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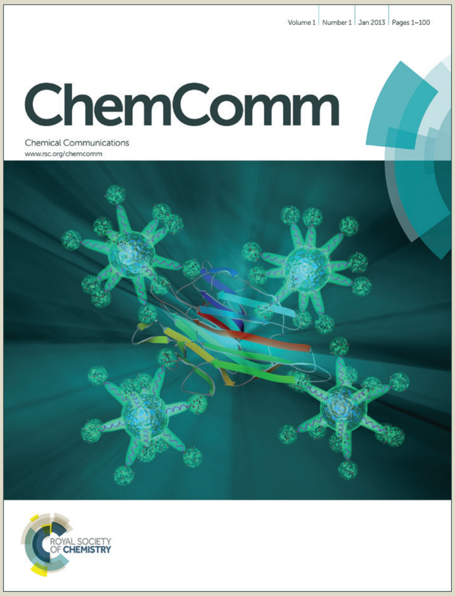

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Surface plasmon-enhanced zeolite catalysis under light irradiation and its correlation with molecular polarity of reactants

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Enhanced catalytic performance of zeoltes *via* the plasmonic effect of gold nanoparticles has been discovered to be closely correlated with the molecular polarity of reactants. The intensified polarised electrostatic field of Na^+ in NaY plays a critical role in stretching the C=O bond of aldehydes to improve the reaction rate.

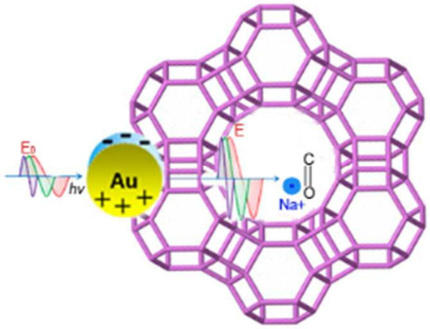
Zeolites are crystalline aluminosilicates and feature a network of molecule-size pores and cages, playing a dominant role in the manufacture of everyday chemicals. However, many processes often require high temperatures and pressures, imposing extra energy consumptions. Thus it is a great challenge to achieve energy-efficient chemical processes.[1]

Photocatalysis offers great promise in the advancement of chemical production, energy storage, environment remediation, and functional materials.[2] For zeolites, the positive charges of extra-framework cations balance the negative charges of the framework aluminium centres, and these accessible cations have polarised electrostatic fields (PFE) and play an important role in adsorbing and activating reactants. Zeolites have been employed as photocatalysts for the degradation of pollutants under UV light. These UV-exciting systems have limited applications because UV light only accounts for 4% of sunlight.[3] Under visible light irradiation, the selective oxidation of hydrocarbons over zeolites has been investigated, whereas the catalytic reaction rate is quite low.[4] To improve the photocatalytic capacity of zeolite-based catalysts, ion-exchange and host-guest structures have been developed to take advantage of porous structures and electron-transfer properties. The host-guest structures, however, have low density and poor distribution of encapsulated photoactive sensitizers. Above all, current zeolite-based photocatalysts suffer from weak abilities to harvest visible light, poor catalytic performance, and unstable catalyst structures.[5]

Efficient "antennas" are required to enhance the light absorption efficiency. Recently, plasmonic nanostructures have been demonstrated to possess remarkable abilities to absorb visible light owing to the localised surface plasmon resonance (LSPR).[6] The plasmonic nanostructures can localise, enhance, and propagate the electromagnetic field of visible light because of the LSPR effect which features a collective oscillation of free conduction electrons on the particle surfaces. The excited 'hot electrons' may have direct or indirect influence on the reaction efficiency.[6] Actually, this LSPR effect can amplify the electromagnetic field intensity of incident light ($|E_0|$) and results in an enhanced electromagnetic field ($|E|$) on the nanometre scale.[7] This enhancing effect is known as the "electric near-field enhancement (ENFE)", and the enhancement factor ($|E|/|E_0|$) can reach *ca* 10^3 at the surface of an isolated particle and *ca* 10^6 at junctions of interparticles (hot spots).[8] These unique characteristics of LSPR and ENFE have been successfully applied in such as the surface-enhanced Raman scattering, photodetectors, photodegradation and photovoltaic solar cells.[9] In zeolite photocatalysis, both the LSPR effect and PEF function of cations have been examined initially.[10] However, the role of PEF strengthened by the ENFE effect has not been well understood as well as the correlation of catalytic performance and the molecular polarity of reactants under irradiation.

This study proposes an innovative plasmonic structure which is composed of NaY zeolites decorated with gold nanoparticles (Au-NPs) as "antennas" to catalyse the acetalisation of aromatic aldehydes with methanol. Au/NaY with various amounts of gold loadings was prepared and the contribution of this "relay enhancement" from ENFE to PEF was identified. The enhanced light absorption was discovered to boost the catalytic activity of zeolites and the enhanced reaction rate directly correlated with the molecular polarity of reactants.

To illustrate in Scheme 1, Au-NPs exhibit the LSPR effect upon visible light irradiation, resulting in enhanced electromagnetic fields of incident light. Taking Au/NaY for example, the LSPR-induced ENFE can intensify the PEF of Na^+ in zeolites, enabling the intensified PEF to stretch the C=O bond of reactants to facilitate their breakage, thus accelerating the reaction rate.

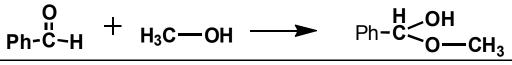


Scheme 1. Proposed mechanism of the acetalisation on Au/NaY under the irradiation of visible light. E_0 refers to the original electromagnetic field of incident light, and E refers to the intensified electromagnetic field. $|E|/|E_0|$ can be up to 10^3 - 10^6.

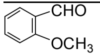
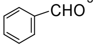
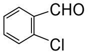
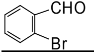
The acetalisation of aromatic aldehydes with methanol can be significantly enhanced by Au-NPs supported on NaY under visible light irradiation, and the experimental results are shown in Table 1. With light off, Au/NaY and NaY showed no obvious difference in conversion, indicating that Au-NPs did not enhance the catalytic performance of NaY without visible light irradiation because the Au-NPs were not active centres for the acetalisation (*Experimental details, Supporting Information, Section S1*).

With light on, the conversions on Au/NaY improved significantly compared with those on NaY, demonstrating that visible light irradiation plays an essential role in boosting the catalytic activity of acetalisation on Au/NaY. The dipole moments of reactants corresponding to molecular polarities were calculated by the DFT method (*Supporting Information, Section S2*). It is noteworthy that the net increase in conversion over Au/NaY, which means the conversion of Au/NaY (light on) deducts the conversion of Au/NaY (light off), increased with the molecular polarities of aldehydes. This tendency demonstrates that photo-excited Au-NPs made more contributions to enhancing the conversion of reactants with larger molecular polarities. Moreover, without Au-NPs, the conversions on NaY with light on were similar to those of NaY with light off, showing that light irradiation alone could not enhance the catalytic performance of NaY and that visible light could not strengthen the PEF of Na^+ strongly enough to boost the catalytic activity.

Table 1. Catalytic conversions of acetalisation of aldehydes with methanol on Au/NaY and NaY[a]



$$\mathrm{Ph{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}H} + \mathrm{H_3C{-}OH} \longrightarrow \mathrm{Ph{-}\overset{H}{C}}\genfrac{}{}{0pt}{}{\mathrm{OH}}{\mathrm{O{-}CH_3}}$$

Reactants	Dipole Moment (Debye)	Net increase (%)	Light off (Conversion, %)		Light on (Conversion, %)	
			Au/NaY	NaY	**Au/NaY**	NaY
	4.81	44.4	**51.9**	50.1	**96.3**	50.9
	3.30	38.2	**48.9**	45.8	**87.1**	49.1
	3.29	38.1	**28.2**	28.4	**66.3**	38.1
	3.25	35.3	**17.6**	16.9	**52.9**	18.2

[a] Reaction conditions: reactant, 0.2 g of aldehyde and 10 g of methanol; 0.025 g of Au/NaY of 3wt% gold loading; atmosphere, air; temperature, 60°C; reaction time 6 h; light intensity, 0.505 W/cm^2; wavelength range (420-800) nm. The selectivity towards diacetal was excellent (>99%) in all reactions.

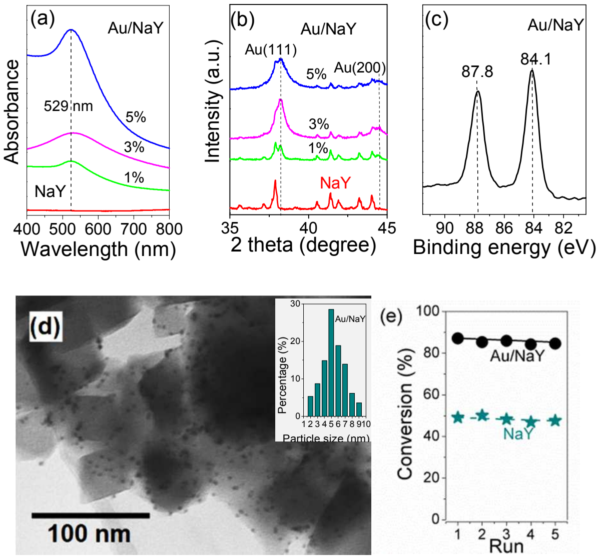


Figure 1. (a) UV/Vis patterns of Au/NaY and NaY; (b) XRD patterns of Au/NaY and NaY; (c) XPS spectra of Au/NaY, (d) the TEM images of Au/NaY of 3wt% gold loading and the size distribution of Au-NPs, and (e) Test of the reusability of catalysts in the acetalisation reaction between benzaldehyde and methanol.

Now one may wonder why the photo-excited Au-NPs can accelerate the acetalisation rate on Au/NaY. The physiochemical properties of catalysts were investigated. UV/Vis spectra (Figure 1a) showed that NaY had no absorption of visible light, whereas Au/NaY exhibited evident absorption of visible light at *ca* 529 nm and the light absorption increases with the amounts of gold loadings because of the LSPR effect. X-ray diffraction patterns (XRD, Figure 1b and Figure S1 in *Supporting Information, Section S3*) confirmed that NaY crystal structures preserved well after loading of Au-NPs, and the gold crystal face of Au(111) and Au(200) can be observed at 38.2° and 44.5°, respectively.[10] X-ray photoelectronic spectra (XPS, Figure 1c) identified the metallic state of gold on zeolites: Au$4f$ spectra confirmed that the binding energies of Au$4f_{7/2}$ and Au$4f_{5/2}$ electrons were 84.1 eV and 87.8 eV, respectively.[11] TEM images (Figure 1d) provided direct information of the size, shape and distribution of Au-NPs on NaY, showing that Au-NPs existed as pseudospherical particles and had a narrow size distribution, ranging from 3 to 8 nm. The test of reusability of NaY and Au/Y confirmed that the catalysts could be recycled and reused after five runs, showing slightly decline in catalytic activity (Fig.1e).

On the basis of the experimental and characterization results, we now tentatively explain the enhancing mechanism. It has been reported that the existence of external electric fields of 12-15 V/nm obviously helps activate the reactants of CO/O_2 and enhances the oxidation process on small gold crystals (20-30 nm)[12]. The reported mechanism of acetalisation demonstrates that the metal ions of zeolites break the C=O bond first to initiate the reaction.[13] Moreover, Density-function-theory (DFT) calculations confirmed that the extra electric field (0-12 V/nm) could stretch the C=O bond of aromatic aldehydes, but did not affect the methanol molecules (*Supporting Information, Section S4*). The strength of extra electric field employed in DFT calculations is on the same order of the PEF strength of Na^+ in NaY (6.2 V/nm)[14]. Therefore, it becomes convincing that the PEF of Na^+ should be directly intensified by the LSPR-induced ENFE, so that the intensified PEF can stretch the C=O bond of aldehydes to boost the reaction rate. Aldehydes with larger molecular polarities can interact more strongly with the intensified PEF, thereby showing higher conversions (Figure S5).

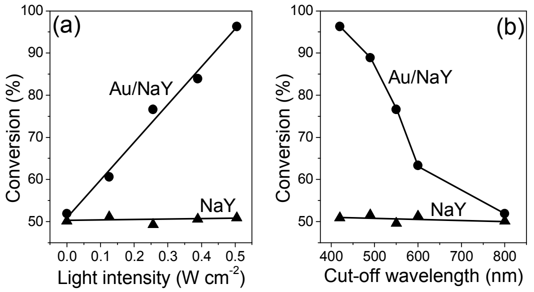


Figure 2. The conversion of the acetalisation between 2-methoxy benzaldehyde and methanol varies as the function of light intensity (a), and cut-off wavelength (b) (e.g. 400 nm means the light wavelength < 400 nm is cut off). Reaction conditions: 2-methoxy benzaldehyde, 0.2 g, methanol, 10 g, catalyst, 0.025 g, atmosphere air, temperature 60°C, and time 6 h. The selectivity towards diacetal was excellent (>99%) in all these reaction conditions.

Light intensity and wavelength also have influence on the catalytic consequences. Figure 2a illustrated that the correlation between measured catalytic conversions as the function of light intensity. A linear increase in the conversion with the light intensity was observed on Au/NaY, whereas no apparent change in conversion was observed on NaY. This linear dependence indicated that the photo-excited Au-NPs were responsible for the observed increase in the catalytic activity, because stronger light intensity resulted in more intensive ENFE-PEF interaction to improve the reaction. In addition, the range of wavelength also affected the catalytic performance (Figure 2b, glass filters were used to remove photons with wavelengths below the filter threshold). The conversion on Au/NaY declined gradually when the light source with longer cut-off wavelengths was used, keeping the light intensity (after filter) constant. However, the wavelength change did not affect the catalytic activity of NaY. All these results demonstrated that photo-excited Au-NPs made essential contribution to boosting the reaction.

Conclusions

The acetalisation of aromatic aldehydes with methanol can be significantly enhanced by supported Au-NPs on NaY under visible light irradiation, and the catalytic activity is directly correlated with the molecular polarity of aldehydes. Au-NPs exhibit the LSPR effect upon visible light irradiation, resulting in enhanced electromagnetic fields of incident light. This LSPR-induced ENFE can intensify the PEF of Na^+ in zeolites, enabling the intensified PEF to stretch the C=O bond of reactants to facilitate their breakage, thus accelerating the reaction rate. Moreover, reactants with a larger molecular polarity convert much fast because of the stronger interaction between the reactant and the intensified PEF. Further work on exchanged zeolites of other ions and tuneable sizes of Au-NPs are conducted. This cascade enhancement effect from electromagnetic fields of visible light to electrostatic fields of zeolite extraframe cations may have extensive applications in adsorption, separation, and catalysis.

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Notes and references

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