Supporting Information

Methyl Ester Synthesis Catalyzed by Nanoporous Gold: From 10^{-9} torr to 1 atm

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Evaluation of the activity and selectivity of npAu catalyst in flow reactor

The reaction conditions were held constant for at least 30 min to reach steady state. All measurements of the activity were repeated at least three times for each specific reaction condition. In principle, the conversion of the reactants should be calculated based on the corresponding concentrations before and after reaction. In this work, however, the reactor configuration does not allow for accurate measurements of the reactant concentrations before reaction ($c_{methanol,0}$ *and* $c_{aldehyde,0}$) via bypass. Furthermore, the conversions could not be calculated simply based on the nominal concentrations as those measured deviate from the nominal values in our experiments due to the fluctuation in the temperature of the condenser (see Experimental Section). In view of the fact that only up to two prominent products are detected in all the experiments, namely, methyl formate and methyl ester (methyl acetate or methyl butyrate), in this paper the conversions of methanol (X_{methanol}) and aldehyde (X_{aldehyde}) were calculated based on the reaction stoichiometry using the expressions:

$$X_{methanol} = \frac{2 \times c_{methyl.formate} + c_{methyl.ester}}{c_{methanol,1} + 2 \times c_{methyl.formate} + c_{methyl.ester}} \times 100\%$$

$$X_{aldehyde} = \frac{c_{methyl.ester}}{c_{aldehyde,1} + c_{methyl.ester}} \times 100\%,$$

where $c_{methanol,1}$ and $c_{aldehyde,1}$ are the concentration of methanol and aldehyde in the gas mixture after reaction, respectively; $c_{methyl.ester}$ and $c_{methyl.formate}$ are the concentration of methyl ester (methyl acetate or methyl butyrate) and methyl formate in the gas mixture after reaction, respectively.

The mass-specific reaction rates of aldehydes (*r*) are calculated as follows:

$$r = \frac{F \times c_{aldehyde} \times X_{aldehyde}}{22.4 \times 10^3 \times m_{catalyst}} = \frac{50ml/\min \times c_{aldehyde} \times X_{aldehyde}}{60s/\min \times 22.4 \times 10^3 ml/mol \times 0.0284g},$$

where F is the total flow rate of the reaction mixture, $m_{catalyst}$ is the weight of the npAu catalyst disk.

The selectivity (*Sel*) of methyl formate and methyl ester (methyl acetate or methyl butyrate) production were calculated using the expressions:

$$Sel_{methyl.ester} = \frac{c_{methyl.ester}}{c_{methyl.ester} + c_{methyl.formate}} \times 100\%$$

$$Sel_{methyl.formate} = 100 - Sel_{methyl.ester}.$$

Note that each data point of the activity and selectivity reported in this work was obtained by calculating the mean value of the last three results. The error bars were determined from the corresponding standard deviation.

Temperature programmed reaction experiments on npAu catalyst in UHV and data evaluation

Mass spectrometry is used to determine products, conversion and selectivity of oxygen assisted reactions in UHV on npAu. In some cases fragments are not unique to a specific product, and in those cases the overlapping contributions are subtracted using the referenced ion yields in Tables S1 and S2.

Table S1 Relative ion yields used for subtractions in quantification of the reaction of methanol and acetaldehyde on O/npAu

Molecule	Mass	Mass fragments reference: *relative intensity*
methyl acetate[2]	74 (parent, unique)	1.00
	29	0.58
methyl formate[1]	60 (parent, unique)	1.00
	32	1.48
	29	1.58
carbon dioxide[1]	44[3] (parent, unique)	1.00
acetaldehyde[2]	44 (parent)	0.56
	29[3] (unique)	1.00
	31	0.08
methanol[2]	31 (parent)	1.39
	29	1.04
	32[3]	1.00

[1] Data reference adopted from NIST (Stein, S. E.; Linstrom, P. J., (Ed.); mallard, W. G., (Ed.); Institute of Standards and Technology, Gaithersburg MD, 20899).

[2] Reference measure from the molecular desorption of the authentic sample from Au(111).

[3] Mass fragments are unique for acetaldehyde, methanol, and carbon dioxide after the relevant subtraction of contributions from products and reactants has been conducted.

Table S2 Relative ion yields used for subtractions in quantification of the reaction of methanol and butyraldehyde on O/npAu

Molecule	Mass	Mass fragments reference: *relative intensity*
methyl butyrate[1]	87 (parent, unique)	1.00
methyl formate[1]	60 (parent, unique)	1.00
	32	1.48
carbon dioxide[1]	44[3] (parent, unique)	1.00
butyraldehyde[2]	72 (parent, unique)	1.00
	44	1.39
methanol[2]	32[3] (unique)	1.00

[1] Data reference adopted from NIST (Stein, S. E.; Linstrom, P. J., (Ed.); mallard, W. G., (Ed.); Institute of Standards and Technology, Gaithersburg MD, 20899).

[2] Reference measure from the molecular desorption of the authentic sample from Au(111).

[3] Mass fragments are unique for carbon dioxide and methanol after the relevant subtraction of contributions from butyraldehyde and methyl formate (respectively) has been conducted.

Procedure for selectivity calculations

Selectivity towards different products is calculated on a molar basis, according to the following formulas for methanol with aldehyde (acetaldehyde or butyraldehyde):

$$Sel_{methyl\ ester} = \frac{n_{methyl\ ester}}{n_{methyl\ ester} + n_{methyl\ formate} + n_{CO_2}}$$

$$Sel_{methyl\ formate} = \frac{n_{methyl\ formate}}{n_{methyl\ ester} + n_{methyl\ formate} + n_{CO_2}}$$

where $Sel_{methyl\ ester}$ and n stand for the selectivity of methyl ester (methyl acetate or methyl butyrate) and the number density of molecules in the ionizer of the mass spectrometer, respectively; n for various species were calculated according to the following formula (The derivation can be found in the supporting information of J. Am Chem. Soc. 2010, 132, 16571.):

$$n_i \approx I_i \approx \sum_j I_{ij} = \sigma_i^{-1} \bullet \sum_j \frac{s_{ij}}{T_{ij} \bullet \delta_{ij}} = \frac{\sigma_i^{-1} \bullet s_{ik}}{T_{ik} \bullet \partial_{ik}} \bullet \left(1 + \sum_{j,j \neq k} \frac{s_{ij} \bullet T_{ik} \bullet \delta_{ik}}{s_{ik} \bullet T_{ij} \bullet \delta_{ij}}\right)$$

where

s_{ij} is the measured mass spectrometer signal of the *j*th mass fragment of molecule *i*,

s_{ij}/s_{ik} is the ratio of signals of the *j*th and *k*th fragments of molecule *i* determined by separate calibrations of the neat parent molecule *i*,

T_{ik} is the transmission coefficient of the *k*th fragment of molecule *i*,

δ_{ik} is the detection coefficient of the *k*th fragment of molecule *i*.

Unique masses are indicated for all species in the quantification as indicated in the table (Table S1-S2). The constants used in the quantification are summarized in Table S3.

Table S3 Constants used in the quantitative mass spectrometry analysis

Mass/amu	T[a]	δ[b]	*Molecule*	σ[d]
0-20	1	1.5	CO_2	3.5[c]
21-30	1	1	Acetaldehyde	7.25
31-40	1	0.9	Methanol	5.01
41-50	1	0.8	Methyl formate	7.25
51-60	1	0.7	Methyl acetate	12.69
61-70	1	0.65	Methyl butyrate	15.41
71-80	0.98	0.6	Butyraldehyde	12.69

[a] Adapted from manual of Hiden analyzer.

[b] Adapted from manual of the UTI 100C mass spectrometer.

[c] Adapted from *J. Phys. B. At. Mol. Opt. Phys.* **2004**, *37*, 445-455.

[d] unless specified, cross sections are from *International Journal of Mass Spectrometry* **2008**, *273*,53-57.

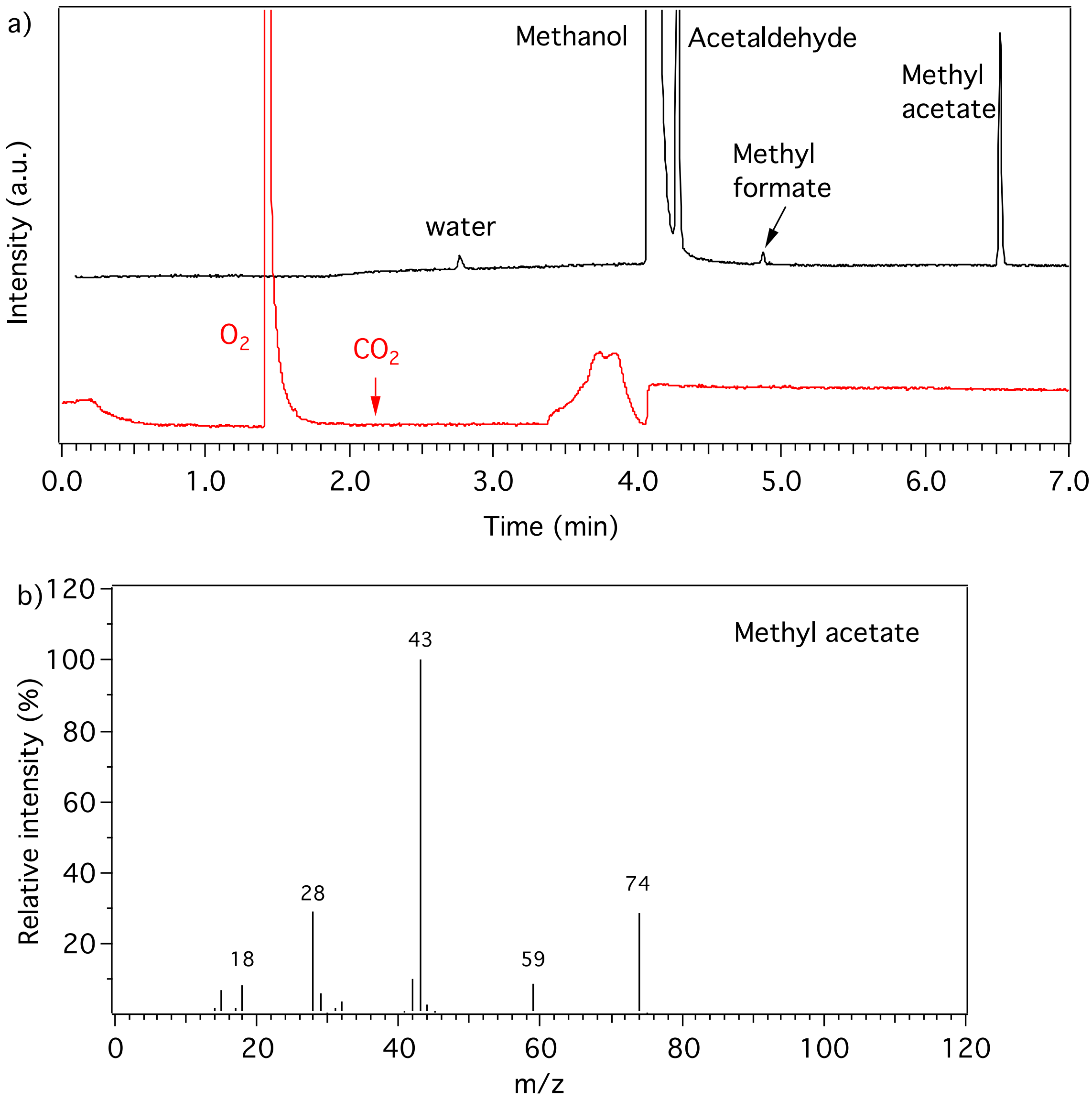

Figure S1 a) Typical chromatograms for reaction of methanol with acetaldehyde in the presence of O_2 over the npAu catalyst and b) the mass spectrum of the cross-coupling product methyl acetate. Reaction conditions: 20 vol.% O_2, 10 vol.% methanol, 0.5 vol.% acetaldehyde, 70°C, 50 mL/min.

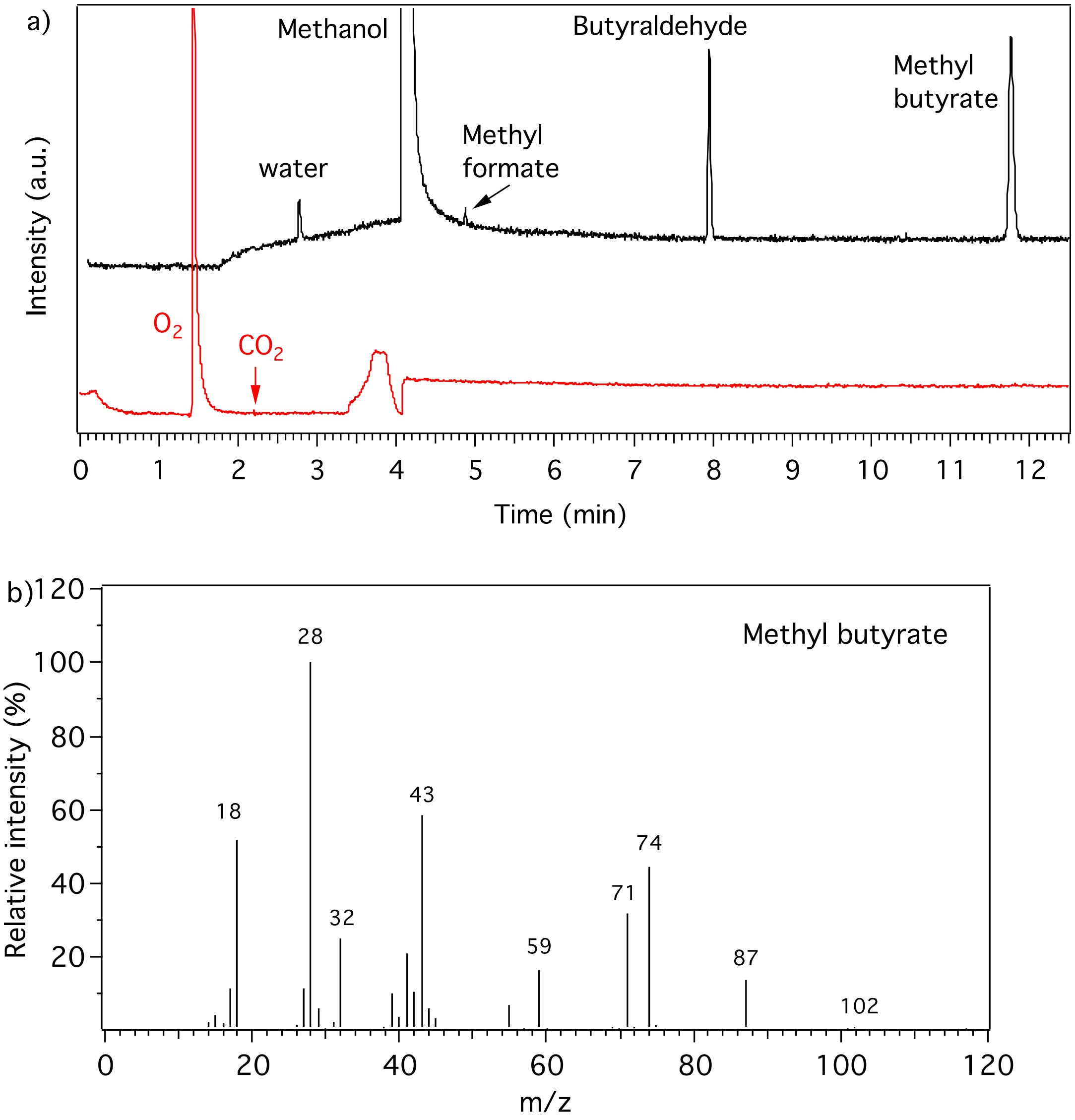

Figure S2 a) Typical chromatograms for reaction of methanol with butyraldehyde in the presence of O_2 over the npAu catalyst and b) the mass spectrum of the cross-coupling product methyl butyrate. Reaction conditions: 20 vol.% O_2, 10 vol.% methanol, 0.5 vol.% acetaldehyde (0.06 vol.% butyraldehyde), 70°C, 50 mL/min.

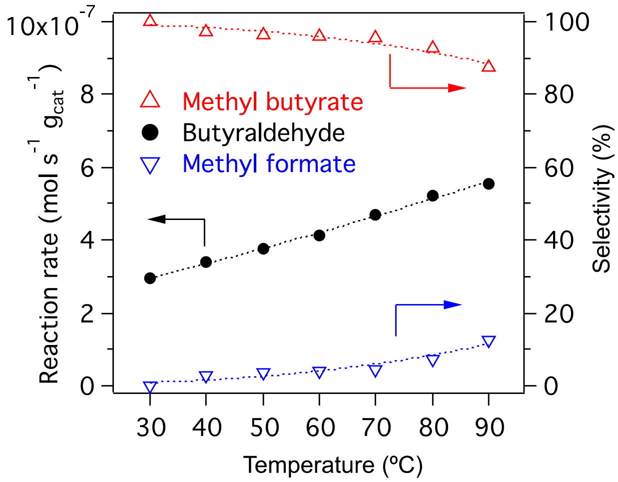

Figure S3 The activity and selectivity of npAu catalyst in methanol-butyraldehyde coupling reaction as a function of reaction temperature. Reaction conditions: 20 vol.% O_2, 10 vol.% methanol, 0.057 vol.% butyraldehyde, 50 mL/min.

Evaluation of the influence of mass transport limitation on the reaction kinetics in the flow reactor

The measured kinetics (activity, reaction orders, activation energy) may be strongly affected by mass transport limitation in the nanoporous Au materials used here.[1] The extent of mass transport limitation was evaluated by using the so-called Weisz modulus (M_w).[2] Assuming first order kinetics, the Weisz modulus M_w is

$$M_w = \frac{r_A L^2}{C_A D_{eff}},$$

where r_A is the *observed* reaction rate, L is the characteristic length (0.5×thickness for flat plate approximation), C_A is the concentration of the reactant (0.223 mol m^{-3} for acetaldehyde), and D_{eff} is the effective diffusion coefficient, which can be derived by the following expression[3]

$$D_{eff} = \varepsilon_p \frac{D_K}{\tau},$$

where D_K is the Knudsen diffusion coefficient ($m^2\ s^{-1}$), ε_p is the porosity of the material (0.7), and τ is the tortuosity factor (set to 5).[1] The Knudsen diffusion coefficient D_K ($cm^2\ s^{-1}$) can be calculated using the relationship:

$$D_K = 4850 d_{pore} \sqrt{\frac{T}{M}},$$

where d_{pore} is the pore diameter (50 nm in our case), T is the temperature (K), and M is the molecular mass of the gas molecules (g mol^{-1}). As a criterion, if M_w is smaller than 0.15, the effect of mass transport limitation can be neglected; if M_w is larger than 4, there is *strong* mass transport limitation effects on the reaction; otherwise, the reaction is diffusion influenced.[2]

Based on the steady-state activity data in Fig. 7, a Weisz modulus of ~0.024, ~0.081, and 0.87 are calculated for O_2, methanol, and acetaldehyde, respectively, in the methanol-acetaldehyde reaction (see also Table S4). For the reaction of methanol and butyraldehyde, Weisz modulus of ~0.024, ~0.32, and 2.42 are obtained for O_2, methanol, and butyraldehyde, respectively (Table S4). Obviously, the reaction of both aldehydes is influenced by diffusion, but negligible diffusion limitation exists for internal access of the npAu for either O_2 or methanol in both coupling reactions.

For strong diffusion control the actual activation energies are approximately 2 times the measured ones; the true reaction orders (n) are given by $n = 2n_{\text{app}} - 1$,[4] where n_{app} is the measured values. Since the Weisz modulus data suggests that the methanol-acetaldehyde coupling reaction is only weekly influenced by pore diffusion, the actual E_a must lie between 20 and 40 kJ mol^{-1} for methanol-acetaldehyde coupling, and the corresponding reaction order of acetaldehyde is essentially first-order. The E_a obtained here is in rough agreement with that obtained on O/Au(111) surface, where an activation barrier of ~33 kJ mol^{-1} was reported.[5] The corresponding data for the methanol-butyraldehyde reaction after taking into account the diffusion limitations are also given in Table S4. Note that the Weisz modulus for butyraldehyde is significantly greater than that for acetalydehyde, indicating that the methanol-butyraldehyde reaction is affected by diffusion to a larger extent, which could be accounted for by the higher molecular weight of butyraldehdye.

Table S4 Estimated Weisz modulus of various reactants in the methanol-aldehyde coupling reactions on the npAu catalyst.

Coupling reaction	Weisz modulus (M_w)		
	O_2	Methanol	Aldehyde
Methanol-acetaldehyde [a]	0.024	0.081	0.87
Methanol-butyraldehyde [b]	0.024	0.32	2.42

[a] Reaction conditions: 0.5 vol.% acetaldehyde, 10 vol.% methanol, 20 vol.% O_2, 70°C, 50 mL/min.

[b] Reaction conditions: 0.057 vol.% butyraldehyde, 10 vol.% methanol, 20 vol.% O_2, 70°C, 50 mL/min.

Table S5 Estimated kinetic parameters of methanol-aldehyde coupling reactions on the npAu catalyst.

Coupling reaction	Conversion of aldehyde (%)	Reaction order			E_a (kJ mol^{-1})
		O_2	Methanol	Aldehyde	
Methanol-acetaldehyde	31 [a]	0.09 ± 0.01	0.11 ± 0.01	1.1 ± 0.22 (~*1.2*) [c]	20 ± 1 (~ *40*)
Methanol-butyraldehyde	67 [b]	0.15 ± 0.01	0.20 ± 0.02	0.83 ± 0.04 (~*0.66*) [d]	15 ± 0.2 (~*30*)

[a] Reaction conditions: 0.5 vol.% acetaldehyde, 10 vol.% methanol, 20 vol.% O_2, 70°C, 50 mL/min. [b] Reaction conditions: 0.057 vol.% butyraldehyde, 10 vol.% methanol, 20 vol.% O_2, 70°C, 50 mL/min. [c] Acetaldehyde concentration: 0.2 ~ 0.7 vol.%. [d] Butyraldehyde concentration: 0.01 ~ 0.06 vol.%. Data in parenthesis are calculated by taking the diffusion limitations into account.

It is useful to consider the effect of pore diffusion on the access of O_2 to the interior of the npAu catalyst. The dissociation probability of O_2 has been measured on npAu to be 2×10^{-4}.[6] From this value the rate of oxygen activation per catalyst bed volume is calculated to be 0.30 mol m^{-3} s^{-1} under reaction conditions, giving a Weisz modulus for oxygen activation in the npAu to be 0.0005, which is much smaller than that calculated using the observed reaction rate (0.015) but is still consistent with no diffusion limitation for O_2 activation under the 'standard' reaction conditions (10 vol.% methanol + 0.5 vol.% aldehyde + 20 vol.% O_2). Given this, the independence of the catalyst activity at high O_2 concentrations (>5 vol.%, Fig. 2) indicates that the surface active sites are essentially saturated by oxygen.

References

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