A Kinetic View on Proximity-dependent Selectivity of Carbon Dioxide Reduction on Bifunctional Catalysts

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ABSTRACT: Multifunctional catalysts with distinct functional components are known to have much improved selectivity. However, the well-known proximity-dependent selectivity observed in several high profile experiments is yet to be understood. Here, we reveal that such dependence is closely associated with the kinetics involved. Based on reaction-diffusion dynamics together with a coarse-grained model, one famous example, namely the proximity-dependent selectivity from carbon dioxide to liquid fuels on a bifunctional catalyst composed of HZSM-5 and In₂O₃, has been systematically examined. It is found that the diffusion kinetics of the intermediate methanol generated on In₂O₃ plays a decisive role for the selectivity. For different In₂O₃/HZSM-5 proximities, the local methanol concentration induce a shift of the dominant process for subsequent methanol-to-hydrocarbon reactions inside HZSM-5, resulting in a preferred reaction window to generate favorable liquid fuels with profound high selectivity. Our findings emphasize the importance of the largely overlooked kinetic in the design of multifunctional catalysts.

Emissions of carbon oxide (CO₂) from burning of fossil fuels are now a global pressing environment issue due to the growing energy demand. As one of the solutions, chemical reduction provides a promising way to convert CO₂ into value-added products. So far, many monofunctional catalysts have been proposed to convert CO₂ into various mono-carbon feedstocks such as carbon monoxide, formic acid, methane or methanol. Nevertheless, the extremely low rate for the direct formation of C-C bonds hinders the reduction of CO₂ into hydrocarbons with multiple carbons on monofunctional catalysts. As an alternate, bifunctional catalysts composed of two distinct functional components may bring new reactivity and/or selectivity to the CO₂ reduction reaction (CO₂RR). Very recently, a bifunctional catalyst composed of H-form Zeolite Socony Mobil-5 (HZSM-5) and reducible indium oxides (In₂O₃) was found to be of excellent performance to directly convert CO₂ into liquid fuels with high selectivity. It was found that, the reactant CO₂ is hydrogenated on In₂O₃ to be the intermediate species, methanol (CH₃OH), which is then transformed into hydrocarbons via methanol-to-hydrocarbon (MTH) reactions inside HZSM-5. Quite interestingly, the authors observed that the selectivity of liquid fuels depends strongly on the proximity between the two components, i.e., high selectivity lies in a moderate range of proximity below or above which CO₂ is mainly reduced into methane. A similar phenomenon was also observed in the experiment of hydrocracking of hydrocarbons on a bifunctional catalyst comprising a mixture of zeolite Y and alumina binder with platinum metal deposited on either the zeolite or the binder, where the closest proximity of bifunctional active sites was found to be detrimental to the hydrocracking selectivity. It thus indicates that the conventional 'the closer the better' rule fails to correctly interpret the effect of the proximity between components of bifunctional catalysts. Apparently, a general mechanistic understanding for the proximity-induced optimal selectivity holds the key for the future development of multifunctional catalysts with controllable organization of catalytic components for new functional purposes.

Herein, we address such a mechanistic issue by proposing a theoretical framework for CO₂RR on the In₂O₃/HZSM-5 bifunctional catalyst. At the inner-component level, we show that the local concentration of CH₃OH for subsequent reactions inside HZSM-5 decreases sharply as In₂O₃/HZSM-5 proximity increases. At the inner- HZSM-5 level, a reaction window for high selectivity of liquid fuels is uncovered as a result of the CH₃OH-concentration-induced shift of dominant reaction process by establishing a full kinetic model for MTH. The proximity-dependent selectivity is thus actually kinetic-controlled for CO₂RR on the In₂O₃/HZSM-5 bifunctional catalyst. Since the local concentration of the intermediate species is determined by the reaction-diffusion dynamics in between the two components of the bifunctional catalyst, the kinetic-controlled mechanism we revealed provides a powerful tool and opens a great opportunity for future design of bifunctional catalysts with special selectivity.

Proximity-dependent concentration of intermediate species for bifunctional catalysts. Generally, for bifunctional catalysts of two components A/B with distinct functional, the reactant R fed in is catalyzed to be an intermediate
species $S$ on component $A$, then $S$ diffuses onto component $B$ and transforms into the product $P$ (Fig.1). Notice that, the intermediate species $S$ can only emerge at the position of component $A$. Due to the diffusion in space, amount of $S$ reaching the position of component $B$ should decrease as the $A/B$ proximity increases. To illustrate clearly the spatial distribution of the intermediate species $S$, a calculation of the reaction-diffusion dynamics containing the production of $S$ at component $A$ with a rate $v_s$ and diffusion across its neighborhood with a diffusion constant $D_s$ is performed (see details in the supplemental information, SI). The obtained 3-dimensional distribution (for $v_s=10^2$ and $D_s=0.1$) and its 2-dimensional cross-section are plotted in Fig. 1a and 1b, respectively. As expected, concentration of $S$ (the color map) fades quickly away from component $A$ (the orange ball), which brings a concentration gradient (black arrows) pointing outwards. For component $B$ located at different positions in the concentration field (such as red balls), the local concentration of $S$ for subsequent reactions on component $B$ decreases sharply as $A/B$ distance increases (Fig.1c). We emphasize that Fig.1 provides a mean-field picture for the relation between $A/B$ proximity and local concentration of the intermediate species near $B$. In other words, the averaged local concentration of $S$ should decreases as the mean proximity decreases. In real systems, there are also other factors affect the diffusion kinetics of the intermediate species, for example, the space distribution of $A$ and $B$. The detailed arrangement of catalyst components may provide a practical way to tune the diffusion kinetics in experiments.

**Kinetic modeling for hydrocarbon selectivity on HZSM-5.** For CO$_2$RR on InO$_2$/HZSM-5 bifunctional catalyst, InO$_2$ provides the intermediate species CH$_3$OH, and hydrocarbons (C$_i$, $i=1,2,3,...$) are produced inside HZSM-5. To explore the effect of proximity between the two components on the hydrocarbon selectivity, we establish a coarse-grained model containing fully kinetics for MTH reactions inside HZSM-5 where the influence of InO$_2$/HZSM-5 proximity is compacted into an efficient CH$_3$OH local concentration near HZSM-5 component. As shown in Fig.2a, HZSM-5 is an aluminosilicate zeolite with 10-membered oxygen ring and two types of channel systems. The straight (5.3x5.6Å) and sinusoidal (5.1x5.5Å) channels are perpendicular to each other and generate intersections (cages with diameters 8.9Å). In our model, cages

![Figure 1. Proximity-dependent concentration of intermediate species on bifunctional catalysts of two components A/B with distinct functional. Reactant R fed in is catalyzed on component A to be intermediate species S which is further catalyzed to be P by component B. Color map shows the concentration profile of S in the neighborhood of component B in (a) 3-dimensional space and (b) a 2D cross-section over the component A, where arrows indicate the concentration gradient. (c) Concentration of S as a function of A/B proximity.](image1)

![Figure 2. Kinetic modeling of methanol-to-hydrocarbons reaction on HZSM-5 zeolite. (a) Coarse-grained lattice for catalytic kinetics where cages and channel segments between two adjacent cages are coarse-grained to be cage sites and channel sites for kinetics. (b) The “dual-cycle” hydrocarbon pool mechanism to produce hydrocarbons with multiple carbons.](image2)
the aromatic cycle tending to occur on the cage sites involves aromatic methylation and dealkylation to form polymethylbenzenes (MB, \( i=0,1,2 \ldots \)) and side chain growth of MB to produce \( C_n \) \(^{32,34} \). The two cycles are connected by cyclization of long-chain hydrocarbons and \( C_3 \) producing via HCP. Besides, MTH also includes the activation and deactivation of the active state for HCP mechanism. The activation concerns about the direct formation of \( C_3 \) from \( CH_3OH \) (the direct way), which is extremely slower than the indirect way via HCP\(^{33-37,31} \). It has also been revealed that the activity of the aromatic pool species decreases with an increasing number of methyl groups on the polymethylbenzene intermediates\(^{34,35} \). At last, \( CH_3OH \) can also be catalyzed directly to \( C_3 \)\(^{36} \). More details about the kinetic model can be found in SI.

Standard “event-list” algorithm of kinetic Monte Carlo simulation\(^{37} \) is applied to calculate the kinetics inside HZSM-5. Involved chemical events are listed in Supplementary Table 1.

**Figure 3.** Local methanol concentration induced optimal \( C_5 \) selectivity. (a) Selectivity and (b) producing rate of hydrocarbons as functions of local \( CH_3OH \) concentration. (c) Schematic of the local-concentration-dependent hydrocarbon producing rates. Inset in (a) is experimental data from Ref. 18.

**Kinetic-controlled hydrocarbon selectivity.** Based on the proposed kinetic model, the experimentally revealed dependence of liquid fuels (\( C_r \)) selectivity on the proximity (inset in Fig.3a) is well reproduced with parameters in Supplementary Table 2. As shown in Fig.3a, the main product is \( C_1 \) for low and high local \( CH_3OH \) concentration \( c_m \) and turns to be \( C_5 \) for medium \( c_m \), corresponding to the experimental observation that high selectivity of \( C_5 \) lies in a moderate range of proximity\(^{48} \). Additionally, it is noted that \( C_1 \) selectivity in our simulation results for large \( c_m \) is smaller than the experimental one in Ref.18, the reason may be that \( C_1 \) can also be produced on \( In_2O_3 \) by reverse water gas shift reactions. Besides the hydrocarbon selectivity, we are also interested in how the producing rates of hydrocarbons depend on \( c_m \). As shown in Fig.3b, the rate for \( C_1 \) increases monotonically with increasing \( c_m \). For \( C_{3,4} \) and \( C_{5,6} \), the rates increase sharply as \( c_m \) increases from a very low value to a moderate range, indicating that these hydrocarbons are generated by a self-catalytic process, i.e., the alkene and aromatic cycles for HCP. For high \( c_m \), producing rates of \( C_{3,4} \) and \( C_{5,6} \) drop to be very slow again. Such a turnover of \( C_{5,6} \) producing rate can be illustrated clearly by the schematic in Fig.3c, where spheres colored in purple denote the local \( CH_3OH \) concentration, and ones in black, blue and red are the producing rates for \( C_0, C_3, \) and \( C_6, \) respectively. This observation indicates that the local-concentration-induced turnover of \( C_{5,6} \) selectivity should be attributed directly to the kinetic events concerning about \( C_{5,6} \), while the production of \( C_1 \) affects the \( C_5,6, \) selectivity only by providing a parallel reaction.

To reveal the mechanism underlying the local-concentration-induced turnover of \( C_{5,6} \) selectivity, the probabilities of events for \( C_1 \) producing (black area in Fig.4a), \( C_3 \) producing via the direct way (blue area in Fig.4a) and that via HCP (red area in Fig.4a), are obtained by a detailed analysis of the kinetic trajectories in steady states. For low local \( CH_3OH \) concentration such as \( c_m<0.008 \), \( C_3 \), the initial species for HCP, is mainly generated via the direct way. Since the direct formation of \( C_3 \) is extremely slow, \( C_3 \) producing event is then of course the dominant one. For \( c_m \) slightly larger than 0.008, producing event of \( C_2 \) via HCP changes to be the dominant one, resulting from the fact that HCP is a self-catalytic process whose rate should increase much faster than producing event of \( C_1 \) as local \( CH_3OH \) concentration increases. Notice that, \( C_3 \) is formed exclusively from the lower polymethylbenzenes in cage sites during the aromatic cycle in HCP\(^{33} \). Nevertheless, the lower polymethylbenzenes may be further methylated to be higher polymethylbenzenes which occupy the catalytic sites to deactivate HCP. In the model, the deactivating species are considered to be pentamethylbenzene (MB) and hexamethylbenzene (MB) for MTH in HZSM-5. The percentage of deactivated cage sites occupied fully by \( MB \) as a function of the local \( CH_3OH \) concentration is also plotted in Fig.4a (the green line). It is observed that, there are no deactivated cage sites when \( C_1 \) production is the dominant event at low \( c_m \). As the HCP changes to be dominant, deactivated cage sites emerge and their percentage increases as \( c_m \) increases, leading to the drop of \( C_3 \) producing event via HCP. For large enough \( c_m \), almost all of cage sites are deactivated, thus, reaction deactivation dominates. The parameter range in between the \( C_1 \) dominant state and the deactivation dominant state provides a reaction window for experimentally observed proximity-induced high \( C_{5,6} \) selectivity. To illustrate clearly the local-concentration-induced shift of the dominant process, the whole reaction network is presented in Fig.4b. Firstly, \( CH_3OH \) transforms directly to be \( C_1 \), \( C_3 \) starts the self-catalytic HCP with the alkene cycle and aromatic cycle. Finally, lower polymethylbenzenes which are active species in the aromatic cycle are methylated to be higher
polymethylbenzenes deactivating the HCP in return. The higher the local CH$_3$OH concentration is, the deeper the reaction network goes. As the local concentration is determined by diffusion process between the two components of the bifunctional catalyst, the high selectivity lying in a moderate range of proximity is actually a kinetic-controlled hydrocarbon selectivity.

**Figure 4.** Mechanism of kinetic-controlled selectivity for methanol-to-hydrocarbon on HZSM-5 zeolites. (a) Stack probability of events for C$_1$ producing, C$_2$ producing via the direct C-C formation (direct C$_2$) and via the hydrocarbon pool (HCP C$_2$), normalized by the total number of the three events. The green line with scatters is the percentage of deactivate cage sites. (b) Schematic of the reaction network and the local-concentration-induced shift of the dominant process, i.e., the dominant process is the producing of C$_n$, the HCP or the deactivation as local concentration increases. Width of green arrows indicates qualitatively the relative rate constant for corresponding events.

**Figure 5.** Effect of the inter-component kinetics on the reaction window for high C$_5^+$ selectivity. The dependence of the shortest proximity $l_o$ for the onset of the reaction window and the window size $\Delta l$ on (a) diffusion constant of CH$_3$OH between In$_2$O$_3$/HZSM-5 and (b) CH$_3$OH producing rate on In$_2$O$_3$.

In summary, we revealed that the proximity-dependent selectivity of liquid fuel (C$_5^+$) from CO$_2$RR is actually kinetic-controlled on the In$_2$O$_3$/HZSM-5 bifunctional catalyst where CO$_2$ is catalyzed to be the intermediate species CH$_3$OH on component In$_2$O$_3$ and hydrocarbons are formed via MTH reactions inside component HZSM-5. A moderate local concentration of CH$_3$OH was found to be the key factor for the reaction window of high C$_5^+$ hydrocarbons selectivity, while the local concentration depends strongly on and can be tuned by the diffusion of CH$_3$OH from In$_2$O$_3$ to HZSM-5. Our finding emphasizes that, along with the energetic, the kinetic is also an important factor in the design of bifunctional catalysts. Since the diffusion of the intermediate species between components is determined by the producing rate, diffusion constant, boundary conditions, the arrangement of catalyst components, etc, the kinetic-controlled selectivity provides many routines for tunable selectivity of bifunctional catalysts, and may inspire a new area for future design of multifunctional catalysts with special selectivity.

**ASSOCIATED CONTENT**

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Possible ways to tune the reaction window for high C$_5^+$ selectivity. As the diffusion of the intermediate species is a key factor for the proximity-dependent selectivity of C$_5^+$ on In$_2$O$_3$/HZSM-5 bifunctional catalyst, it is expected that the reaction window for high selectivity should be tunable by kinetic parameters concerning the diffusion process. The shortest proximity $l_o$ for the onset of the reaction window and the window size $\Delta l$ as functions of the diffusion constant $D_o$ in between In$_2$O$_3$ and HZSM-5 and the CH$_3$OH producing rate $v_o$ on In$_2$O$_3$ are plotted in Fig.5. As $D_o$ increases, the shortest onset proximity $l_o$ decreases monotonically. Quite interestingly, it is observed that the size of the reaction window firstly increases to a maximal value and then decreases, presenting an optimal size for the reaction window of high C$_5^+$ selectivity (Fig.5a). Such an optimal size can also be found as the CH$_3$OH producing rate $v_o$ increases, while the shortest onset proximity $l_o$ monotonically increases. Besides, the detailed arrangement of the two components can also affect the reaction window, which may provide new routines for tunable selectivity of bifunctional catalysts and deserve further systematic investigation in future.
Supporting Information. The Supporting Information is available.

Supplementary Notes of simulation details of the intermediate species distribution for A/B bifunctional catalysts; kinetic modeling details for hydrocarbon selectivity on HZSM-5; Determination of parameters for the kinetic model; figure for dependence of the diffusion constant on the number of carbon atoms for alkanes; tables for chemical events and kinetic parameters for simulation of kinetics in HZSM-5 (PDF).

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H.-J.J., Z.-H.H., and Y.L. conceived the idea and co-wrote the paper. Z.-H.H., and Y.L. supervised the project. H.-J.J. established the kinetic model and performed the theoretical simulations. All the authors discussed the results and commented on the manuscript.

Notes
The authors declare no competing financial interest.

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