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Enhanced Methane Activation on Diluted Metal–Metal Ensembles under an Electric Field: Breakthrough in Alloy Catalysis

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Methane activation on diluted metal ensembles is a challenging task in the field of alloy chemistry. This report describes that synergy between an electric field and Pd–Zn alloy allows improved catalytic activities in the steam reforming of methane. Because of surface protonics, Pd–Pd ensembles are no longer needed. Ligand effects facilitate methane conversion.

Alloying has been used widely as a strategy to modify and improve physical and chemical properties of metallic materials such as magnetism, superconductivity, hydrogen storage capacity, and catalysis.^{1–13} For catalytic properties, the effect of alloying has been classified into two classical roles: so-called ligand¹⁴ and ensemble¹⁵ effects. Ligand effects often appear as improved catalytic activity originating from electronic density or d-band structure of active main metals modified by second metals.^{1,9,16} Ensemble effects are typically observed for active metal–metal ensembles diluted by second metals. Bond dissociation ability of active metal is generally weakened, thereby suppressing undesired side reactions to increase the selectivity to desired products.^{4,17,18} However, the rate of the desired reaction is concurrently diminished because of the weaker activity.^{4,5,13,19} This tradeoff relation has long limited to developing highly active transition metal catalysts based on alloying strategy. Therefore, it is attractive but highly challenging to discover a general concept that can overcome the limitation described above.

One possible approach to this issue is application of an external field such as a magnetic, photonic, or electric field, to the reaction environment to modify the chemical behavior. We

earlier reported that imposing an electric field can drastically decrease the catalyst working temperature for various industrially important reactions such as ammonia synthesis, water gas shift reaction, and steam reforming of methane (SRM).^{20–25} Under an electric field, proton hopping via surface hydroxyl groups or adsorbed water (Grotthuss mechanism) is markedly facilitated, enabling strong proton collision to robust reactant molecules such as N₂ or CH₄ and its activation, even at low temperatures (so-called surface protonics).^{22–24} Consequently, electric field application can strongly modify the mode of molecular transformation.

For this study, we attempted to apply an electric field to SRM over Pd-based catalysts and discovered a specific synergy effect affording increased catalytic activity on an alloyed surface (Fig. 1). This report describes a breakthrough in the catalysis of alloys and presents a novel concept for catalyst design.

For this study, Pd-based catalysts were prepared using a conventional impregnation method with Ce_{0.5}Zr_{0.5}O₂ (CZO) as a support. For alloying, Zn was chosen as a second metal because of its strong ligand effect on Pd,^{16,26} inertness for methane conversion, and various alloying fashion (solid-solution or intermetallic). We prepared a series of Pd–Zn/CZO catalysts with Pd:Zn atomic ratios of 9:1, 4:1, and 1:1: respectively denoted hereinafter as Pd₉Zn₁, Pd₄Zn₁, and Pd₁Zn₁.²⁷

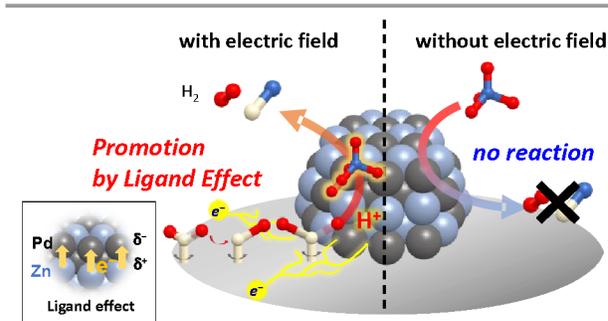


Fig. 1. Synergy between an electric field and Pd–Zn alloy allows improved catalytic activities in the steam reforming of methane: Ligand effect and surface protonics promote catalysis.

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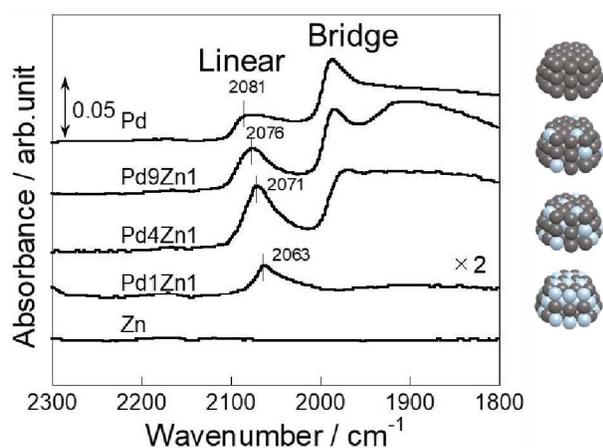


Fig. 2. DRIFT spectra of adsorbed CO on Pd–Zn/CZO catalysts.

Formation of the corresponding solid-solution ($\text{Pd}_{0.9}\text{Zn}_{0.1}$ and $\text{Pd}_{0.8}\text{Zn}_{0.2}$) and intermetallic (Pd_1Zn_1) phases was confirmed using X-ray diffraction and adsorption spectroscopy analyses (Figs. S1 and S2, and Table S1). We also performed a diffuse reflectance Fourier transform infrared (DRIFT) study with CO adsorption to evaluate the surface structure. Figure 2 presents DRIFT spectra of CO adsorbed onto these catalysts. For monometallic Pd, peaks are assignable to the stretching vibration of CO adsorbed in linear ($2100\text{--}2000\text{ cm}^{-1}$) and bridge ($2000\text{--}1800\text{ cm}^{-1}$) conformations,¹³ reflecting the presence of Pd–Pd ensembles. The peak intensity of the bridge CO relative to that of linear CO decreased with the Zn content and the bridge CO peak disappeared at Pd:Zn = 1:1, clearly illustrating the dilution of Pd–Pd ensembles with inert Zn. Therefore, we confirmed the alloying of Pd with Zn not only in the bulk but also at the surface. We also observed that the peak position of the linear CO red-shifted with increased Zn content, which indicates that the electron density of Pd increased because of charge transfer from Zn,^{16,26} i.e., the ligand effect by alloying.

We tested the catalytic activity of the prepared catalysts in SRM with or without an electric field (described as electroforming: ER or steam reforming: SR, respectively). A schematic image of reactor is presented in Fig. S3. For 5 wt%Pd/CZO, methane conversion in ER at 423 K (11.2%) was comparable to that in SR at 673 K (8.74%, Table S2), highlighting the remarkable effect of electric field. In this study, the catalytic activity in SR was evaluated by the turnover frequency based on Pd dispersion, i.e., the number of Pd atoms at the surface of nanoparticles (TOF-s). This is true simply because the surface Pd sites are the true active sites for SR of methane.^{28,29} By contrast, for ER, we reported earlier that ER of methane proceeded at the Pd–CZO interface with the aid of surface protonics.^{23,24} Therefore, TOF for ER was calculated based on the number of Pd atoms at the nanoparticle perimeter (TOF-p, see ESI for details). We confirmed that this evaluation method was valid for PdZn: TOF-p in ER was constant even though the metal loading amount was changed (Fig. S4). Figure 3 portrays the change in TOF-s and TOF-p obtained for SR and ER, respectively, as functions of Zn/Pd atomic ratio (detailed information including methane conversion is presented in Tables S2 and S3). For SR,

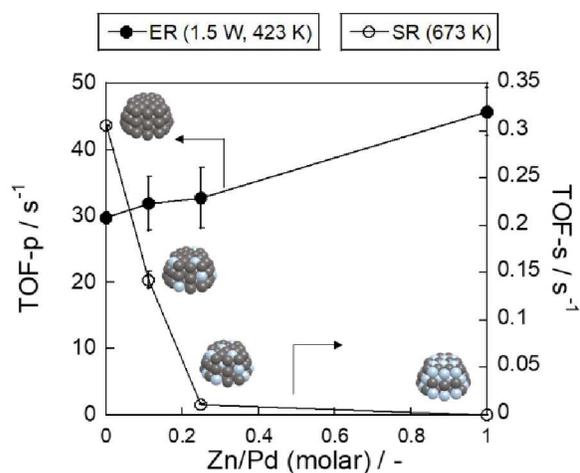


Fig. 3. Relation between Zn/Pd atomic ratio in Pd–Zn/CZO catalysts and TOF-p in ER (1.5 W) or TOF-s in SR (673 K). Reaction conditions: $\text{CH}_4:\text{H}_2\text{O}:\text{Ar} = 1:2:7$, total flow rate = 100 SCCM; furnace temperature, 423 K (ER) and 673 K (SR); input power, 1.5 W (ER).

the catalytic activity dropped to near zero with only a small amount of Zn (Pd:Zn = 4:1). No reaction occurred when 1:1 alloy was used. These results reflect that large Pd–Pd ensembles are necessary to activate the strong C–H bond of methane, which is the rate-determining step.^{30,31} Moreover, this trend is consistent with those reported in the relevant bimetallic systems such as Ni–Ag^{4,17} and Ni–Sn,¹⁸ where TOF decreased by addition of the second metals inert for SR. By contrast, for ER, the catalytic activity increased monotonically as the Zn content increased. Emphasis must be placed on the fact that the highest catalytic activity in ER was obtained for Pd1Zn1, which was inactive in SR. The observed opposite trend suggests that methane activation in ER requires no Pd–Pd ensemble. As described above, the ER reaction proceeds through a unique reaction mechanism: proton hopping and collision to methane with the aid of electric field. The strong impact at the proton collision to methane could be the driving force activating the robust C–H bond of methane even with diluted Pd ensembles as the active site. Therefore, conventional C–H activation on large metal ensembles might no longer be necessary when using surface protonics. This report presents this point as an innovative observation of catalysis of alloys.

Another surprising result is that the catalytic activity in ER increased as the Zn content increased. This trend agrees closely with that found for Pd electron density, as presented in Fig. 2. The electron-richness of Pd might contribute to the enhanced catalytic performance. An earlier study demonstrated the formation of a methanium cation ($[\text{CH}_3\text{--H--H}]^+$) intermediate via the proton collision to methane as the rate-determining step in ER of methane.²⁴ Therefore, such a cationic intermediate should be stabilized on electron-enriched Pd sites. Therefore, its formation can be promoted. Results show that the ligand effect by Zn works positively for methane activation in the electric field. Consequently, the combination of electric field and alloying with Zn exhibited a unique synergy effect on methane conversion. An important consideration is that the positive

ligand effect appeared in ER, which has typically been cancelled out in SR by the negative ensemble effect. These findings are expected to expose a novel concept of catalyst design that is not influenced by conventional ensemble effects. For instance, a wider variety of bimetallic composition including second-metal-rich conditions would be allowed, thereby expanding the choices and possibilities of catalyst design for relevant chemical conversions.

In summary, we prepared Pd–Zn alloys supported on CZO to develop a highly active catalyst for steam reforming of methane in an electric field. Results show that Pd₁Zn₁/CZO catalyst is inactive for SR, even at high temperatures, although it is highly active for ER. The active sites for SR and ER differ: they are, respectively, large Pd–Pd ensemble at the surface of nanoparticle and Pd atoms at the metal-support interface. Under an electric field, no large Pd–Pd ensemble is necessary for methane activation. Moreover, the catalytic activity is enhanced further by virtue of the ligand effect by Zn, i.e., increased electron density of Pd. Insights obtained through this study not only provide improved catalytic performance and present an unconventional synergy effect of electric field and alloying. These insights unlock a novel approach for unrestricted catalyst design derived from ensemble effects.

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Conflict of interest

The authors have no conflicts to declare related to this report or the study it describes.

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- The geometric effect, called the “ensemble effect,” is a change in the geometrical environment of the parent metal (M) decreasing the coordination number of M–M and the M ensemble size.
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