Tuning of Catalytic Activity by Thermoelectric Materials for Carbon Dioxide Hydrogenation

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An innovative use of a thermoelectric material (BiCuSeO) as a support and promoter of catalysis for CO₂ hydrogenation is reported here. It is proposed that the capability of thermoelectric materials to shift the Fermi level and work function of a catalyst lead to an exponential increase of catalytic activity for catalyst particles deposited on its surface. Experimental results show that the CO₂ conversion and CO selectivity are increased significantly by a thermoelectric Seebeck voltage. This suggests that the thermoelectric effect can not only increase the reaction rate but also change chemical equilibrium, which leads to the change of thermodynamic equilibrium for the conversion of CO₂ in its hydrogenation reactions. It is also shown that this thermoelectric promotion of catalysis enables BiCuSeO oxide itself to have a high catalytic activity for CO₂ hydrogenation. The generic nature of the mechanism suggests the possibility that many catalytic chemical reactions can be tuned in situ to achieve much higher reaction rates, or at lower temperatures, or have better desired selectivity through changing the backside temperature of the thermoelectric support.

1. Introduction

Thermoelectric (TE) materials have recently attracted widespread interest in research because they can convert a temperature difference directly into an electrical voltage via the Seebeck effect, \( S = -V/\Delta T \), where \( V \) is the voltage between the two ends of the TE material and \( \Delta T \) the temperature difference, \( S \) is the Seebeck coefficient. The performance of a TE material is ranked by its figure of merit \( ZT = S^2\sigma T/\kappa \), where \( \sigma \) is the electrical conductivity, \( \kappa \) the thermal conductivity, and \( T \) the absolute temperature. Most currently used TE materials are heavy-metal-based, such as Bi₂Te₃ and PbTe, due to their high ZT. However, these materials are not best suited for medium to high temperature, large scale applications, because of problems such as their low melting, or decomposition, or oxidation temperatures. They are also harmful to environment and contain scarce constituent elements. On the other hand, oxide TE materials, such as p-type layered BiCuSeO, cobalt oxide \( A_xCoO_2 \) \((A = Na, Ca, Sr)\), and n-type NaTaO₃-Fe₂O₃, CaMnO₃ and SrTiO₃ based perovskites, can overcome these disadvantages. TE devices are usually configured in modules by connecting the p-type and n-type TE legs electrically in series and thermally in parallel. We report here an innovative use of TE materials as a catalyst support and show its substantial promotional effect on catalytic activity. BiCuSeO (BCSO) was selected as the thermoelectric materials for this investigation because it possesses good TE properties to over 900 K, an extraordinary low intrinsic thermal conductivity of less than 0.5 W m⁻¹ K⁻¹; therefore, a high temperature difference can easily built up across this material; high Seebeck coefficient up to 500 μV K⁻¹ at room temperature and greater than 300 μV K⁻¹ at high temperatures, and no decomposition below 773 K. Catalyst promoters improve the activity, selectivity, or lifetime of a catalyst and can generally be divided into structural and electronic promoters. Structural promoters enhance and stabilize the dispersion of the catalyst on the support. Electronic promoters induce changes of electronic state of the catalyst near the Fermi level. These promoters are added and fixed during the catalyst preparation and therefore can be subject to degradation during the catalytic process. On the other hand, electrochemical promotion, also called non-Faradaic electrochemical modification of catalytic activity (NEMCA), which allows for controlled in situ introduction of promoters on catalyst surfaces under operating conditions. NEMCA has proved to be an excellent research technique but its large scale industrial use has been limited due to its shortcomings: (i) low efficiency of catalyst materials (which are often expensive noble metals) because it requires a continuous electrode to maintain conductivity, (ii) need to maintain electrical connection under often harsh conditions, and (iii) the incompatibility of its reactor configuration (often a fuel cell configuration) with typical chemical reactors (fixed bed, monolithic, and fluidized bed).

We report here the realization of in situ, reversible, and significant modification of catalytic activity for both continuous
thin film and highly dispersed (nanoscale particles) metal catalysts, by using TE materials as a catalyst support for CO₂ hydrogenation. Furthermore, we show that this profound promotional effect on catalytic activity by the TE effect also enables the oxide TE material itself to possess high catalytic activity for CO₂ hydrogenation.

The concentration of carbon dioxide in the atmosphere has risen from ≈280 ppm before the industrial revolution to ≈400 ppm in 2013 and is projected to be ≈500 ppm by 2050.[6] This contributes to the increase in global temperature and climate changes due to the “greenhouse effect.” Hence there are extensive efforts to reduce CO₂ emissions around the world. Generally speaking, there are three strategies to achieve this: (i) reduce CO₂ production, (ii) storage, and (iii) usage. The first two options, which involve improving energy efficiency, switching to renewable energy, and CO₂ capture and sequestration, have been the major focus in the past. The third strategy, i.e., using CO₂ as a feedstock for making useful chemicals, is regarded as the most feasible and effective solution to our carbon conundrum.[7] The CO₂ hydrogenation may undergo two main processes, the first is the reverse water-gas shift (RWGS) reaction (Equation (1)) and the other leads to the formation of hydrocarbons (Equation (2))

\[
\begin{align*}
\text{CO}_2 + \text{H}_2 & \rightarrow \text{CO} + \text{H}_2\text{O} \quad (1) \\
x\text{CO}_2 + (2x-z+y/2)\text{H}_2 & \rightarrow \text{C}_x\text{H}_{2y} + (2x-z)\text{H}_2\text{O} \quad (2)
\end{align*}
\]

For \(x = 1, y = 4, \) and \(z = 0\) (i.e., the inlet gas ratio \(\text{CO}_2/\text{H}_2 = 1:4\)) one has the methanation reaction. RWGS reaction is one of the most established reactions to convert CO₂ into CO and H₂O, from which liquid hydrocarbons conversion via Fischer–Tropsch synthesis can be achieved.

2. Theoretical Consideration

NEMCA, which involves a reversible change of catalytic properties of metal catalysts deposited on solid electrolytes, can be obtained by applying a small external electric current or voltage. NEMCA is due to the back spillover of ionic species from electrolytes to form a double layer at the catalyst surface, which leads to a change of the work function and chemisorption properties of the catalyst.[1,8] The effective change of surface work function leads to an exponential change of chemical reaction,[9] i.e.,

\[
\ln \left( \frac{r}{r_0} \right) = \alpha \Delta \phi / k_b T
\]

where \(r\) is the new reaction rate, \(r_0\) is the open-circuit reaction rate, \(k_b\) is the Boltzmann constant, \(\alpha\) is an empirically determined constants, and \(\Delta \phi\) is the change of work function due to the applied external voltage. Under certain conditions, \(\Delta \phi\) is linearly proportional to the non-Ohm drop of external potential.[3,4,9]

The basic idea of this work is to use a thermoelectric material to change the effective work function of catalyst particles to achieve a significant increase of the catalytic activity. First, consider the change of the Fermi level for TE material BCSO when there is a temperature change (Figure 1). BCSO is a p-type TE material, holes at the hot side diffuse into the cold side upon heating, forming an internal electrical field. Once equilibrium is reached the Fermi level (also called electrochemical potential) at the hot side \(E_{F,h}\) is higher than at the beginning and cold side \(E_{F,c}\) and \(\Delta E_F = E_{F,h} - E_{F,c} = -eV\), here \(e\) is the charge of an electron and \(V\) is the Seebeck voltage.

As no external charges exist, the change of the work function at the surface is the inverse change of the Fermi level, i.e., \(\Delta \phi = -\Delta E_F\), so \(\Delta \phi = eV\) at the hot surface \(T_h\). If a metal particle is deposited on the TE material, at the hot surface, its Fermi level \(E_{F,m}\) must be the same as the Fermi level of the TE at the surface, i.e., \(E_{F,m} = E_{F,h}\) (Figure 1). Therefore, \(\Delta E_{F,m} = \Delta E_F\) and the change of work function \(\Delta \phi_m = eV\) is also true for metal particles supported on the TE material.

Apply the generalized dependence of catalytic rate on catalyst work function Equation (3), then we have

\[
\ln \left( \frac{r}{r_0} \right) = -\gamma eV / k_b T
\]

Here \(\gamma\) is a constant, to be determined by experiment. The introduction of a minus sign makes \(-eV\) the extra energy of an electron at the surface due to the Seebeck voltage \(V\). Combining Equation (4) and the definition of Seebeck coefficient \(S\) gives

\[
\ln \left( \frac{r}{r_0} \right) = \gamma e S \Delta T / k_b T = \gamma e S (T_h - T_c) / k_b T_h , \text{ at hot side } T_h
\]

And

\[
\ln \left( \frac{r}{r_0} \right) = \gamma e S \Delta T / k_b T = \gamma e S (T_c - T_h) / k_b T_c , \text{ at cold side } T_c
\]

where \(S\) is not a constant, \(S(T_h - T_c)\) should be replaced by \(\int_{T_c}^{T_h} S(T) dT\).
Equations (4)-(6) link catalytic activity with Seebeck voltage and temperature for a metallic catalyst supported on a TE material.

3. Results and Discussion

3.1. Thermoelectric Property of BiCuSeO

Figure 2 shows the temperature dependence of (a) Seebeck coefficient and electrical conductivity, (b) thermal conductivity, and (c) power factor and dimensionless figure of merit $ZT$ for the BCSO pellets after spark plasma sintering (SPS). The Seebeck coefficient was highest at room temperature with a value 516 $\mu$V K$^{-1}$, then decreased with increasing of temperature, and reached 328 $\mu$V K$^{-1}$ at 764 K. The electrical conductivity $\sigma$ decreased with increasing temperature from room temperature to about 460 K, then increased with further increasing temperature, and reached its highest value of 18.8 S cm$^{-1}$ at 764 K. The thermal conductivity $k$ was found to decrease continuously with temperature, being 0.84 W m$^{-1}$ K$^{-1}$ at 315 K and 0.42 W m$^{-1}$ K$^{-1}$ at 764 K; these values are very low even for TE materials. The highest power factor $(S^2 \sigma)$ of 230 $\mu$W m$^{-1}$ K$^{-2}$ was obtained at $\approx$665 K. $ZT$ values were found to increase with increasing temperature and reached 0.37 at $\approx$764 K. The Seebeck coefficient and electrical conductivity of the samples had lower values but similar trends with temperature as BCSO prepared using self-propagating high-temperature synthesis (SHS), but higher than those of BCSO prepared using solid state reaction (SSR). The thermal conductivity values were lower than both SHS and SSR prepared BCSOs$^{[10,11]}$ As a result, our BCSO showed similar $ZT$ values (0.36 at 665 K and 0.37 at 764 K) as SHS (0.33 at 675 K and 0.49 at 775 K)$^{[10]}$ but higher than SSR (0.09 at 725 K and 0.15 at 775 K) samples$^{[11]}$

3.2. Thin Film and Nanoparticle Catalysts on BiCuSeO

The surface microstructures of the catalysts on BCSO were investigated using scanning electron microscopy (SEM). Figure 3 shows SEM images for the surface of: (a) BCSO, (b) Pt(15)/BCSO, (c) Pt(80)/BCSO, and (d) Pt(NP)/BCSO. Here, Pt(15), Pt(80), and Pt(NP) refer to the nominal Pt film thicknesses of 15, 80 nm, and as nanoparticles, respectively. The surface of BCSO was relatively smooth. Many Pt particles (indicated by arrow heads) could be observed on the grains of Pt(80)/BCSO and some Pt particles could be seen on the grains of Pt(15)/BCSO as well (indicated by arrow heads). Pt(NP)/BCSO had smaller grains and more voids. This was probably due to its lower sintering temperature (823 K), compared with 923 K used for the other three samples. X-ray diffraction pattern (XRD) patterns for all of the four samples are shown in Figure 3e, indicating that the BCSO in every sample was almost a single phase (PDF#45-0296) with the ZrSiCuAs structure. No second phases were observed in BCSO, but a small peak at $\theta$ = 27.2 suggested some Bi$_2$O$_3$ was present as a second phase in the XRD patterns for the other three samples. Also, the Pt(111) peak was apparent for Pt(80)/BCSO, but could not be seen in the XRD patterns for Pt(15)/BCSO and Pt(NP)/BCSO, indicating that the Pt particle sizes in the latter two samples were too small to be detected by XRD, probably less than 20 nm in diameters.

3.3. Promotion of Catalytic Activity by Thermoelectric Effect

3.3.1. The Thermoelectric and Reduced Thermoelectric (RTE) Effect Conditions

The schematic diagram of the single chamber reactor which combines TE effect with catalytic chemical reaction is shown in Figure 4a and Figure S1 (Supporting Information). The
reaction chamber was placed on top of a hot-plate to create a large temperature difference (≈ 200–300 K when \( T_h > 500 \) K) between the bottom floor of the chamber and the hot surface \( T_h \) of the sample (Figure 4b). A large temperature gradient in the chamber can induce strong convection along the vertical direction, which can bring in the reactants and remove the products quickly from the reaction surface \( T_h \). Figure 3a–d shows that the samples were not porous; hence, there was no pore-diffusion limitation. For these reasons, it was assumed that there was no mass transportation limitation, and the intrinsic chemical reaction was the rate limiting step for all the reactions investigated. Disc samples with a diameter of 20 mm and thickness of 2 mm were tested for catalytic activity as represented by \( \text{CO}_2 \) hydrogenation conversion \( X(\%) \) at different temperatures (\( \text{CO}_2 \) conversion \( X \) is proportional to the \( \text{CO}_2 \) reaction rate \( r \) if the backward reaction of Equation (1) is ignored, this will be discussed later). Catalytic activities are then compared between the TE and RTE conditions, at the same front (hot) surface temperature. Under normal TE conditions, the backside of the disc was in contact with water cooled stainless steel cap (with a thin mica sheet in between for electrical insulation), so its temperature was never higher than 373 K. A large temperature gradient across the disc thickness was created when the front surface reached a high temperature. Under RTE conditions, the backside of the disc was not in contact with the cooled cap, so the temperature gradient across the disc thickness was much smaller. At a particular hot-plate temperature, after reaching thermal equilibrium, the bottom surface of the disc sample was stabilized at a temperature \( T_h \), while the top surface was at a temperature \( T_c \). Hence, for the same sample at the same temperature \( T_h \) under TE and RTE conditions, the only differences were that the top surface temperature \( T_c \) was different, which led to a different Seebeck voltage across the sample. The Seebeck voltage \( V \) between the surfaces \( T_c \) and \( T_h \) was monitored continuously during the whole period of the experiment (Figure 4b, Figures S2 and S3 in the Supporting Information).

The \( \text{CO}_2 \) hydrogenation reactions could have taken place on the hot surface \( T_h \) (nominal surface area 100 \( \pi \) mm\(^2\)), cold
surface $T_c$ (nominal surface area $100 \pi \text{ mm}^2$), and the side wall of the disc (nominal surface area $40 \pi \text{ mm}^2$) sample. From Tables S1 and S2 (Supporting Information), it can be seen that when $T_h$ was below 403 K no CO$_2$ conversion was obtained, and $T_c$ was never higher than 331 K. Especially at high temperatures, $T_h$ was much higher than $T_c$, and the temperature of the side wall was between $T_c$ and $T_h$. For these reasons we assume that for all of the samples, the measured CO$_2$ conversion rate was contributed from the hot surface $T_h$ only, and the contributions from the cold surface $T_c$ and the side wall of the disc sample were negligible.

### 3.3.2. Higher Catalytic Activity at the Same Temperature under TE than RTE Conditions

The reaction products observed were only CO and CH$_4$, with the vast majority (>90%) being CO (Figure 5a). Figure 5b shows the CO$_2$ conversion as a function of temperature $T_h$ under the TE and RTE conditions for Pt(80)/BCSO and bare BCSO with an inlet gas ratio of CO$_2$/H$_2$ = 1:1. It can be seen that for the same sample at the same temperature, the CO$_2$ conversion $X$ under TE conditions was much greater than under RTE conditions. For example, for Pt(80)/BCSO at 573 K, the CO$_2$ conversion under TE condition was 12.4%, 42 times higher than 0.3% under RTE conditions. At 673 K, the CO$_2$ conversion under TE condition was 10 times higher than under RTE conditions. Also, CO$_2$ conversion (0.8%) was first obtained at 420 K under
the TE conditions, much lower than 553 K when it was first measured under the RTE conditions (0.2%). It is plausible to assume that relative to conditions without any TE effect, the promotional effect should be even higher. It is worthy to point out that similar experiments were repeated at least once and the results were reproducible (the same samples were used for oxidized ethylene to form CO₂ and H₂O, and a repeatable and similar thermoelectric promotional effect was observed; these are the subjects for a separate publication), this ruled out the possible explanation that the conversion difference between the TE and RTE was due to the particle aggregation at the surface.

Another observation was that the BCSO TE sample, without any Pt catalyst, was also catalytically active for CO₂ hydrogenation (Figure 5b). This may not be a total surprise, as BCSO is electrically conductive, and other conductive oxides have been found to be good catalysts. Moreover, Cu and CuO catalysts are widely used for CO₂ hydrogenation, so the CuO containing BCSO itself could have very low catalytic activity even without thermoelectric promotion. The first measured CO₂ conversion (0.3%) was at 493 K under TE conditions and 633 K under RTE conditions (0.8%). As for Pt(80)/BCSO, at the same temperature T_h the CO₂ conversion under TE conditions was much higher than under RTE conditions. At 698 K, the CO₂ conversion was 20.8% under TE conditions compared to 553 K when it was first measured under the RTE conditions (0.2%). It is plausible to assume that relative to conditions without any TE effect, the promotional effect should be even higher. It is worthy to point out that similar experiments were repeated at least once and the results were reproducible (the same samples were used for oxidized ethylene to form CO₂ and H₂O, and a repeatable and similar thermoelectric promotional effect was observed; these are the subjects for a separate publication), this ruled out the possible explanation that the conversion difference between the TE and RTE was due to the particle aggregation at the surface.

3.3.3. Promotion of CO₂ Conversion by Thermoelectric Effect

To further investigate the relationships between the temperature, Seebeck voltage, and catalytic activity, the CO₂ reduction reactions were studied for different samples under different inlet gas compositions, all under TE conditions. Figure 6a displays the measured thermoelectric voltage as a function of the temperature difference ΔT across the sample thickness for four samples, namely Pt(80)/BCSO, Pt(15)/BCSO, Pt(NP)/BCSO, and bare BCSO, at the inlet gas ratios of CO₂/H₂ = 1:1 and 1:4. All of the four samples were weighted as 5.8 g. All of the samples had zero voltages when their bottom and top surfaces were at the same (room) temperature. The measured voltage for each sample increased linearly with temperature difference. The linear gradient for Pt(80)/BCSO was 319 μV K⁻¹ for ΔT < 200 K, and then decreased with increasing ΔT. The gradients for BCSO and Pt(15)/BCSO were similar and did not change with the change of the inlet gas compositions. These are typical values for Seebeck coefficient of BCSO. Note that the Seebeck coefficient of 319 μV K⁻¹ here is lower than the values reported in Figure 2a for SPS processed material. The main reason for this was that the BCSO used for the above catalysis experiments was not densified by SPS but using conventional sintering, so an inferior crystallinity and density of this sample was expected, which led to a smaller Seebeck coefficient. Another reason was that the Seebeck coefficient obtained through the linear gradient here was the average value over a large temperature range, while those in Figure 2a were obtained by changing the temperature over a smaller range (∼50 K over a 13 mm long sample), and generally speaking,

![Figure 6](https://www.advenergymat.de)
the Seebeck coefficient is temperature dependent. The gradient for the Pt(NP)/BCSO was much lower, at about 136 µV K⁻¹, again, it also kept the same value when the inlet gases ratio was changed from 1:1 to 1:4. This much lower Seebeck coefficient was due to the fact that this sample was sintered at a much lower temperature (823 K as compared to 923 K for other BCSO), and there were still some second phases such as Bi₂O₃ and void in the sample (Figure 3d). These results demonstrate that the measured voltage was determined by the intrinsic thermoelectric properties of the sample and the temperature difference only, and was not affected by the gas compositions.

Again, the reaction products were found to be CO and CH₄, with the majority (>80%) being CO. Higher H₂ concentration in the inlet gases led to lower CO selectivity. The temperature dependences of CO selectivity for six cases are shown in Figure 6b, while the other two, BCSO 1:1 TE and Pt(80)/BCSO 1:1 TE, are shown in Figure 5a. Generally speaking, at T > 600 K, the CO selectivity increased with temperature and voltage. Figure 6c shows the CO₂ conversion as a function of the hot-surface temperature Tₛ for different samples at the inlet gas ratios of CO₂/H₂ = 1:1 or 1:4. All of the samples showed a similar trend, i.e., the conversion increased with temperature. It can be seen that for the same sample, higher H₂ concentration leads to higher CO₂ conversion. Pt(80)/BCSO reached 48.4% conversion at 656 K, the highest for all of the samples, indicating that the Pt surface had the highest catalytic activity. Remarkably, even without any Pt catalyst, the TE material BCSO (CO₂/H₂ = 1:4) itself reached a conversion of 41.2% at 703 K.

Excellent linear relationships were observed between Ln(X) and -eV/k_bTₛ for all ten cases (four for Figure 5c and six for Figure 6d). The best-fit trend line gradients γ were obtained as: 6.6 for BCSO @ 1:4 and 6.22 for BCSO @ 1:1 TE; 6.06 for Pt(15)/BCSO @ 1:4 and 7.46 for Pt(15)/BCSO @ 1:1; 7.2 for Pt(80)/BCSO @ 1:1 and 7.15 for Pt(80)/BCSO @ 1:4; 9.09 for Pt(NP)/BCSO @ 1:4 and 9.73 for Pt(NP)/BCSO @ 1:1; 46 for Pt(80)/BCSO @ 1:1 RTE and 25.4 for BCSO @ 1:1 RTE. Generally speaking, as can be seen from Figures 5c and 6d, γ had similar values for all the TE conditions and much higher values for the RTE conditions.

Combining the results as shown in Figures 5c and 6d, we can summarize the observed relationship in Equation (7)

\[
\text{Ln} \left( \frac{X}{X_0} \right) = -\gamma eV / k_bT_s.
\]

Here, X₀ is the conversion rate when V equals zero, i.e., when Tₛ = Tₐ. For the p-type TE material BSCO, V at Tₛ surface is negative, so -eV is positive and the conversion rate at the hot side Tₛ could be much higher with a TE voltage than without, we call this thermoelectric promotion of catalysis (TEPOC), or thermoelectrocatalysis as the TE material itself can be catalytic active. Take an experimental data point for Pt(80)/BCSO @ 1:4, Tₛ = 656 K, V = -86 mV, and γ = 7.15, so Ln(X/X₀) = -eV/k_bTₛ = 10.88, and X/X₀ = 53103. This means that at 656 K, the conversion with a Seebeck voltage of -86 mV was more than 53 thousand times higher than without a Seebeck voltage.

Equation (4) can lead to Equation (7), and vice versa, if the conversion X is proportional to the reaction rate r. This requires the conversion X to be much lower than the thermal equilibrium conversion (TEC) of the reactions in Equation (1) and Equation (2), so that the backward reactions were negligible. The TECs at 673 K for CO₂ conversion in RWGS reaction without methanation (to CO only) are about 22% and 42% for an inlet gas ratio CO₂/H₂ = 1:1 and 1:4 respectively; with methanation, the corresponding values are about 23% and 80%, respectively.[14,15] Under RTE conditions, the conversion rate was very low; hence, the CO₂ conversion on both Pt(80)/BCSO and BCSO was far away from the TEC, so it is safe to assume that the backward water-gas-shift reaction can be ignored and the CO₂ conversion X was linearly proportional to the reaction rate r. So for the two cases under RTE conditions, the experimental results confirmed the prediction of Equation (4).

The rate of chemical reactions usually follows the Arrhenius law, so r₀ = k₀ exp(-Eₐ/k_bTₛ), here k₀ is a constant, Eₐ the activation energy of the reaction. Equations (4) and (7) apparently suggest that the activation energy is reduced by -eV, i.e., Eₐ = Eₐ + eV. Eᵣ is the new activation energy when there is a TE voltage V (a negative value for our case, as the reaction take place at the hot side of a p-type TE material).

Figures 5b and 6c show that at high temperatures around 673 K, when there was a high Seebeck voltage, the CO₂ conversion rate reached TEC (22.9% for Pt(80)/BCSO @ 1:1 TE at 673 K), or just slightly below TEC (17.6% for BCSO @ 1:1 TE at 673 K; 37.2% for Pt(15)/BCSO @ 1:4 at 678 K; 36.3% for BCSO 1:1 at 683 K), even above the TEC (48.4% for Pt(80)/BCSO 1:4 at 656 K) without methanation. For the purpose of comparison, the TEC values for CO₂ conversion in RWGS reactions with and without methanation at CO₂/H₂ ratios 1/1 and 1/4 at 673 K are also presented in Figure 6c. To the best of our knowledge, 48.4% is the highest reported CO₂ conversion to CO (with 100% CO selectivity) at atmosphere pressure below 673 K with an inlet gas ratio CO₂/H₂ no larger than 4.[13,15,16] How can the CO₂ conversion to CO exceeds the TEC at 673 K? It can be seen from Figure 6b that at temperatures Tₛ > 678 K, the CO selectivity was >95% for all the samples. Notably for Pt(80)/BCSO @ 1:4, the CO selectivity was 100% at 656 K. The CO selectivities observed at these temperatures were also much higher than the predicted values under the consideration of thermal equilibrium.[13,15,16] These results indicate that the Seebeck voltage promoted the conversion to CO and forward reaction in Equation (1), hence changed the TEC. This agrees with the observation that an electric field (via the NEMCA mechanism) shifted the chemical equilibrium, increased the RWGS reaction, and decreased the (backward) water-gas-shift reaction.[15] With the assistance of an electric voltage of 1.6 kV, CO₂ conversion to CO on a Pt/La-ZrO₂ catalyst reached 40.6% with an inlet gas ratio CO₂/H₂ = 1:1 at 648 K, much higher than the TEC of about 20% without electric field at the same temperature.[15] This shifted the chemical equilibrium and TEC by an electrochemical energy of -eV and may also be the reason why we observed the linear relationships in Figures 5c and 6d. Strictly speaking, if the conversion rate is close to the TEC and the backward water-gas-shift reaction cannot be ignored, and the conversion X is not determined by the reaction rate, and Equation (4) cannot lead to Equation (7). Nevertheless, a very good linear relationship between Ln(X) and -eV/k_bTₛ was observed for all the cases investigated. The most plausible
3.4. Discussion

Referring to Figure 6a,c,d, all the samples, either bare BSCO or BCSO with a continuous Pt thin film Pt(80)/BCSO, or BCSO with discontinuous Pt nanoparticles Pt(15)/BCSO and Pt(NP)/BCSO, showed similar CO₂ conversion dependence with the temperature $T_b$ and Seebeck voltage $V$ (Figures S4 and S5, Supporting Information). The four samples with similar Seebeck voltage at a particular temperature, i.e., BCSO @1:4, Pt(15) BCSO @1:1, Pt(15)/BCSO @1:4, and Pt(80)/BCSO @1:4, also had similar $\ln(X) \sim -eV/k_BT_b$ relationships. The sample Pt(80)/BCSO @1:1 and 1:4 had the lowest Seebeck voltage and also had a similar $\ln(X) \sim -eV/k_BT_b$ relationship. This suggests that the Seebeck voltage, not specific surface property, was the most important factor in determining the catalytic activity. This also agrees with the observation that the CO₂ conversion stronger dependence on the effect of the electric field than the nature of the catalyst.⁶ These results also agree with the observations in NEMCA of CO₂ hydrogenation in that a negative (reduced) potential increased the selectivity and reaction rate to CO, and a positive (increased) potential increased the selectivity and reaction rate to CH₄.⁸⁻¹⁵

From the above discussion, all the above observed results can be explained by Equation (4), i.e., the change of work function lead to the promotion of catalytic activity. This mechanism based on the change of work function through the in situ and controlled TE effect suggests that TEPOC is an effective mechanism for any metallic catalysts, regardless of their properties such as particle size or total amount of the metal. This is because whatever the particle size or chemisorption property, the Fermi level of the metallic particle will be the same as that of the surface TE materials supporting them. The total amount of the metal particles, indeed any second phase materials, will affect the TE properties such as Seebeck coefficient and electrical conductivity, as the whole system can be regarded as a TE composite. This is because all of the samples, with or without metal Pt, are just thermoelectric materials with a different Seebeck coefficient. Of course, the metal particle surface and TE surface may have different adsorption properties, which may lead to different catalytic properties.

Since the TE effect can be realized independently of chemical reactions, its modification to the catalytic activity can be in situ under operational conditions, and controlled through the control of the backside temperature, e.g., changing the water cooling to liquid nitrogen cooling. For n-type TE materials, the Fermi level at the cold side is higher than at the hot side, but the relationship $\varphi_{ph,b} - \varphi_{ph,c} = -eV$ is still valid, so is $\Delta\varphi = eV$, but $V$ is now positive.

The significant promotional effect of the TE effect when there is a large Seebeck voltage can be understood from the energy point of view. $-eV/k_BT_b$ can be regarded as the ratio between the extra electrochemical energy induced by TE effect and the thermal energy of an electron at the reaction surface. At 300 K, the thermal energy $k_BT_b$ is 25.9 meV. So, 104 mV of Seebeck voltage gives 104 meV extra electrochemical energy to an electron at the Fermi level, which is equivalent to the thermal energy of an electron at 1200 K, but a 104 mV Seebeck voltage can be generated by a temperature difference of 347 K by a TE material (such as BCSO) with an average Seebeck coefficient of 300 μV K⁻¹. So, TE effect is a very efficient way to enhance the electrochemical energy of an electron at the reaction surface.

Considering $\Delta\varphi = eV$ in TEPOC, note that Equation (4) is similar to the rate equation for NEMCA¹⁸⁻²⁰, which is $\ln(r_o/r_i) = \alpha(\Delta\varphi - \Delta\varphi^o)/k_BT$, where $r_i$ is the open-circuit reaction rate, $\alpha$ and $\Delta\varphi^o$ are empirically determined constants, $\Delta\varphi$ is the change of work function due to the applied external voltage. Under certain conditions, $\Delta\varphi$ is linearly proportional to the non-Ohm drop of external potential,¹⁸ so the rate Equation (4) for TEPOC looks exactly the same as the rate equation for NEMCA. However, there are a few important differences between NEMCA and TEPOC. (i) No electrolyte nor external voltage are needed in the TEPOC system, while for NEMCA, an electrical insulating electrolyte layer is crucial otherwise a non-Ohm drop of potential (or ionic current) cannot be established. In fact, the unusually low thermal conductivity of BCSO has been attributed to its negligible ionic conductivity, so the back spill-over of ionic species in BCSO would have been negligible.¹⁸ Also, we did not observe any change of reaction rate when an external voltage (positive or negative) was applied to the Pt(80)/BCSO or other samples. (ii) Unlike in NEMCA, the catalyst in TEPOC (e.g., Pt) does not need to be continuous, as TE materials are electrically conductive. Highly, separately dispersed catalysts, including nanoparticle catalysts, can be promoted by TEPOC. (iii) The constant $\alpha$ in NEMCA is smaller than unity, but the values for the constant $\gamma$ in TEPOC have been found to be larger than 1. The fact that $\gamma > 1$ in the Equations (4)–(7) for TEPOC indicates that there is an amplification effect when the extra electrochemical energy $eV$ is present during catalytic chemical reactions. The mechanism for this is not clear yet, but we speculate that this is related to the increase of the number of electrons available for catalytic reaction with the increasing temperature, as no change of electron density with temperature should mean $\gamma = 1$. (iv) The TE material itself can be used as a catalyst when there is a large Seebeck voltage. (v) Furthermore, more importantly, the mechanism for the change of work function at the catalyst surface in TEPOC is different from that in NEMCA. In NEMCA, the external voltage induces the diffusion of ionic species, which form a double layer on the catalyst surface, and produce a change of the work function.¹⁸ Hence, the change of work function $\Delta\varphi$ is an indirect consequence of the external voltage $V$, and the linear relationship between $\Delta\varphi$ and $V$ is true only under certain conditions and may be sample dependent.¹⁸ In TEPOC, the relationship between $\Delta\varphi$ and Seebeck voltage $V$ is directly linked by the change of Fermi level, not through the formation of a double layer.

4. Conclusions

The thermoelectric oxide BiCuSeO has been produced using a facile solid state reaction method using Bi₂O₃ as a flux agent in
air. An innovative use of the thermoelectric material as a catalyst support and promoter has been proposed and investigated through the CO₂ hydrogenation to produce CO and CH₄. A very high CO₂ conversion of 48.4% to CO with 100% CO selectivity under atmosphere at temperatures below 673 K with the inlet gas ratio CO₂/H₂ = 1.4 was obtained.

It is proposed that the thermoelectric effect can change the Fermi level and therefore the work function of the electrons in the catalyst particles supported on a thermoelectric material. This change of work function leads to exponential increase of catalytic activity. It was indeed observed in experiments that the catalytic activity of metallic particles supported on the thermoelectric materials, as represented by the CO₂ conversion, was significantly promoted by a Seebeck voltage generated through the temperature difference across the thickness of the thermoelectric support. This thermoelectric promotion of catalysis also enabled the BiCuSeO itself to possess high catalytic activity. It was further confirmed by experimental results that there exists a linear relationship between the logarithm of the catalytic activity, and −eV/k_B T, which can be regarded as the ratio of extra electrochemical energy (−eV) induced by thermoelectric effect and thermal energy (k_BT) of an electron. This extra electrochemical energy can also change the chemical equilibrium and selectivity of the reaction.

The general nature of the mechanism suggests that thermoelectric promotion of catalysis could be a universal phenomenon.

5. Experimental Section

Thermoelectric Material Preparation: The TE material BCSO was synthesized by solid-state reaction using boron oxide (B₂O₃, Alfa Aesar, 99%) as a flux agent in air. During the flux synthesis, the melted B₂O₃ served as a liquid-seal on the top of the crucible. The obtained product of each sample was then ground to a fine powder. The latter was densified at 150 MPa using a hydraulic press system to form a dense pellet of 20 mm in diameter and 2 mm in thickness. Then, the green pellet was sintered at 923 K for 10 h under argon atmosphere. Further sintering by SPS was carried out before thermoelectric property measurements, using a HP D 25/1 (FCT Systeme GmbH, Frankenblick, Germany).

Preparation of Catalysts: The film catalysts were deposited on BCSO by magnetron sputtering method (Nordiko). The Pt films were prepared using pure Pt (99.99%) as the sputtering target. The thicknesses of the Pt films were ~80 nm for three min and ~15 nm for 20 s of sputtering time, respectively named Pt8(80)/BCSO and Pt15(15)/BCSO. Another platinum nanoparticle sample (Pt(NP)/BCSO) was synthesized using an impregnation method. For this sample, the green pellet was calcined at 823 K for 2 h under argon atmosphere and then reduced under 5% H₂ in Ar at 773 K for 4 h. The microstructural investigations were carried out using XRD (Siemens 5000) at 40 kV with a Cu Kα source and a scanning electron microscope (Philips, FEI XL30 SFEG).

Thermoelectric Property Measurements: The thermal diffusivity (D) was measured by using laser flash method (LFA-457, Netzsch, Germany) under a continuous argon flow. The total thermal conductivity (κ_total) was calculated by the formula ∇ = DC_p, where ρ was the mass density measured by the Archimedes method, while the specific heat (C_p) was determined using a differential scanning calorimeter instrument. The electrical conductivity and Seebeck coefficient were simultaneously measured (LSR-3/1100, Linseis) in a He atmosphere.

The Reaction Chamber: Chemical reactions were performed in a single chamber reactor. A schematic diagram of the reactor can be seen in Figure 1. The cover plate was cooled with continuous running water. Gold wires (Agar Scientific, Ø 0.2 mm) were used as electrical contacts, and temperatures were measured with K-type thermocouples (Ø 0.25 mm, TC Direct) placed directly on the sample surfaces. The reaction chamber was placed directly onto a high temperature hot plate (HP99XY, Wenesco, Inc.) with a temperature controller. The Seebeck voltage was measured continuously (Figures S1 and S2, Supporting Information) between the bottom surface and the top electrode (Au) using a potentiostat-galvanostat (VersaStat 3F, Princeton Applied Research).

Catalytic Activity Measurement: The catalytic activity measurements of different catalysts were carried out at atmospheric pressure in a continuous flow apparatus equipped with the stainless steel reactor (Figure 1b). The reaction reactants and products were continuously monitored using online gas chromatography (GC8340, CE instruments) and online IR analyzer (GT150 CO₂, Gem Scientific) to quantify the concentration of H₂, CO, CH₄, and CO₂. To monitor the temperature, a K-type thermocouple was attached (and fixed using a high temperature tape) onto the catalyst surface for the Tc measurement. Another K-type thermocouple was placed in proximity of the top surface for the Ty measurement. Carbon mass balance for all of the experiments was found to be within 6%.

The catalyst activities were investigated with the composition of carbon dioxide and hydrogen at a ratio of CO₂:H₂ = 1:1, and CO₂:H₂ = 1:4. All samples were tested at an overall flow rate of 100 mL min⁻¹. The conversion of CO₂ and the selectivity of CO and CH₄ were evaluated from the outlet carbon percentage values obtained by the gas analysis. H₂O vapor was condensed before entering the GC to prevent deterioration of the GC column. CO₂ conversion XCO₂, and the selectivity of CO and CH₄ were calculated as

\[
\text{CO}_2 \text{ Conversion} \% = \frac{\text{Y}_\text{CO} + \text{Y}_\text{CH}_4}{\text{Y}_\text{CO} + \text{Y}_\text{CH}_4 + \text{Y}_\text{CO}_2} \times 100
\]

(8)

\[
\text{CO Selectivity} \% = \frac{\text{Y}_\text{CO}}{\text{Y}_\text{CO} + \text{Y}_\text{CH}_4} \times 100
\]

(9)

\[
\text{CH}_4 \text{ Selectivity} \% = \frac{\text{Y}_\text{CH}_4}{\text{Y}_\text{CO} + \text{Y}_\text{CH}_4} \times 100
\]

(10)

where Y_CO, Y_CO₂, and Y_CH₄ were the molar fractions of CO₂, CO, and CH₄ in the outlet, respectively. The CO₂ reaction rate \( r_{\text{CO}_2} = \frac{X_{\text{CO}_2} \times f_r}{22400 \times 80} \) where \( f_r = 100 \text{ mL min}^{-1} \) is the volumetric flow rate at the outlet of the reactor and \( r_{\text{CO}_2} \) is the CO₂ reaction rate.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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