Surface Chemistry of Carbon Dioxide on Copper Model Catalysts Studied by Ambient-Pressure X-ray Photoelectron Spectroscopy

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In-situ analysis of heterogeneous catalysts under reaction condition is indispensable to understand reaction mechanisms and nature of active sites. Ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) is one of the powerful methods to investigate chemical states of catalysts and reaction intermediates adsorbed on the surface. In this review, reaction of carbon dioxide on Cu(997) and Zn-deposited Cu(997) surfaces are discussed as an example of surface chemistry of weakly adsorbed molecules, together with a brief overview of recent progress in AP-XPS methods.

Keywords Ambient-pressure X-ray photoelectron spectroscopy; Carbon dioxide; Copper; Zinc

I. INTRODUCTION

Recycling of carbon dioxide (CO2) emitted by fossil fuel consumption is an important issue for sustainable usage of carbon resources [1, 2]. One of difficulties in the use of CO2 as a chemical feedstock is a catalytic activation of chemically inert CO2 molecules. Cu-ZnO based catalysts has been developed for methanol synthesis from CO2 and hydrogen [3]. An active site for the methanol synthesis is a metallic copper surface. Surface zinc atoms, which are migrated from ZnO onto Cu particles, play an important role in the reaction. The reaction mechanism of methanol synthesis on the Cu-ZnO catalyst has been widely studied, but the nature of the active site is still under debate. Studies on Zn-deposited Cu(111) model catalysts have suggested that a Zn-Cu surface alloy is active for the methanol synthesis [4−6]. This is supported by experimental studies of an industrial Cu/ZnO/Al2O3 catalyst [7]. In addition, first-principle calculations of the methanol synthesis on Cu-Zn surface alloys reveal that the active site consists of Cu steps decorated with Zn atoms, and that atomic oxygen and all intermediates bind to the surface through oxygen atoms are stabilized in the presence of oxophilic zinc at the surface [8, 9]. On the other hand, it has been proposed that an interface between copper surface and zinc-oxide thin film provides an active site for the methanol synthesis [10−12]. In order to reveal the reaction mechanism of CO2 hydrogenation and chemical states of catalysts during the reaction, it is necessary to characterize the surface of catalysts in the presence of reaction gases.

Various experimental techniques have been developed for real-time observation of heterogeneous catalysts under operation conditions [13−15]. Vibrational modes of adsorbates and substrates are measured by sum-frequency generation [16], Raman spectroscopy [17], and polarization-modulation infrared reflection absorption spectroscopy (PM-IRAS) [18]. Analysis of surface vibrational modes provides useful information not only for identification of adsorbed species, but also for elucidation of the nature of active sites by measuring vibrations of adsorbed probe molecules [19] and/or surface phonon modes of catalysts [20].
Operando observation of morphology and surface structure of catalysts during reaction is another important research topic since they can be affected by reaction environment, e.g. gas composition, pressure, and temperature [21, 22]. Atomic force microscopy (AFM) [23, 24] and scanning tunneling microscopy (STM) [25–27] are widely used for atomic-scale measurements of surface structures under reaction conditions. Transmission electron microscopy (TEM) is also applied for observation of catalyst particles exposed in reactant gases using a special environmental cell [28, 29].

Chemical analysis of catalysts under reaction condition is required to understand electronic properties and chemical states of catalysts, which significantly affect catalytic activity and selectivity. X-ray absorption spectroscopy (XAS) [30] and X-ray emission spectroscopy [31–33] provides information about valence electronic states of catalysts and adsorbates. On the other hand, X-ray photoelectron spectroscopy (XPS) directly probes binding energy of core levels. The binding energy is sensitive to chemical and geometrical environments of atoms [34]. In addition, XPS is a surface-sensitive technique because of shorter escape depth of photoelectron compared to photon. Thus, high-resolution XPS measurements with synchrotron radiation can be used for the quantitative analysis of chemical reaction occurring on a surface of catalysts.

These experimental techniques are combined with gas-phase analysis such as quadrupole mass spectrometry and gas chromatography. The real-time monitoring of reaction products in gas phase is quite important to elucidate correlation between the surface states of catalysts in reaction conditions and catalytic activity (conversion, yield and selectivity).

In this review, a brief overview about the ambient-pressure XPS (AP-XPS) method is first presented, together with an introduction of a soft X-ray AP-XPS system at SPring-8 BL07LSU used in this study. Then, a summary of our recent research on activation and hydrogenation of CO2 on single-crystal Cu(997) model catalysts is described as an example of application of AP-XPS for the investigation of surface chemistry of CO2 under well-defined experimental conditions [35, 36]. The Cu(997) surface consists of regularly spaced close-packed (111) terraces (terrace width = 18.7 Å), and each terrace is separated by a monoatomic (111) step. The effects of feed gas composition on the reaction of CO2 were examined. In addition, the role of zinc atoms on Cu surfaces is also discussed by comparing AP-XPS results of Cu(997) and Zn-deposited Cu(997) surfaces as a model system of the stepped Cu surfaces decorated with zinc atoms [8, 9].

II. AMBIENT-PRESSURE X-RAY PHOTOELECTRON SPECTROSCOPY

A. Recent progress in AP-XPS

AP-XPS can measure electronic states of catalyst surfaces and analyze adsorbed species quantitatively in the presence of reactant gases [37–41]. A soft X-ray AP-XPS was first developed by Siegbahn to measure electronic states of a liquid sample [42, 43]. Nowadays, a number of AP-XPS systems are installed in synchrotron-radiation facilities [38] and laboratories with conventional X-ray sources around the world [44].

In the typical AP-XPS apparatus [Figure 1(a)], differential pumping stages are equipped to keep electron analyzer under ultrahigh vacuum (UHV). In
addition, a small aperture (opening diameter typically less than 1 mm) at the entrance of an analyzer lens part reduces gas flow into lens/analyzer chambers. A silicon nitride X-ray window is equipped in a light path to avoid pressure increase of X-ray source. During an AP-XPS measurement, the sample is kept at an appropriate distance (similar to aperture diameter) from the aperture to avoid pressure drop near the sample surface [45]. The short sample–aperture distance is quite important for the AP-XPS measurement because electron mean free path is very small under elevated gas pressure. For example, a mean free path of electron with 100 eV kinetic energy is calculated to be 0.3 mm in 1 mbar CO₂.

One of the advantages of using soft X-ray is large cross sections for light elements, such as carbon, nitrogen, and oxygen. This leads to sensitive detection of adsorbed reaction intermediates on surfaces of heterogeneous catalysts. In addition, the soft X-ray photoelectron signal is surface sensitive due to short inelastic mean free path (IMFP) of photoelectron. Thus, the soft X-ray AP-XPS is a suitable method for investigation of surface chemistry on heterogeneous catalysts. However, note that attenuation of the photoelectron signal in the presence of gas-phase molecules becomes significant with increasing gas pressure. Figure 2 shows simulated C 1s photoelectron intensity as a function of photon energy and methane gas pressure by taking into account attenuation of X-ray by gas (travel length of X-ray = 23 mm) [46], C 1s photoionization cross section [47], and scattering of photoelectron by gas phase (sample–nozzle distance is fixed to 0.3 mm) [48]. The XPS intensity is exponentially decreased with increasing gas pressure. This is mainly caused by the scattering of emitted photoelectron by gas-phase molecules. In order to reduce the scattering effect at higher pressures, it is required to shorten the sample–nozzle distance. In addition, the aperture size of nozzle should be smallened to suppress pressure increase at the lens/analyzer parts. Another way to measure soft X-ray XPS at ambient pressure conditions is utilization of electron-transparent membranes [Figure 1(b)]. Recently, AP-XPS measurements of samples in liquids [49] or under gas above 1 bar [50, 51] have been achieved by physically separating a sample from analyzer parts with the membrane. A few monolayer graphene oxide [52], single-layer or bilayer graphene [53, 54], 15-nm-thick silicon [55], and 5-nm-thick silicon nitride [56] have been used as the electron-transparent membrane to perform the AP-XPS measurement in various environmental conditions.

Ambient-pressure measurements with hard X-ray (or tender X-ray [57]) photoelectron spectroscopy (AP-HAXPES) have been also developed. High photoelectron kinetic energy by hard X-ray excitation causes larger IMFP compared to experiments using the soft X-ray. For example, IMFP of graphite C 1s photoelectron at photon energy of 8 keV is estimated to be 9.61 nm [58]. The large IMFP is advantageous for measurements of buried interfaces, such as solid-liquid and solid-solid interfaces [59, 60], and thus AP-HAXPES has been applied for in-situ measurements of operating devices, such as a fuel cell [61] and a photoelectrochemical cell [62]. In addition, the scattering cross section of electron by gas-phase molecules becomes smaller with increasing kinetic energy. This makes it easier to measure XPS under high-pressure gas environment, compared to the case of soft X-ray AP-XPS. In fact, AP-HAXPES measurements in 1 bar air [63], and in 2 bar He [64] have been already reported.

### B. AP-XPS apparatus at SPring-8 BL07LSU

An AP-XPS system at the soft X-ray undulator beamline BL07LSU of SPring-8 [65] has been under operation since 2014. So far, studies on gas-solid interfaces were mainly conducted: CO₂ adsorption on epitaxial graphene/SiC(0001) [66], CO₂ activation and hydrogenation on Cu model catalysts [35, 36], and hydrogen adsorption/absorption in Pd-Cu [67] and Pd-Ag foils [68]. Figure 3 shows a schematic diagram of the AP-XPS system [35]. The UHV apparatus consists of an electron analyzer chamber, an analysis chamber, a preparation chamber, a load-lock chamber, and a fast-entry chamber for sample installation. Soft X-ray AP-XPS experiments were carried out using a near ambient-pressure electron analyzer (SPECS, PHOIBOS 150 NAP) with a three-stage differentially pumped lens system. A one-dimensional delay-line detector (DLD) is equipped in the electron analyzer. In the preparation chamber, sample preparation can be done through argon ion sputtering, electron-bombardment heating, and vacuum-deposition of metals on the sample surface. Cleanliness of the sample is checked by LEED equipped in the preparation chamber and/or XPS measurements.

The retractable ambient-pressure gas cell is installed in the load-lock chamber with a 4-axis manipulator. The
gas-cell is docked with the entrance of the pre-lens of the analyzer when the AP-XPS experiment is performed. The gas-cell has a Si$_3$N$_4$ window for X-ray transmission (200 nm thickness, double-side coated by 100 nm Al), and a nozzle with small aperture (0.3 mm in diameter), which is the entrance to the differentially pumped electrostatic pre-lens. The gas-cell can be currently pressurized up to 20 mbar. During measurements under near ambient pressure, the sample is placed close (~0.3 mm) to the entrance aperture in order to reduce photoelectron scattering by gas-phase molecules. The X-ray incident angle is 68°, and traveling distance of X-ray in the gas-cell is 23 mm. A prepared sample can be manipulated in UHV. Thus, it is transferred into the gas cell without exposing to air. In the gas-cell, the sample can be heated up to around 900 K and cooled to 170 K on a sample stage under near-ambient pressure conditions.

Feed gases are introduced in the gas-cell through a mass flow controller or a manual variable leak valve connected to a vacuum gas line pumped by a turbo molecular pump and an oil-free scroll pump. For ambient-pressure experiments under well-defined condition, it is quite important to reduce the amount of impurity for avoiding a sample contamination problem. To reduce the amount of impurity in the feed gas, a careful bakeout of the gas line and the AP-XPS chambers including the gas-cell is carried out before conducting experiments. In addition, a liquid-nitrogen cold trap is equipped in the case of non-condensable feed gases (like H$_2$) to reduce the amount of condensable impurities, such as water and large hydrocarbon. For condensable feed gases (CO$_2$, water, etc.), they are further purified through freeze-pump-thaw cycles.

### III. CASE STUDIES

#### A. Activation of CO$_2$ on Cu model surfaces

Activation of inert CO$_2$ molecule on Cu surfaces is an important initial step for the methanol synthesis. Very low reactivity of CO$_2$ on single-crystal flat copper surface has been reported [69–72], whereas the dissociation of CO$_2$ into CO was detected on vicinal Cu surfaces by temperature programmed desorption (TPD) [73, 74]. These results indicate that defect sites on the surface plays an important role for the CO$_2$ activation. However, the reaction condition in UHV is quite different from a real catalytic reaction which is normally operated at higher pressure and temperature. Such differences in the reaction condition may lead to distinct reactivity and/or selectivity under ambient conditions from UHV. Thus, the reaction process of CO$_2$ on a vicinal Cu(997) surface was investigated by AP-XPS measurements.

Figure 4 shows series of (a) O 1s and (b) C 1s AP-XPS spectra ($h\nu = 630$ eV) of the Cu(997) surface as a function of elapsed time [35]. During the measurements, the sample was kept at 340 K under CO$_2$ pressure of 0.8 mbar. Gas-phase CO$_2$ peaks were initially observed at 536.6 eV in an O 1s XPS spectrum at $t = 376$ s and at 292.8 eV in a C 1s XPS spectrum at $t = 507$ s. These gas-phase peaks were shifted to 536.4 eV at 292.6 eV, respectively, at $t > 5500$ s. The shift of gas-phase peaks to lower binding energy originates from an increase of a substrate work function [75].

XPS peaks of adsorbate on the Cu(997) surface were first observed at 531.3 eV in the O 1s region and at 284.4, 289.0, and 284.4 eV in the C 1s region. The C 1s peak at 284.4 eV is assigned to neutral carbon contamination such as carbon atoms and hydrocarbons impurity, and the other adsorbate
peaks are assigned to a reaction product from CO$_2$. In the O 1s spectra, a new peak at 529.5 eV gradually increased in intensity. This peak is attributed to oxygen atoms on the surface [76].

As for assignment of the peaks observed at 531.3, 289.0, and 288.4 eV, quantitative analysis of the composition ratio between oxygen and carbon can be carried out from the area intensity of the O 1s peak (531.3 eV) and those of the C 1s peaks (289.0 and 288.4 eV). In the analysis, the O 1s and C 1s intensities of the adsorbate peaks were normalized by those of the gas-phase CO$_2$ peaks (O/C ratio = 2) to cancel out differences in the analyzer transmission function and the core-electron ionization cross section between O 1s and C 1s.

The O/C ratio of the adsorbate was then estimated to be 3.1 ± 0.1. Thus, the peaks at 531.3, 289.0 and 288.4 eV are assigned to CO$_3$. The produced CO$_3$ and O atoms are stable; they remained on the surface after evacuation [Figure 4(c, d)].

X-ray induced reaction is often observed in AP-XPS measurements with an intense synchrotron radiation. The influence of X-ray irradiation on CO$_2$ chemistry in the present study was minimized by decreasing photon flux density and changing sample position during the measurement. Furthermore, a control experiment was performed, in which the Cu(997) sample was exposed to the CO$_2$ gas under a completely dark condition, i.e., no X-ray irradiation during the reaction. After the gas introduction, the gas cell was evacuated to UHV. Figure 4(c, f) shows post-reaction O 1s and C 1s spectra after the CO$_2$ reaction in the dark condition. The formation of CO$_3$ and an O atom was observed, as in the case of the AP-XPS experiment. Thus, the effect of the X-ray irradiation on the CO$_2$ reaction on Cu(997) is negligible, and the observed reactions are intrinsic thermal processes on the surface.

The intensity of the O 1s peaks of the adsorbates as a function of elapsed time is plotted in Figure 5. The peak intensity of CO$_3$ is nearly saturated at t ~2500 s. The saturation coverage of CO$_3$ was roughly estimated to be 0.05 monolayers (ML). Considering that a Cu substrate surfaces are reactive for CO$_2$ dissociation [73, 74], the dissociation should preferentially take place at the defect site of the Cu(997) surface under ambient conditions to form atomic oxygen and CO. Formed CO is immediately desorbed from the surface at 340 K. Then, the produced atomic oxygen reacts with CO$_2$ to form CO$_3$. The peak shift of gas-phase CO$_2$ in AP-XPS spectra [Figure 4(a, b)] indicates the increase of the work function, with increasing the CO$_3$ coverage. Therefore, adsorbed CO$_3$ is negatively charged by charge transfer from the Cu substrate. The estimated saturation coverage of CO$_3$ is small (0.05 ML). This means that formed CO$_3$ does not cover the whole surface, but they stay at some specific sites and probably block the further CO$_3$ formation. The present results clearly show a facile formation of CO$_3$ on the Cu surface, indicating that CO$_3$ is a key intermediate in the CO$_2$ activation process.

**B. Hydrogenation of CO$_2$ on Cu model surfaces**

CO$_2$ hydrogenation reaction on Cu and Zn-deposited Cu surfaces were also investigated by the soft X-ray AP-XPS [36]. Figure 6 shows (a) O 1s and (b) C 1s AP-XPS spectra of Cu(997) measured in the presence of 0.8 mbar CO$_2$ and 0.4 mbar H$_2$ as a function of sample temperature. The spectra at $T_s \leq 340$ K are similar to the AP-XPS spectra of Cu(997) in the presence of 0.8 mbar CO$_2$ shown in Figure 4, indicating that hydrogen has negligible influence on the CO$_2$ activation, and that the CO$_2$ hydrogenation does not occur at the hydrogen pressure of 0.4 mbar. This is probably because of very small sticking probability for dissociative adsorption of H$_2$ on Cu surfaces [77–79]. The observed adsorbates below 340 K have been attributed to CO$_2$ and atomic O. At 393 K, O atoms were completely removed from the surface and the CO$_3$ coverage also decreased considerably. Above 423 K, the main adsorbate on the Cu(997) surface was the neutral carbon species (C$^0$) such as atomic carbon and hydrocarbon.

Under the real catalytic condition, water molecules should exist in addition to CO$_2$ and H$_2$ gases, since water is a coproduct of methanol synthesis (CO$_2$ + 3H$_2$ $\rightarrow$ CH$_3$OH + H$_2$O) and reverse water-gas shift reaction (CO$_2$ + H$_2$ $\rightarrow$ CO + H$_2$O). Thus, the influence of water on the hydrogenation of CO$_2$ was examined. Figure 7(a, b) shows AP-XPS spectra of the Cu(997) surface measured under 0.8 mbar CO$_2$, 0.4 mbar H$_2$, and 0.05 mbar water gas mixture. In the C 1s spectrum at 299 K, the CO$_3$ and C$^0$ peaks were observed. In O 1s, a broad peak was observed at 531.2 eV, which can be assigned to overlapping hydroxyl and CO$_3$ peaks. There was no O atom peak probably due to the formation of hydroxyl species by the reaction of oxygen with water (H$_2$O + O $\rightarrow$ 2OH). Heating the sample to 340 K leads to decrease of the CO$_3$ coverage and appearance of formate (HCOO) which is a hydrogenation product. The formate coverage decreased.
continuously with the increasing temperature above 373 K and almost disappeared at 423 K. This is due to the hydrogen-promoted decomposition of formate [80, 81]. A series of control experiments on Cu(997) indicates that the CO\textsubscript{2} hydrogenation to formate is promoted by the presence of water. This is consistent with recent studies on the effect of water in the CO\textsubscript{2} activation [82, 83].

Reactivity of CO\textsubscript{2} on the Zn-deposited Cu(997) surface was also studied to reveal the effect of zinc on the CO\textsubscript{2} hydrogenation. Figure 8 shows AP-XPS spectra of Zn (0.33 ML)/Cu(997) under the gas mixture of 0.8 mbar CO\textsubscript{2} and 0.4 mbar H\textsubscript{2}. As in the case of Cu(997), CO\textsubscript{3}, hydroxyl, and oxygen atoms were formed on the Zn/Cu(997) surface at 299 K [36]. As a result of the CO\textsubscript{2} reactions, the Zn atoms were oxidized at 299 K under this pressure condition [see Zn 2p\textsubscript{3/2} spectra in Figure 8(c)], while the Cu substrate retained its metallic state [Figure 8(d)]. When the sample was heated to 423 K, the peak at 289.8 eV in C 1s decreased in intensity, indicating that the CO\textsubscript{3} species corresponding to 289.0 eV were more stable. At 473 K, most adsorbates (CO\textsubscript{3}, hydroxyl, and atomic O) except for the C\textsuperscript{0} species were desorbed from the surface, and Zn was reduced to the metallic state again.

Figure 9(a, b) shows O 1s and C 1s AP-XPS spectra of Zn (0.25 ML)/Cu(997) in the presence of 0.8 mbar CO\textsubscript{2}, 0.4 mbar H\textsubscript{2}, and 0.05 mbar water. The reaction products from CO\textsubscript{2} are similar to those observed on the bare Cu(997) surface. CO\textsubscript{3}, hydroxyl and O atom species were mainly formed on the surface at lower temperatures, and formate was observed above 423 K. In addition, a peak at ~285.5 eV was found in the C 1s region at 340–393 K, which had slightly higher binding energy than the neutral carbon species. From the peak energy, this can be attributed to carbon singly bonded to oxygen (C–O). The C–O species might be assigned to the oxidized graphitic layer (C\textsuperscript{0} species) or adsorbed methoxy, which was also observed on the Zn-deposited Cu film under CO\textsubscript{2} and H\textsubscript{2}O gases [84]. The Zn 2p\textsubscript{3/2} and Cu 2p\textsubscript{3/2} core-level spectra of the Zn/Cu(997) substrate are shown in Figure 9(c, d). Deposited zinc on Cu(997) was oxidized by the adsorbates, such as atomic oxygen, hydroxyl, and formate, even at 473 K [Figure 9(c)].
Figure 8: AP-XPS spectra of Zn (0.33 ML)/Cu(997) surface in the presence of 0.8 mbar CO$_2$ and 0.4 mbar H$_2$: (a) O 1s, (b) C 1s ($h\nu = 630$ eV), (c) Zn 2p$_{3/2}$ and (d) Cu 2p$_{3/2}$ ($h\nu = 1100$ eV). AP-XPS measurements were first performed at 299 K, then the sample was heated up to 473 K under the ambient-pressure condition. Adapted with permission from Ref. 36. Copyright 2019, American Chemical Society.

Figure 9: A series of XPS spectra of Zn (0.25 ML)/Cu(997) surface: (a) O 1s, (b) C 1s ($h\nu = 630$ eV), (c) Zn 2p$_{3/2}$ and (d) Cu 2p$_{3/2}$ ($h\nu = 1100$ eV). AP-XPS measurements were first performed at 299 K in the presence of 0.8 mbar CO$_2$, 0.4 mbar H$_2$, and 0.05 mbar water, then the sample was heated up to 473 K under the ambient-pressure condition. Adapted with permission from Ref. 36. Copyright 2019, American Chemical Society.
This is in contrast to the case of the reaction condition without water where the Zn-deposited Cu(997) surface is significantly reduced at 473 K. Thus, the surface oxidation state is sensitively affected by the composition of gas phase. Note that the reaction products on the Zn-deposited Cu(997) were observed at the sample temperature of 473 K which is close to operation temperature of industrial catalysts of the methanol synthesis. The stabilization of the reaction products from CO$_2$, i.e., reaction intermediates for the methanol synthesis (carbonate, formate, etc.), by the presence of zinc may play an important role in catalysis, since it leads to the increased coverage of the intermediates at the operating temperature of the catalysts (~500 K).

IV. CONCLUSIONS AND FUTURE PROSPECTS

The systematic investigation of the CO$_2$ reactions on Cu(997) model catalysts by soft X-ray AP-XPS reveals the importance of water molecules and zinc atoms on the Cu surface. The addition of water to the feed gas leads to the formation of formate on the Cu surfaces, indicating that water is probably the source of hydrogen for the CO$_2$ hydrogenation under the present reaction conditions. The control experiments on bare Cu(997) and Zn-deposited Cu(997) revealed that the effects of zinc are the stabilization of reaction products, such as carbonate and formate, which leads to increased coverage of reaction intermediates.

The oxidation states of the Zn-deposited Cu surfaces dynamically changed during the AP-XPS measurements depending on the gas-phase composition and surface temperature. This clearly shows the importance of in-situ measurements of the chemical states of catalyst’s surface in order to elucidate the nature of the active site for the methanol synthesis (Zn-Cu alloy or ZnO-Cu interface). Unfortunately, formation of methanol was not observed by a quadrupole mass spectrometer (QMS) in this study because partial pressure of the products is too low and below a detection limit of QMS. The operando spectroscopic study is indispensable to settle the debate on the chemical state of the Cu-ZnO catalyst under the operation condition [6, 12, 85].

The recent progress in the AP-XPS technique makes it possible to measure electronic states of catalysts under real ambient pressure conditions. It is of great advantage for operando measurements of less reactive catalytic systems as is the case for the methanol synthesis. Improving the detection sensitivity of reaction products in gas phase is also necessary for the operando measurements of catalytic conversion of inert molecules. In the case of the methanol synthesis, produced methanol can be condensed and separated from the reactant gases using a cold trap [86]. The separation of produced molecules from reactants by gas chromatography is another way to the quantitative analysis of catalytic reactivity.

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