Bifunctional Synergy in CO Hydrogenation to Methanol with Supported Cu

Nielsen, Niels D.; Thrane, Joachim; Jensen, Anker D.; Christensen, Jakob M.

Published in:
Catalysis Letters

Link to article, DOI:
[10.1007/s10562-019-03036-7](https://doi.org/10.1007/s10562-019-03036-7)

Publication date:
2020

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):
Nielsen, N. D., Thrane, J., Jensen, A. D., & Christensen, J. M. (2020). Bifunctional Synergy in CO Hydrogenation to Methanol with Supported Cu. *Catalysis Letters*, 150, 1427–1433. <https://doi.org/10.1007/s10562-019-03036-7>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Bifunctional synergy in CO hydrogenation to methanol with supported Cu

Niels D. Nielsen, Joachim Thrane, Anker D. Jensen and Jakob M. Christensen*

Department of Chemical and Biochemical Engineering, Technical University of Denmark,
Søltofts Plads B229, 2800 Kgs. Lyngby (Denmark).

*Correspondence to: jmc@kt.dtu.dk

Abstract

Future energy storage could be distributed at local plants and involve production of methanol from reaction of sustainably derived hydrogen with CO or CO₂ from locally available carbon sources. Such decentralized production would benefit from milder operating conditions than found in the current large-scale industrial process. We propose that a route via CO hydrogenation deserves consideration for this purpose, as it will be free of water, which is unavoidable from CO₂-containing gas and strongly inhibiting to the methanol synthesis at lower temperatures. On pure Cu the rate of methanol synthesis from CO is an order of magnitude lower than the rate from CO₂, but active CO hydrogenation catalysts can emerge from a bifunctional mechanism in catalysts that combine copper with a basic oxide. Mechanistic studies are consistent with the bifunctional Cu/support synergy arising from a mechanism, where basic oxide sites activate CO as formates at the metal/oxide interface followed by metal assisted hydrogenation of the interfacial formates. Active catalysts for CO hydrogenation are strongly inhibited by CO₂, which forms carbonates that block the basic oxide sites and thereby prevent the synergistic pathway from CO.

Keywords: Methanol, CO and CO₂ hydrogenation, Support effects, Copper catalyst, Bifunctional mechanism

1. Introduction

Methanol synthesis from syngas (CO/CO₂/H₂) at 500-600 K and 5-10 MPa over Cu/ZnO/Al₂O₃ catalysts is a major industrial process [1]. However, future uses of the reaction to store renewable energy in the form of methanol [2] could involve a decentralized production of methanol, where milder reaction conditions would be especially beneficial. While there is a major research focus on CO₂ hydrogenation [1, 3-5], the synthesis of methanol from CO/H₂ should not be neglected in the search for improved low-temperature systems. An advantage of the route from CO/H₂ is that the atmosphere will be free of water, which is unavoidable from CO₂-containing gas and strongly inhibiting to the methanol synthesis – especially at lower temperatures [6-9]. At lower temperatures (< 473 K) a few kPa of water partial pressure is sufficient to eliminate the majority of the activity for Cu-based methanol synthesis catalysts [6, 7]. As H₂O adsorption isotherms on Cu[10] or Cu/ZnO/Al₂O₃ [10-12] also suggest that a high coverage is reached at H₂O pressures of a few kPa the inhibition can largely be attributed to competitive adsorption (illustrated in supplementary information, figs. S1 & S2). This is likely to be one of the factors that confine the industrial process to higher (> 500 K) temperatures. Consequently, from CO₂ it could be difficult to reach a high yield with a high reaction rate at lower temperatures due to inhibition from the co-produced water.

Future energy storage could involve synthesis of methanol from sustainably derived hydrogen and CO₂ from locally available point sources. The inhibition by water means that it is difficult to achieve a high methanol yield directly from a CO₂/H₂ feed, but there are process concepts [13, 14] where the CO₂/H₂ feed is first partially shifted to CO/CO₂/H₂ (and formed water is removed) and then converted to methanol. This allows methanol synthesis with the conventional catalyst, as the

CO in the syngas can help to remove water formed during methanol synthesis by the shift reaction. However, these concepts are still limited to the harsher synthesis conditions (500-600 K, 5-10 MPa) of the current industrial process. When seeking a process for synthesis of methanol at milder conditions it is worth considering a process, where the CO₂ is fully converted to CO (e.g. by water-gas shift or electrolysis) followed by methanol synthesis from CO/H₂. The pathway from CO/H₂ will both have a more favorable equilibrium [15] and as water is not formed from CO/H₂ the reaction will be free of water inhibition. Both of these factors could lead to improved low-temperature performance, and some Cu-based catalysts are able to achieve considerable methanol synthesis rates from CO/H₂ at lower temperatures [16, 17]

These considerations imply that it is of potential importance to elucidate the active sites and mechanism for CO hydrogenation on Cu-based catalysts. Additionally, the CO hydrogenation can offer fundamental insights into support effects, as single crystal studies [15, 18] suggest that Cu itself has little or no activity for CO hydrogenation, whereas supported Cu catalysts can exhibit catalytic activity with a strong support effect [19]. Here we seek to elucidate the reaction mechanism and the support effect.

2. Methods

Here Cu/MgO (20 wt%), Cu/ZnO/Al₂O₃ (56 wt%), Cu/Al₂O₃ (50 wt%), unsupported Cu and Cu/C (15 wt%) were all prepared by precipitation methods (nominal Cu loading in parentheses). Cu-MOR was prepared by ion-exchanging Cu into mordenite, and Cu/SiO₂ (20 wt%) and MgO/C were prepared by incipient wetness impregnation. Raney Cu was acquired from Strem Chemicals. Catalytic tests were conducted using two different high-pressure setups. One of these is described elsewhere [20] and the other is described in detail in the supporting information. CO chemisorption, temperature programmed reactions (TPR) on model systems and Cu surface area measurements by N₂O uptake with the reactive frontal chromatography method [21] were performed with a Quantachrome Autosorb iQ₂ setup. Combined TPR and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was conducted in a Harrick Scientific domed reaction chamber and Praying Mantis DRIFTS unit. This was done with a Nicolet iS50 FTIR Spectrometer with a liquid-N₂ cooled MCT detector. X-ray photoelectron spectroscopy (XPS) analyses were performed with a monochromatic and micro-focused Al K-Alpha source equipped with a 180° double focusing hemispherical analyzer with a Thermo Scientific 128-channel detector. Further experimental details are provided in the supporting information.

3. Results and discussion

Fig. 1 illustrates that in high pressure methanol synthesis the CO hydrogenation is around an order of magnitude slower than CO₂ hydrogenation for unsupported Cu, Raney Cu and Cu-rich Cu/Al₂O₃. These samples are all expected to approximate the intrinsic properties of Cu. This is in good agreement with the negligible CO hydrogenation observed in Cu single crystal studies performed at low pressure [15, 18]. Ex situ XPS analyses on the fresh and spent unsupported Cu showed that the surface only contained Cu (and O due to the ex situ analysis) and showed that no Ni or Fe deposition from carbonyls occurred (see supplementary information). For Cu-catalyzed methanol synthesis by CO₂ hydrogenation there is a strong support effect [22, 23], but there is generally also a linear correlation between activity and metallic Cu surface area [24-26], which indicates that the reaction occurs on the metallic surface. However, this (fig. S8) and other studies [24, 27] observe no such correlation for CO hydrogenation in good agreement with the limited ability of the metallic Cu surface to form methanol from CO (fig. 1). Some theoretically

hypothesized mechanisms [28-30] suggest a faster pathway from CO compared to CO₂ on Cu, but both high pressure (fig. 1) and low pressure [15, 18] studies contradict this view, and this emphasizes the continued need for theoretical studies of methanol synthesis reactions.

Fig. 1. The relative methanol production rates from CO/H₂ (blue) and CO₂/H₂ (white) over unsupported Cu, Cu-rich (50 wt% Cu) Cu/Al₂O₃, Raney Cu and 20 wt% Cu on MgO. The methanol production in the most reactive atmosphere is assigned as 100 for each sample. Reaction conditions: 5 MPa, H₂/CO_x/inert = 68/3/29, and 523 K (498 K for unsupported Cu due to poor thermal stability). Details on absolute productivity levels are provided in supporting information figs. S3-S7.

Fig. 1 also illustrates the role of the support in achieving CO hydrogenation activity. When compared to the three samples expected to represent the intrinsic properties of Cu the relative rates of the industry-type catalyst Cu/ZnO/Al₂O₃ correspond to the intrinsic behavior of Cu. However, the relative rates of the CO and CO₂ pathways are completely inverted for Cu on an MgO support. Fig. 2 shows that this CO hydrogenation activity in Cu/MgO emerges from a Cu/oxide synergy. Co-precipitated Cu/MgO is of high activity for CO hydrogenation, and whereas Cu/C and MgO/C are of negligible activity, MgO/Cu/C prepared by impregnating Mg(HCOO)₂ onto the essentially inactive Cu/C catalyst shows a clear improvement in activity. This illustrates that the activity emerging in the Cu/MgO combination is the result of a synergy between two components (Cu and MgO) of low individual activity.

Fig. 2. Methanol synthesis rate in CO hydrogenation as a function of time on stream for various supported Cu catalysts. Reaction conditions: $T = 523$ K, $P = 5$ MPa, flow = 300 NmL/min, 0.5 g cat., $H_2/CO = 67/33$.

Previous studies [31-33] have established a correlation between Cu^+ -type surface sites and methanol synthesis activity from CO/H_2 . On metallic Cu CO desorbs at sub-ambient temperatures, and stable chemisorption at ambient temperature is only achieved on Cu^+ -type sites, where CO is more strongly bound [34, 35]. CO chemisorption at 303 K and subsequent TPD shows that with the exception of Cu/C all the catalysts investigated in fig. 2 have Cu^+ -type sites ascribed to bridging “ $Cu^{\delta+}$ -O-support” sites at the metal/oxide interface (table S1 and fig. S9). The CO chemisorption capacities of Cu/MgO (143 $\mu\text{mole/g}_{\text{cat.}}$) and MgO/Cu/C (25 $\mu\text{mole/g}_{\text{cat.}}$) suggest that a major reason for the difference in activity between the two Cu-MgO systems (fig. 2) is the number of these interfacial $Cu^{\delta+}$ -O-Mg sites, which indicates that a key to making active CO hydrogenation catalysts is to maximize the number of interfacial sites. However, a material such as Cu/SiO₂ has a relatively high $Cu^{\delta+}/Cu^0$ ratio in the surface (table S1), but only a modest activity (fig. S7), and an ion-exchanged Cu-mordenite sample (Cu-MOR) prepared specifically as a Cu^+ model system is completely without activity (fig. 2) despite a large number of the CO adsorption sites attributable to Cu^+ species (table S1 and fig. S9). Consequently, Cu^+ sites are most likely not an exclusive requirement for activity. It is therefore not only the extent of the metal/oxide interface that is important, but also the nature of the interfacial sites. The importance of the sites at the metal/oxide interface most likely arises, as it is here that the two elements of a bi-functional mechanism come together.

The argument for the existence of a bifunctional mechanism comes from the results in fig. 3. Fig. 3a shows that Cu/MgO exposed to CO/H_2 at 523 K exhibits infrared bands characteristic of formate (1340, 1625, 2847 and 2925 cm^{-1}) [36] and methoxide (1086, 2600 and 2810 cm^{-1}) [37] on the MgO. The formation of formate (HCOO) by reaction of CO with basic OH species is a well established reaction on oxide surfaces [38, 39], and the oxide can thereby activate CO as formate. We propose that the facile CO hydrogenation on materials such as Cu/MgO proceeds via formate (HCOO) created from insertion of CO into a basic OH group from the oxide as illustrated in fig. 4. This mechanism will take place at the interface between metal and oxide.

There are several arguments for a mechanism via formate. Fig. 3b shows that temperature programmed hydrogenation (TPH) of the surface species on Cu/MgO after exposure to CO/H₂ leads to methanol production in two peaks centered at 423 K and 523 K. Fig. 3c shows that a model system, where magnesium formate was impregnated onto pre-reduced (and passivated) Cu/SiO₂ and then subjected to TPH, produced methanol at the same two temperatures. This would be consistent with the methanol-forming intermediates from CO/H₂ being formate species. Figs. 3b and 3d show that the 423 K methanol formation peak coincides with the disappearance of a species with IR bands (1360 cm⁻¹ and 2834 cm⁻¹) typical [40, 41] of H-C and symmetric O-C-O stretches in bidentate formate. This suggests that such a formate is the origin of the most facile methanol formation at 423 K. Efficient CO hydrogenation catalysts such as Cu/MgO (fig. 2) and Cu/CeO₂ [16, 17] include oxides that efficiently produce formate from CO + OH reactions (see fig. 3a for MgO and Li et al.[42] for CeO₂). A reliance on basic OH groups explains why the supports/promoters providing higher CO hydrogenation activity, such as MgO and ZnO (fig. 2), alkali oxides [43] and rare earth oxides [16, 17] all are of a basic character [44, 45]. Additionally, previous C¹⁶O/C¹⁸O isotope labeling studies [46] with Na₂O-Pd/SiO₂ have shown that in such systems combining a metal with a basic oxide the C-O bond in methanol is scrambled compared to the CO reactant. This is consistent with a mechanism via the two-oxygen formate intermediate, where either oxygen can end in the product molecule.

Fig. 3 a) FTIR spectra of Cu/MgO at 523 K and atmospheric pressure in flowing CO/H₂ (full line) or CO₂/CO/H₂ (dotted line) with indications of formate (F), methoxide (M) and carbonate/bicarbonate (C). Conditions: CO/H₂/inert = 3/68/29, CO₂/CO/H₂/inert = 1.5/1.5/68/29. b) Methanol (m/z = 31) MS intensity as a function of temperature during TPH of the Cu/MgO catalyst after the exposure to CO/H₂ or CO₂/CO/H₂ at 523 K and atm. pressure (and cooling in this gas). Numbers indicate the positions of the spectra in fig. 3d. 2 K/min, 50 NmL/min H₂ flow, 10 mg catalyst. c) Normalized methanol (m/z = 31) MS intensity as a function of temperature comparing CO/H₂ treated Cu/MgO to Mg(HCOO)₂·2H₂O impregnated to 5 wt% Mg on pre-reduced and passivated 20 wt% Cu/SiO₂. Ramp in both cases: 2 K/min, 50 NmL/min H₂ and 10 mg catalyst for Cu/MgO, 30 NmL/min H₂ and 0.5 g catalyst for Mg(HCOO)₂/Cu/SiO₂. d) FTIR

spectra at points 1-4 along the TPH experiments in fig. 3b. The arrows mark 1360 cm^{-1} and 2834 cm^{-1} .

An alternative pathway via the mono-oxygenated intermediates formyl (HCO), formaldehyde (H_2CO) and methoxide (CH_3O) is the basis of several [4, 28-30] proposed mechanisms for CO hydrogenation. For unsupported Cu such a mechanism seems like the only option, since there is no oxide support to facilitate the creation of a two-oxygen species. That unsupported Cu does have a low, but non-zero formation of methanol from CO (fig. 1) suggests that such a direct mechanism exists. However, for an efficient CO hydrogenation catalyst like Cu/MgO it is formate-type IR bands (assigned to interfacial species) that correlate to methanol formation in fig. 3d whereas a characteristic IR band of formyl ($2660\text{-}2680\text{ cm}^{-1}$) [47] was absent in the methanol forming situations in fig. 3d. While the present results therefore offer support to the intermediate role of interfacial formate species there is nothing in the present results to suggest an important role of formyl for an active catalyst such as Cu/MgO.

The Cu/MgO catalyst exposed to CO/H_2 produces methanol in two peaks during TPH (fig. 3b). Fig. 3d suggests that the 423 K methanol formation coincides with a species having IR bands characteristic of formate (1360 cm^{-1} and 2834 cm^{-1}). These bands are different from those of formate entirely on MgO [36], but Fig. 3d shows that this species is formed from CO implying a role of surface OH from the oxide. Fig. 3d also shows that this species is not formed from $\text{CO}_2/\text{CO}/\text{H}_2$. This counts against it being formate entirely on the metallic surface, where it is well established that formate is produced from CO_2 and H_2 [48]. Consequently, the species forming methanol at 423 K , which does not appear to be entirely on either metal or oxide, is attributed to formate at the metal/oxide interface, possibly a bridging formate across the interface. This species is assigned as the primary reaction intermediate, as it can form methanol at a relatively lower temperature. A pathway to methanol via interfacial formates is supported by studies [49-51] of Cu on ZrO_2 . The higher temperature (523 K) methanol formation coincides with the general disappearance of formates and methoxides entirely on the MgO (figs. S10 and S11) and is thus assigned to the less facile conversion of such species entirely on the oxide.

Fig. 4. The proposed oxide assisted mechanism for methanol synthesis via formate and methoxide. Here X can represent both Cu or Mg with X = Cu implying a bridging formate across the Cu/oxide interface. The scheme also illustrates the deactivating effect of CO₂. Although illustrated for MgO other oxides with basic sites should perform similarly.

Contrary to the behavior of Cu itself (fig. 1) both this (fig. S12) and other studies [19, 29, 52] observe that catalysts with a high activity from CO/H₂, such as Cu/MgO, are strongly inhibited by CO₂. The inhibition is largely reversible upon removal of CO₂ (fig. S6). Fig. 3a shows that when Cu/MgO is exposed to CO₂/CO/H₂ IR bands characteristic of carbonates and bicarbonates appear. An experiment, where Cu/MgO was exposed to CO₂ alone to produce carbonates (fig. S13), clearly illustrates that carbonates contribute to the bands at 858, 1078, 1340 and 1630 cm⁻¹ in good agreement with the literature [53, 54]. The band at 1254 cm⁻¹ occurring in CO₂/CO/H₂ is most likely carbonate in a particular configuration bridging two metal atoms/ions [54], but this species is only formed by CO₂/CO/H₂ and not by CO₂ alone (fig. S13) – possibly because it is a bicarbonate species. The Cu/MgO catalyst exposed to CO₂/CO/H₂ produces considerably less methanol in the subsequent TPH, which suggests that inhibition is due to a blocking effect of the carbonates that displaces the methanol forming intermediates. Most importantly, the absence of the 423 K methanol formation (fig. 3b) and the 1360 and 2834 cm⁻¹ IR bands (fig. 3d) shows that the more reactive species assigned as interfacial formates are completely displaced in conjunction with the carbonate formation. This can explain the inhibiting effect of CO₂. In the presence of CO₂ the basic oxide sites that are necessary for the bifunctional synergy are blocked as inactive carbonates (as indicated in fig. 4), and the formation of the mechanistically important interfacial formates relying on basic OH groups is prevented. The inhibiting effect of CO₂ on a bifunctional pathway from CO might not be limited to the highly basic oxide supports such as MgO. It is possible that such a CO-pathway is also inhibited on less basic oxides, when CO₂ is present. It only appears to be the bifunctional pathway from CO that is inhibited by CO₂. In the presence of CO₂ the methanol formation rate suggests that Cu metal surface produces methanol from the CO₂ with its expected rate (table S2).

Whereas the interfacial formate species are assigned as the key intermediates in the CO hydrogenation the formate and methoxide species entirely on the MgO are only expected to play a limited role in the methanol synthesis, perhaps that of complete spectators. Firstly, these species are only converted at higher temperatures during TPH (figs. S10 and S11). Secondly, the IR bands of formate on MgO are not strongly affected by the presence of CO₂ (fig. 3a), which affects productivity significantly. The interfacial formates are more reactive, but also less stable and more easily displaced by carbonates (fig. 3d), whereas the majority of formates entirely on the MgO are more stable and less reactive and therefore not displaced by carbonates (fig. 3a.). Consequently, the methanol formation is assigned to formate species specifically at the metal/oxide interface that are displaced by carbonates in the presence of CO₂. It is thus likely that formate is both a spectator on the oxide surface further away from the metal particles and an actual intermediate on interfacial sites. The IR bands of methoxide on MgO drop significantly in the presence of CO₂ (fig. 3a.). This is most likely because water is produced from the CO₂-containing gas. The removal of methoxide on an oxide by hydrolysis with water is far more facile than hydrogenation [55]. The methoxide on MgO is most likely formed, when produced methanol is re-adsorbed on the oxide, and the combination of the slower methanol production in the presence of CO₂ and the faster removal of methoxide by hydrolysis can explain the lower methoxide coverage in the CO₂-containing gas. While it cannot be fully excluded that methoxide on the MgO can play a mechanistically important

role under some conditions its disappearance in the presence of CO₂ may just result from the presence of water that hydrolyzes the methoxide species.

The present results clearly show that the CO hydrogenation to methanol relies on a metal/oxide synergy and suggest that one pathway to methanol is the activation of CO as formate by the oxide followed by a metal-assisted hydrogenation of formate into methanol. The presence of CO₂ interrupts the bifunctional synergy, as the necessary basic oxide sites are blocked as carbonates. Although developed here with Cu/MgO the present mechanistic conclusions are expected to be valid also for other catalyst systems. As an example another system with high activity from CO/H₂ is Cu/CeO₂ [16, 17], where the oxide is also able to activate CO as formate [42], and where the presence of CO₂ also inhibits the methanol synthesis and leads to carbonate formation [52, 56]. Similarly, Pd-based catalysts for CO hydrogenation generally exhibit the same support and promoter effect where basic oxides are beneficial [19, 46].

4. Conclusion

In conclusion, we propose that it is worth considering methanol synthesis from CO/H₂ in the search for methanol synthesis at milder conditions. The pathway from CO/H₂ has a more favorable equilibrium and is free of co-produced water, which is strongly inhibiting to methanol synthesis at lower temperatures. Both factors could be advantageous for low temperature operation. The present results show that active CO hydrogenation catalysts such as Cu/MgO emerge from a synergy between metal and oxide, which is attributed to a bifunctional mechanism focused at the metal/support interface. The mechanistic investigations are consistent with interfacial formates, produced by reaction of CO with basic OH groups from the oxide surface, as the important reaction intermediates. Active CO hydrogenation catalysts are strongly inhibited by CO₂ and the results suggest that this occurs because CO₂ forms carbonates at the basic oxide and thereby blocks the oxide sites that enable the bifunctional pathway. The results suggest that the key to making active CO hydrogenation catalysts is to engineer systems that maximize the number of interfacial sites, where Cu and basic oxide sites come together while ensuring the absence of species such as CO₂ that can block the oxide sites. The combination of optimally engineered catalysts and the water free conditions of CO hydrogenation could lead to improved low temperature performance in methanol synthesis and pave the way for remote and small scale methanol-based energy storage facilities.

Acknowledgements

The Villum Foundation V-SUSTAIN grant 9455 to the Villum Center for the Science of Sustainable Fuels and Chemicals is gratefully acknowledged for funding. We thank Saint Gobain for providing the SiO₂ support.

References

- [1] Behrens M (2015) *Recycl Catal* 2:78-86.
- [2] G.A. Olah, A. Goepfert, G.K.S. Prakash, *Beyond Oil and Gas: The Methanol Economy* (Germany, Wiley-VCH, 2006).
- [3] Studt F, Sharaftudinov I, Abild-Pedersen F, Elkjær CF, Hummelshøj JS, Dahl S, Chorkendorff I, Nørskov JK (2014) *Nature Chem* 6:320-324.
- [4] Graciani J, Mudiyanseelage K, Xu F, Baber AE, Evans J, Senanayake SD, Stacchiola DJ, Liu P, Hrbek J, Fernandez Sanz J, Rodriguez JA (2014) *Science* 345:546-550.

- [5] Martin O, Martín AJ, Mondelli C, Mitchell S, Segawa TF, Hauert R, Drouilly C, Curulla-Ferré D, Pérez-Ramírez J (2016) *Angew Chem Int Ed* 55:6261-6265.
- [6] Bardet R, Thivolle-Cazat J, Trambouze Y (1984) *Compt Rend Acad Sci Paris* 299:423-425.
- [7] Cherifi O, Monteverdi S, Bettahar MM, Forissier M, Perrichon V (1985) *Bull Soc Chim Fr*:405-409.
- [8] Sahibzada M, Metcalfe IS, Chadwick D (1998) *J Catal* 174:111-118.
- [9] Saito M, Fujitani T, Takeuchi M, Watanabe T (1996) *Appl Catal A* 138:311-318.
- [10] Słoczyński J, Grabowski R, Janas J, Skrzypek J (1991) *Chem Eng Sci* 46:2611-2623.
- [11] Słoczyński J, Grabowski R, Janas J, Skrzypek J (1991) *Chem Eng Sci* 46:2599-2610.
- [12] Tarasov A, Seitz F, Schlögl R, Frei E (2019) *ACS Catal* 9:5537-5544.
- [13] Goehna H, Koenig P (1994) *Chemtech* 24:36-39.
- [14] Joo O-S, Jung K-D, Moon I, Rozovskii AY, Lin GI, Han S-H, Uhm S-J (1999) . *Ind Eng Chem Res* 38:1808-1812.
- [15] Maack M, Friis- Jensen H, Sckerl S, Larsen JB, Chorkendorff I (2003) *Top Catal* 22:151-160.
- [16] Owen G, Hawkes CM, Lloyd D, Jennings JR, Lambert RM, Nix RM (1987) *Appl Catal* 33:405-430.
- [17] Shen W-, Ichihashi Y, Matsumura Y (2005) *Appl Catal A* 282:221-226.
- [18] Nerlov J, Chorkendorff I (1998) *Catal Lett* 54:171-176.
- [19] Fujita S, Usui M, Hanada T, Takezawa N (1995) *React Kinet Catal Lett* 56:15-19.
- [20] Christensen JM, Mortensen PM, Trane R, Jensen PA, Jensen AD (2009) *App Catal A* 366:29-43.
- [21] Chinchin GC, Hay CM, Vandervell HD, Waugh KC (1987) *J Catal* 103:79-86.
- [22] Fujitani T, Saito M, Kanai Y, Kakumoto T, Watanabe T, Nakamura J, Uchijima T (1994) *Catal Lett* 25:271-276.
- [23] Chaumette P, Courty P, Barbier J, Fortin T, Lavalley JC, Chauvin C, Kiennemann A, Idriss H, Sneed RPA, Denise B (1988) *Proc 9th Intl Congr Catal* 2:585-593.
- [24] Robbins JL, Iglesia E, Kelkar CP, DeRites B (1991) *Catal Lett* 10:1-10.
- [25] Baltes C, Vukojević S, Schüth F (2008) *J Catal* 258:334-344.
- [26] Joyner RW, Burch R, Golunski SE, Spencer MS (1990) *Catal Lett* 6:151-156.
- [27] Robinson W, Mol J (1988) *Appl Catal* 44:165-177.
- [28] van Rensburg WJ, Petersen MA, Datt MS, van den Berg J-A, van Helden P (2015) . *Catal Lett* 145:559-568.
- [29] Studt F, Behrens M, Kunkes EL, Thomas N, Zander S, Tarasov A, Schumann J, Frei E, Varley JB, Abild-Pedersen F, Nørskov JK, Schlögl R (2015) *ChemCatChem* 7:1105-1111.
- [30] Behrens M, Studt F, Kasatkin I, Kühl S, Hävecker M, Abild-Pedersen F, Zander S, Girgsdies F, Kurr P, Knief BL, Tovar M, Fischer RW, Nørskov JK, Schlögl R (2012) *Science* 336:893-897.
- [31] Monnier JR, Hanrahan MJ, Apai G (1985) *J Catal* 92:119-126.
- [32] Sheffer GR, King TS (1989) *J Catal* 116:488-497.
- [33] Chu PJ, Gerstein BC, Sheffer GR, King TS (1989) *J Catal* 115:194-204.
- [34] Cox DF, Schulz KH (1991) *Surf Sci* 249:138-148.
- [35] Dandekar A, Vannice MA (1998) *J Catal* 178:621-639.
- [36] Busca G, Lamotte J, Lavalley JC, Lorenzelli V (1987) *J Am Chem Soc* 109:5197-5202.
- [37] Kondo J, Sakata Y, Maruya K, Tamaru K, Onishi T (1987) *Appl Surf Sci* 28:475-478.
- [38] Shido T, Iwasawa Y (1991) *J Catal* 129:343-355.

- [39] Gopal PG, Schneider RL, Watters KL (1987) *J Catal* 105:366-372.
- [40] Chutia A, Silverwood IP, Farrow MR, Scanlon DO, Wells PP, Bowker M, Parker SF, Catlow CRA (2016) *Surf Sci* 653:45-54.
- [41] Dubois LH, Ellis TH, Zegarski BR, Kevan SD (1986) *Surf Sci* 172:385-397.
- [42] Li C, Sakata Y, Arai T, Domen K, Maruya K, Onishi T (1989) *J Chem Soc Faraday Trans 1* 85:1451-1461.
- [43] Herman RG (1991) *Stud Surf Sci Catal* 64:265-349.
- [44] Martin D, Duprez D (1996) *J Phys Chem* 100:9429-9438.
- [45] Auroux A, Gervasini A (1990) *J Phys Chem* 94:6371-6379.
- [46] Kikuzono Y, Kagami S, Naito S, Onishi T, Tamaru K (1981) *Faraday Discuss* 72:135-143.
- [47] Saussey J, Lavalley J-C, Lamotte J, Rais T (1982) *J Chem Soc Chem Commun*:278-279.
- [48] Taylor PA, Rasmussen PB, Ovesen CV, Stoltze P, Chorkendorff I (1992) *Surf Sci* 261:191-206.
- [49] Fisher IA, Bell AT (1998) *J Catal* 178:153-173.
- [50] Larmier K, Liao W-C, Tada S, Lam E, Verel R, Bansode A, Urakawa A, Comas-Vives A, Copéret C (2017) . *Angew Chem Int Ed* 129:2358-2363.
- [51] Lam E, Larmier K, Wolf P, Tada S, Safonova OV, Copéret C (2018) *J Am Chem Soc* 140:10530-10535.
- [52] Jennings JR, Lambert RM, Nix RM, Owen G, Parker DG (1989) *Appl Catal* 50:157-170.
- [53] Cornu D, Guesmi H, Krafft J-M, Lauron-Pernot H (2012) *J Phys Chem C* 116:6645-6654.
- [54] Busca G, Lorenzelli V (1982) *Mater Chem* 7:89-126.
- [55] Fujita S, Ito H, Takezawa N (1993) *Bull Chem Soc Jpn* 66:3094-3096.
- [56] Lin L, Yao S, Liu Z, Zhang F, Na L, Vovchok D, Martinez-Arias A, Castaneda R, Lin JY, Senanayake SD, Su D, Ma D, Rodriguez JA (2018) *J Phys Chem C* 122:12934-12943.