 2.25 mL of 0.38 mol/L sodium hydroxide aqueous solution (NaOH). The mixture was stirred continuously for 2 h and aged statically for 24 h. Finally, the solid was washed with deionised water three times and ethanol once; and the obtained solids were dried at 60°C for 16 h. The dried solids were used directly as photocatalysts, denoted as Au/NaY catalysts.

Characterisation of catalysts. XRD (X-ray Diffraction) patterns were obtained on the Philips PANalytical X'Pert PRO diffractometer, using Cu *Ka* radiation (λ =1.5418 Å) at 40

kV and 40 mA. The diffraction data were collected from 5° to 75° with a resolution of 0.01° (2 θ). UV/Vis spectra were recorded on the Cary 5000 UV/Vis-Nir Spectrophotometer, using light source of (200-800) nm in wavelength. XPS (X-ray Photoelectron Spectroscopy) data were collected on the ESCALAB 250 spectrometer, using the Al *Ka* radiation as the X-ray source. The C_{1s} peak at 284.8 eV was used as the reference for the calibration of the binding energy scale. TEM (Transmission Electron Microscopy) images were taken with a JEOL JEM-2100 transmission electron microscope employing an accelerating voltage of 200 kV. The specimens were fine powders deposited onto a copper microgrid coated with a holey carbon film. The element composition of some samples was determined by energy-dispersive X-ray spectroscopy (EDS) attached on a JEOL JSM-7001f field emission scanning electron microscopy.

Catalytic test. All the raw chemicals were purchased from Sigma-Aldrich and used without further treatment. As for a typical batch reaction, 0.2 g of aldehyde was added into 10 g of methanol, and then 0.025 g of catalysts was added. The reaction was conducted in a round-bottomed 50-mL transparent glass flask equipped with a sealed spigot and a magnetic stirrer. The reaction temperature was controlled in a silicone oil bath. The flask was irradiated with a 500-Walt Halogen lamp, and the UV light was removed by a glass filter to cut off the light with the wavelength shorter than 420 nm. The light intensity was controlled from 0 (light off) to 0.505 W/cm². In particular, to investigate the influence of cut-off wavelength, light irradiation was adjusted to keep the light intensity (after filters) constant. Aliquots (0.5 mL) were collected at given time intervals and filtrated through a Millipore filter (pore size 0.45 μ m) to remove the catalyst particles. Control experiments were performed without light irradiation, maintaining the other conditions identical. The filtrates were analysed by a Gas Chromatography (GC, HP6890, HP-5 column) and the components of products were analysed on a GC-MS (6890-5793, HP-5MS column). Quantification of the products was obtained from the peak area ratios of the components.

Section 2: Calculations of dipole moments of reactants

The dipole moments of the molecules were theoretically predicted within the framework of Density Functional Theory (DFT) with B3LYP^[s2, s3] functional provided by Gaussian09 package^[s4]. The 6-31G(d) basis set was selected to describe the atomic orbitals for all atoms involved. All the molecules were optimized at this B3LYP/6-31G(d) level first and then the dipole moments were calculated.

Section 3: XRD patterns, EDS analysis and TEM images of Au/NaY and NaY.

The number of Au nanoparticles has a significant influence on conversion efficiency owing to the surface plasmonic-enhanced effect. With various amounts of gold loading (1%, 3%, and 5%), the corresponding data of materials characterization have been provided, including UV-Vis spectra, XRD patterns, and TEM images. With the increasing loading of Au-NPs from 1% to 3% and then to 5%, the light absorption increases significantly (Table S1, Figure S2). The conversion efficiency of 3% Au/NaY exceeded that of 1% Au/NaY, but the conversion efficiency over 5% Au/NaY decreased considerably, which can be ascribed to that the high density of Au NPs covers the active centers on zeolites and thus impedes the access of reactants to the active sites.

According to the TEM images of zeolites, the size of nanozeolite NaY is 70-120 nm (Figure S3). Smaller zeolites (70-120 nm) are preferred in this study because gold nanoparticles are closer to active centres in zeolites and the Na⁺ cations, thus exerting stronger influence on them under light irradiation.



Figure S1 XRD patterns of NaY and Au/NaY with various loadings of gold nanoparticles (weight ratio).

Table S1. Catalytic conversions of acetalisation of 2-methoxy benzaldehyde with methanolon Au/NaY with various loadings of gold nanoparticles.CatalystsNominal loadingEDS analysisConversion, %Selectivity, %

Catalysts	Nominal loading	EDS analysis	Conversion, %	Selectivity, %
1% Au/NaY	1%	0.9%	68.6	>99
3% Au/NaY	3%	2.7%	96.3	>99
5% Au/NaY	5%	4.8%	58.4	>99



Figure S2 Typical EDS patterns of Au/NaY with various loadings of gold nanoparticles (1%, 3%, and 5%; weight ratio).



Figure S3 TEM images of NaY (Left) and Au/NaY of 3wt% of gold loading (Right).

Section 4: Calculations of the effect of extra electric fields on C=O bonds.

The Density Functional Theory (DFT) was used to calculate the influence of extra electric field on the C=O bond length. All the *ab* initio calculations were performed with the Gaussian09 package.^[s5] The Density Functional Theory level method B3IYP with basis set of 6-31G(d,P) was employed.^[s6, s7] Geometry optimizations were first performed in the absence of electric field for aldehyde and methanol, respectively. Then a finite field at various sizes was added along a specific axis and all the geometries were fully relaxed in the presence of an electric field until a tight convergence reached.

The DFT calculations unambiguously demonstrated that increasing the strength of external electric field stretched the C=O bond of aldehydes, whereas had no effect on methanol molecules, probably because the molecular polarity of aldehydes are larger than that of methanol (1.70 Debye). The relationship between the C=O bond length and the electric field strength was linear (Figure S1). For instance, the C=O bond length of benzaldehyde was 1.218 Å, 1.223 Å, 1.229 Å, 1.236 Å, and 1.245 Å, when the electric field strengths was 0 V/nm, 2.58 V/nm, 5.16 V/nm, 7.74 V/nm, and 10.32 V/nm, respectively. The C=O bond length of other three reactants were calculated using the same method.

To be clear, the C=O bond polarity can affect the molecular polarity, but they are not equal; namely, a larger C=O bond length does not necessarily mean a larger molecular dipole moment because of the existence of another substitute functional group, such as -Br, -Cl and $-OCH_3$. For instance, the dipole moment of benzaldehyde (3.3027) is smaller than that of 2-methoxy benzaldehyde (4.8129), but DFT calculations showed that the extra electric field

could stretch the C=O bond of benzaldehyde more strongly than it stretched the C=O bond of 2-methoxy benzaldehyde, probably because of the influence of other unidentified factors, such as the difference in the electron withdrawing ability, and the interaction between the function group of -CHO and the substitute functional groups. Generally, for 2-bromo benzaldehyde and 2-chloro benzaldehyde, their dipole moments are smaller, and the extra electric field had a slighter effect on stretching the C=O bonds.



Figure s4. The relationship between the C=O bond length (Angstrom) of selected aldehydes and the intensity of extra electrostatic fields simulated by the density functional theory (DFT) method.

It can be noted that the bond length is subjected to the strength of imposed electric-field (light effect in this case), thus directly correlating with total conversion efficiency (Figure S5).



Figure S5. The conversions of reactants on Au/NaY with light on and the C=O bond length of reactants (as listed in Table 1). Here the C=O bond length was calculated from Figure S4 when the extra electric field was 6.2 V/nm.

References

- [s1] S. Mintova, N. H. Olson, V. Valtchev, T. Bein, Science 1999, 283, 958 960
- [s2] A. D. Becke, Density-functional thermochemistry. III. The role of exact exchange, J. Chem. Phys. 98 (1993) 5648-5652.

- [s3] C. Lee, W. Yang, R. G. Parr, Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density, Phys. Rev. B 37 (1988) 785-789.
- [s4] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision C. 01, Gaussian, Inc., Wallingford, CT, 2010.
- [s5] M. J. Frisch, G. Trucks, H. Schlegel, G. Scuseria, M. Robb, J. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, and G. Petersson, Gaussian 09; Gaussian. Inc., Wallingford, CT 2009.
- [s6] A. D. Becke, J. Chem. Phys. 1993, 98, 5648-5652.
- [s7] C. Lee, W. Yang and R. G. Parr, Phys. Rev. B 1988, 37, 785-789.