

Hydrogenation of CO₂ to Methanol and CO on Cu/ZnO/Al₂O₃: Is there a Common intermediate or not?*

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Keywords: H/D substitution, methanol, copper, reverse water gas shift, DFT, kinetics, mechanism, CO₂ hydrogenation

Abstract

H/D exchange experiments on a Cu/ZnO/Al₂O₃ catalyst have shown that methanol synthesis and RWGS display a strong thermodynamic isotope effect, which is attributed to differences in the zero point energy of hydrogenated vs. deuterated species. The effect is larger for methanol synthesis and substantially increases the equilibrium yield in deuterated syngas. In the kinetic regime of CO₂ hydrogenation, an inverse kinetic isotope effect of H/D substitution was observed, which is stronger for methanol synthesis than for CO formation suggesting that the two reactions do not share a common intermediate. Similar observations were also made on other catalysts like Cu/MgO, Cu/SiO₂ and Pd/SiO₂. In contrast to CO₂ hydrogenation, the CO hydrogenation on Cu/ZnO/Al₂O₃ did not show such a strong kinetic isotope effect indicating that methanol formation from CO₂ does not proceed via consecutive reverse water gas shift and CO hydrogenation steps. The inverse KIE is consistent with formate hydrogenation being the rate-determining step of methanol synthesis from CO₂. Differences in the extent of product inhibition by water, observed for methanol synthesis and reverse water gas shift indicate that the two reactions proceed on different surface sites in a parallel manner. The consequences for catalyst design for effective methanol synthesis from CO₂ are discussed.

Introduction

The Cu/ZnO-catalyzed methanol synthesis process has been extensively studied due to its high industrial relevance since this technology was established in the 1960s [1, 2] and the industrial and

* This work is dedicated to the memory and achievements of Dr. Haldor Topsøe.

academic labs in the environment of Dr. Haldor Topsøe have been major players in this field responsible for substantial technological and scientific progress. Today, this reaction is still in the focus of many researchers as renewed interest has been aroused, because of the potential of the CO₂ hydrogenation to methanol as a source of clean synthetic fuels [3] and as an energy storage molecule [4]. The great importance of syngas chemistry for the global energy challenge was highlighted by Dr. Haldor Topsøe in his 2010 interview [5]. On Cu-based catalysts, methanol synthesis from CO₂ (equation 1) is usually accompanied by undesired CO formation via the reverse water gas shift reaction (RWGS, equation 2).



In recent literature reports, various hypotheses for the identity of the active sites and the nature of the reaction mechanism are presented, in particular with regard to the intermediates and precursors of methanol formation [6-12]. Different conclusions regarding the active site and the reaction mechanism have been drawn based on the different materials studied, such as clean and oxide-promoted Cu catalysts. One of the major mechanistic questions is related to whether methanol synthesis and RWGS are parallel pathways [13, 14], share a common intermediate [8], or if methanol formation proceeds by sequential RWGS and CO hydrogenation as recently suggested for Cu/CeO_x catalysts [15] and Cu/ZnO/Al₂O₃ catalysts at very high pressure [10]. Knowledge of these mechanistic details is a decisive design criterion for CO₂ hydrogenation catalysts. Chances to suppress the undesired CO formation for an increased methanol yield are higher and different strategies can be applied if the two reactions are known to proceed independently via parallel pathways (and on different surface sites). In turn, it will be a harder task to suppress CO formation for catalyst that produces methanol by a mechanism that shares a common intermediate with CO formation or even uses CO as a reactant. Here, we focus on industrially applied Cu/ZnO/Al₂O₃ catalyst to identify its potential as a highly selective CO₂ hydrogenation catalyst.

In order to answer the question of a common intermediate, we employ H/D isotope substitution experiments. The effect of H/D substitution on the reaction rates, i.e. the kinetic isotope effect (KIE) [16], has been proven as a useful mechanistic tool on other industrially relevant hydrogenation processes like, e.g., ammonia [17] and Fischer-Tropsch synthesis (FTS) [18-21]. Both kinetic and thermodynamic isotope effects (TIE) are observed as a result of zero-point vibrational energy effects and differences in the rates of hydrogen transfers, respectively (Fig. S1). A KIE may occur even if the rate-determining step (RDS) does not directly involve cleavage of a bond to hydrogen, but involves a hydrogenated transition state. This secondary KIE, is generally weaker than the primary KIE, and might be normal ($R_H/R_D > 1$) or inverse ($R_H/R_D < 1$) depending on whether bond force constants are decreased or increased, respectively.

Interestingly, H/D substitution studies of methanol synthesis are relatively sparse. The first two studies on the subject was performed by Belysheva et al. in 1978 and consisted of an examination of the effect of H/D substitution on the equilibrium and kinetics of methanol synthesis [22, 23]. The later study was performed on an industrially relevant Cu/ZnO/Al₂O₃ catalyst with a CO/CO₂ mixture, but it was carried out at atmospheric pressure. In a recent paper, Yang et al. briefly alluded to a kinetic isotope effect in CO₂ hydrogenation on Cu/SiO₂, in the context of a comprehensive mechanistic study, conducted mostly through spectroscopic means [8]. Otherwise, we could not find a study of the effect of H/D substitution in WGS on Cu-based catalysts in the academic literature.

Herein, we report an H/D substitution study of the KIE and TIE for methanol synthesis and RWGS over industrial-like Cu/ZnO/Al₂O₃ catalysts and discuss the results in the context of the debate on the reaction mechanism of methanol synthesis from CO₂ and accompanying RWGS. The relevance to catalyst design for CO₂ hydrogenation based on modified industrial catalysts is also addressed.

Materials and Methods

The Cu/ZnO/Al₂O₃ catalyst studied in this work has been synthesized from a zincian malachite precursor (Cu,Zn)₂(OH)₂CO₃ (Cu:Zn = 70:30) with additional 13 mol% Al (metal basis) by co-precipitation using the concept of the industrial catalyst [24]. The catalyst is similar to the materials described in detail in previous contributions [25, 26]. The Cu surface area as determined by N₂O decomposition was 30 m²/g_{cat}. The Cu/MgO catalyst and its physicochemical properties have been presented previously in [13]. The Cu/SiO₂ and Pd/SiO₂ catalysts have been synthesized by incipient wetness impregnation of silica gel with Cu and Pd nitrate salt solutions respectively, to attain metal loadings of 10 wt.%. Subsequently the catalysts were dried at 373 K and calcined at 573 K in a muffle furnace. All catalytic tests were carried out in fixed bed flow reactor. The fresh catalyst (sieve fraction 100 - 200 μm) was mixed with 0.7 g of crushed SiO₂ chips and loaded into a 10 mm inner diameter stainless steel reactor tube. It was reduced at 523 K (1 K min⁻¹) for at 2 hours in 20 % H₂ in He (100 mL min⁻¹) prior to methanol synthesis. Upon completion of the reduction, the feed gas containing was introduced into the reactor and the reaction was carried out at different conditions as indicated in the next section. For the determination of the KIE the same experiments were conducted with a deuterated version of the feed gas at otherwise identical conditions, once the reaction has reached steady state. Online analysis of products was performed with a gas chromatograph Agilent 7890A equipped with a Haysep Q-Column and a thermal conductivity detector for analysis of non-condensable gases and an Agilent DB1 column interfaced to a flame ionization detector for analysis of methanol. To determine the error of the measurements, repeated experiments have been performed at a selected set of conditions (523 K, 30 bar, 200 m catalyst, flow 100 ml/min), both during the same run (at same conditions, and different times on stream) and with fresh batches of catalyst at same conditions. The relative error in methanol formation rates with both H₂ and D₂ was approximately 8%. The same magnitude of error was assumed for the CO hydrogenation experiments. The combined error involved in R_H/R_D calculation was on the order of 11%. Possible catalyst deactivation effects were excluded based on a representative run of CO₂ hydrogenation. It was started at 523 K and 30 bar in H₂ and was allowed sufficient time to reach steady state. The temperature study involved switching the feed from H₂ to D₂ at each of the temperatures studied and allowing sufficient time (4 h) for steady state to be achieved after each change. A space velocity study followed the temperature study, after which the catalyst was returned to initial conditions after more than 60 h on stream. During this time an 8% change in methanol synthesis activity and a 0.5% change in RWGS activity was observed, both in the range of the estimated error.

A vibrational analysis of the intermediates and transition states involved in the hydrogenation of CO₂ to methanol on Cu/ZnO/Al₂O₃ catalysts was performed. The structures and energetics are taken from recent work [6, 25]. Here, we only consider the effect of deuterium substitution on the vibrational frequencies and thus zero-point energies (ZPE) and entropies. The vibrational frequencies used to determine the ZPE and the entropic contribution S^T are calculated within the harmonic approximation to the total energy curve. In the calculations all hydrogen atoms are replaced by the isotope deuterium, thus increasing the reduced mass of the intermediates in the methanol synthesis resulting in an overall downshift of the vibrational modes.

Results and Discussion

The TIE for methanol synthesis and reverse water gas shift was first quantified under industrial-like conditions. For this purpose, a large amount of Cu/ZnO/Al₂O₃ catalyst (7g) was used to drive the reaction into equilibrium at 30 bar. We have chosen methanol synthesis from CO₂ (equation 1) and RWGS (equation 2) as two independent reactions to describe the thermodynamics of the system. The equilibrium constants of these reactions, as calculated from reactor outlet concentrations in normal and fully deuterated syngas (6% CO, 8% CO₂, 26.5% He or Ar and 59.5% H₂ or D₂) is shown in Tab. 1 (see SI for further information). A strong TIE was observed both for methanol and RWGS. The increase in equilibrium methanol yields is consistent with the observations of Belysheva and coworkers for the methanol synthesis equilibrium yields, measured at 1 bar [22]. DFT calculations show an increase and decrease in zero-point-energy contributions for deuterated species leading to an increase in ΔH of the reaction in fair agreement with the experimental results (Tab. 1).

Tab.1: Comparison of measured and calculated values for the thermodynamics of methanol synthesis and RWGS in hydrogen- and deuterium-containing syngas (at 30 bar in 6% CO, 8% CO₂, 26.5% He or Ar and 59.5% H₂ or D₂ measured in the temperature range 523–573 K).

	Methanol synthesis			Reverse water gas shift		
	K^{523K}	$\Delta H^{Exp} /$ kJ/mol	$\Delta H^{DFT} /$ kJ/mol ^[a]	K^{523K}	$\Delta H^{Exp} /$ kJ/mol	$\Delta H^{DFT} /$ kJ/mol ^[a]
CO/CO ₂ /H ₂	1.43×10^{-5}	-52.1	-53.5	6.72×10^{-3}	47.6	40.2
CO/CO ₂ /D ₂	6.17×10^{-4}	-82.5	-88.0	3.40×10^{-2}	30.2	30.1

[a] DFT calculations were performed employing the BEEF-vdW functional; the details are reported elsewhere.[24] The value for CO₂ in the gas-phase for which BEEF-vdW performs poorly has been corrected as described in references [5,24].

The KIE was quantified in the CO₂ hydrogenation reaction (CO₂:H₂/D₂ = 1:3) with 200 mg catalyst in the kinetically limited regime. Figure 1 shows the results obtained for methanol synthesis and CO formation as a function of temperature (variation of space velocity and pressure are shown in the SI, Fig. S3). It can be seen that the KIE is inverse with a slower reaction in case of H₂ compared to D₂ ($r_H/r_D < 1$). The KIE for methanol is significantly larger than for RWGS and calculated to be approximately 0.6 vs. 0.9 at 503 K. **The increase in the magnitude of the KIE of methanol formation with increasing reaction temperature may at first be justified by the dominance of the TIE as the reaction approaches equilibrium. This may be the case for measurements made at 523 K, where the approach to equilibrium of the methanol synthesis reaction is around 50% (60% for RWGS, see SI). However, the relative constancy of the KIE for methanol synthesis (0.6) with changing space velocity at 503 K (Fig. S3c) and pressure at 493 K (Fig. S3e) implies that the effect persists even as the reaction is driven away from equilibrium.**

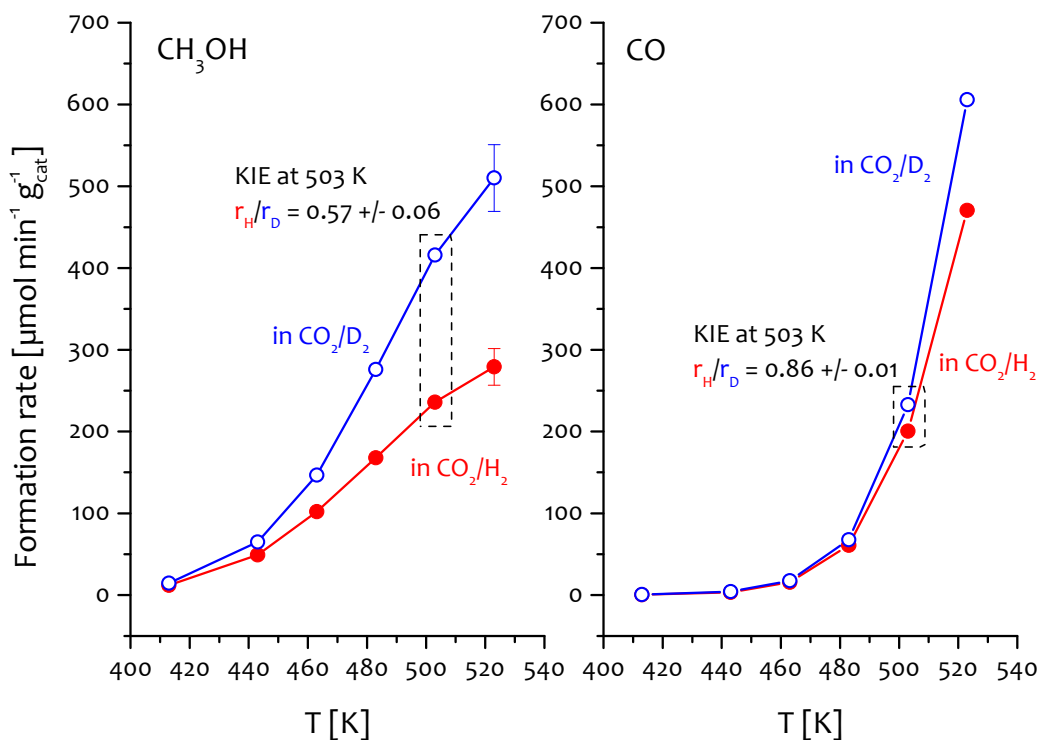


Fig. 1: Formation rates of methanol (left panel) and CO (right panel) on a Cu/ZnO/Al₂O₃ catalyst as a function of temperature (200 mg catalyst at 30 bar and 100 ml/min) in CO₂/H₂ (red, filled circles) and CO₂/D₂ (blue, open circles), respectively. The KIE (r_H/r_D) at 503 K is indicated. *The error for methanol formation was estimated based on repetition experiments at 523 K (8%). In case of CO formation the symbol size exceeds the error bar (1%).*

Conversely, Yang and co-workers measured a weak normal KIE for methanol synthesis ($R_H/R_D = 1.2$) and CO production ($R_H/R_D = 1.5$) for CO₂ hydrogenation at 6 bar and 469-546 K on Cu/SiO₂ [8]. It is interesting to note that although the curvatures of Arrhenius plots constructed by Yang et al. with aforementioned kinetic data are affected by equilibrium at the higher temperatures, an inverse TIE is also not observed. Belysheva et al., however, also observed an inverse KIE for methanol synthesis in a CO₂:CO:H₂/D₂ mixture (5:32:63) over a Cu/ZnO/Al₂O₃ catalyst conducted at atmospheric pressure and obtain an $R_H/R_D = 0.65$ and 0.75 at 473 K and 453 K, respectively [23]. According to the authors, these measurements are not significantly affected by equilibrium since the approach to equilibrium of the methanol synthesis reaction was 0.13 at 473 K with hydrogen. The aforementioned magnitude and the temperature dependence of the KIE for methanol synthesis are in good agreement with our results.

The difference in KIE between methanol and CO formation strongly suggests a different RDS for the two reactions. The weak KIE for RWGS generally indicates a lower number of H atoms involved in the RDS of RWGS than methanol synthesis. This is in good agreement with the surface redox and carboxyl mechanisms of RWGS. In the RDS of the surface redox mechanism, dissociation of CO₂ at the catalyst surface is the RDS [27, 28]. This step does not involve hydrogen and no KIE is expected. In the carboxyl mechanism, carboxyl decomposition (COOH* + * \rightleftharpoons CO* + OH*) is proposed as the RDS, where only one H atom is involved [8, 29] (* = adsorbed surface species or free surface sites). It is noted that the decomposition of formate (HCOO* \rightleftharpoons OH* + CO*), also with presence of a single H

atom, has been discussed as an alternative RDS [30], but formate likely is a spectator in the shift chemistry [7, 31]. Experimentally, we observe a slight evolution toward an inverse KIE with increasing pressure, which might point to a beginning change in mechanism of CO formation, possibly due to higher formate coverage (Fig. S3f). Accordingly, the kinetic model for methanol synthesis proposed by Askgaard *et al.* [32], predicts that the formate coverage increases by a factor of fifty when pressure increased from 2 to 50 bar at 500 K. Variation in space velocity (Fig. S3c,d) did not provide new results in terms of KIE, but revealed that product inhibition is clearly less significant for CO formation. The relative stability of the CO rate during space velocity variation, which at the same time caused a change in the methanol and water concentration by a factor of four, shows that the CO formation is not linked to the methanol concentration and thus cannot result from methanol decomposition, but from RWGS.

Generally, the clear difference in the extent of inverse KIE for methanol and for CO formation – R_D/R_H for the former is always significantly lower than for the latter – proves that the two reactions do not proceed via a common intermediate for the RDS. This supports the view that methanol is formed on Cu/ZnO via formate hydrogenation [13, 25, 32, 33], while formate is a spectator in RWGS, which in turn likely proceeds through the carboxyl or surface redox mechanism.

The strong KIE for methanol synthesis is also observed in density functional theory (DFT) calculations (Fig. 2). The effect stems from the differences in the vibrational modes of the intermediates and transition-states that are introduced upon substitution with the heavier deuterium. Due to the increase in mass, the vibrational frequencies are decreased thus resulting in a lesser zero-point energy (ZPE) of deuterated species compared to their hydrogen counterparts. In addition, a reduction in vibrational frequencies does also lead to smaller entropy. This effect is, however, less pronounced than the change in ZPE (see Tab. S2 for all values,). Figure 2 shows the free energy diagram of CO₂ to methanol on the model of the active site of the Cu/ZnO/Al₂O₃ catalyst that was established recently [25]. The effect of deuterium substitution is shown as the blue diagram. It can be seen that both, intermediates and transition-states that involve one or more hydrogen atoms are reduced in their free energy (relative to the educts CO₂ and 3 H₂) upon substitution with deuterium. This effect is becoming more pronounced the more hydrogen/deuterium are involved, ranging from a few kJ/mol for one deuterium up to 40 kJ/mol at the end of the pathway (6 deuterium). Interestingly, it can not only be seen that all barriers are lowered upon deuteration, but there is also some indication that the rate-determining step changes from the third hydrogenation to the second hydrogenation (that is hydrogenation of DCOO*). These barriers are rather similar, however, and certainly within the error of DFT [34], so no conclusive argument can be put forward.

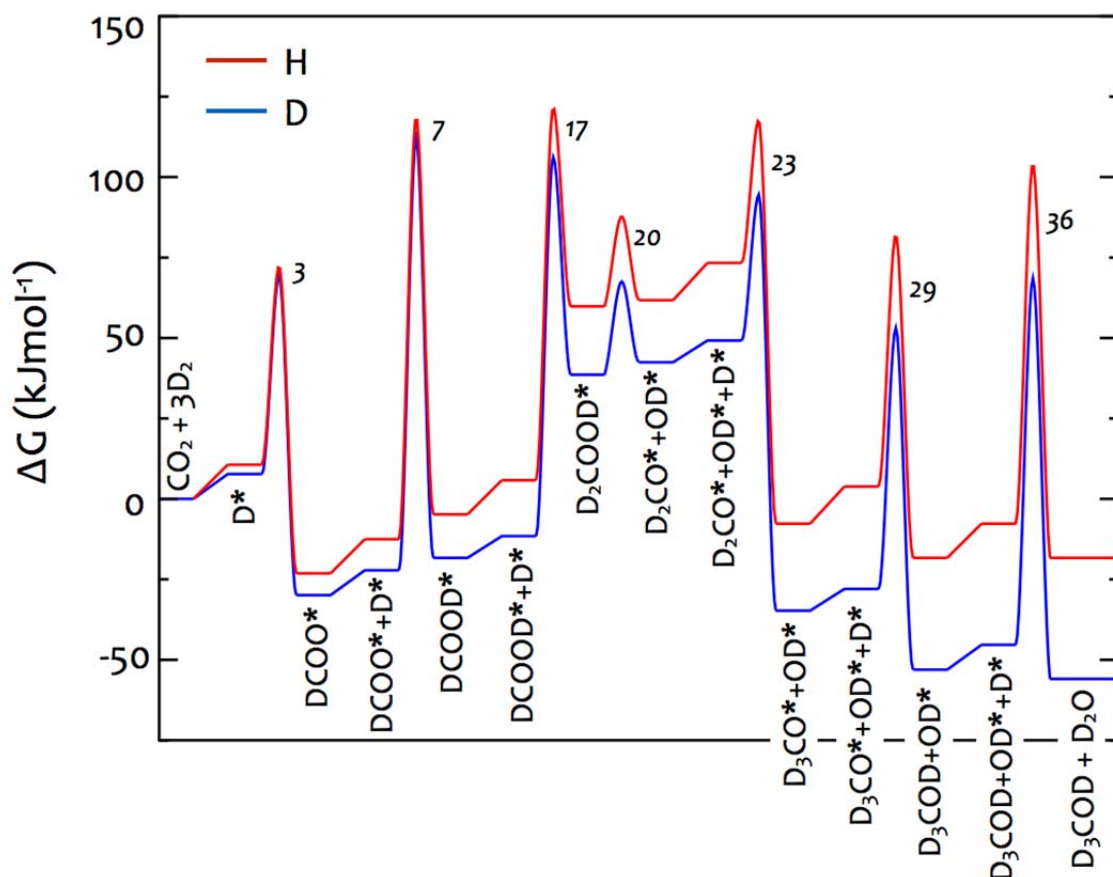


Fig. 2. Effect of H/D substitution on the Gibbs-free energy diagram for the hydrogenation of CO_2 to methanol over a stepped CuZn surface. All energies are relative to $\text{CO}_2 + 3 \text{H}_2$ (red diagram) and $\text{CO}_2 + 3 \text{D}_2$ (blue diagram). Intermediates marked with a star are adsorbed on the surfaces. Gibbs-free energies were calculated at 503 K.

Comparative measurements were additionally performed on a number of different catalysts, namely Cu/SiO₂ (10 wt%), Cu/MgO (80 wt%) and Pd/SiO₂ (10 wt%). The reaction rates and KIEs are compiled in Tab. 2 and show similar general behavior for all catalysts with regard to the presence of a significant inverse KIE for methanol synthesis and values close to unity for RWGS on all catalysts. This shows that the KIE and thus the nature of the RDS of CO_2 hydrogenation to methanol is not affected by different supports or different active metals within the range of tested materials despite very different performance in methanol synthesis. This observation provides support for the view that the widely observed promotional effect of ZnO on Cu-based catalysts [2, 35-37] affects the activity of methanol synthesis, but does not change its mechanism. We have recently shown that this promotion effect can be successfully modeled by assuming the active site to be a fully Zn decorated surface step of Cu [25].

Tab. 2 Formation rates of methanol and CO and KIEs in H₂- or D₂-containing feed on different catalysts in $\mu\text{mol}/(\text{min g}_{\text{cat}})$. The conditions of reaction were 200 mg catalyst in 100 ml/min of a CO₂/H₂(D₂) feed (1:3) at 30 bar and 523 K.

Catalyst	MeOH (H ₂)	CO (H ₂)	MeOH (D ₂)	CO (D ₂)	KIE MeOH	KIE CO
10 wt % Cu/SiO ₂	2.1	8.4	2.7	8.6	0.75	0.98
80 mol% Cu/MgO	47.1	147.5	74.9	158.3	0.63	0.93
10 wt% Pd/SiO ₂	0.3	5.2	0.5	5.0	0.57	1.04

The temperature variation study of Fig. 1 was repeated with a CO:H₂/D₂ feed (1:3) as shown in Fig. 3. The KIE of methanol formation at 503 K is 0.90 and thus, similar to RWGS, much less significant compared to methanol formation from CO₂. This result was confirmed by a feed gas variation study performed at 413 K, and thus far away from the equilibrium (Fig. S7). Comparison of the methanol formation rates in H₂ and D₂ as a function of CO₂ content showed absence of a significant KIE for a pure CO feed (KIE > 0.95) and stronger inverse KIE values between 0.75 and 0.85 as the relative CO₂ content was increased toward 100 %. The methanol formation rates showed a linear dependence on the CO₂ content as expected for direct CO₂ hydrogenation at differential reaction conditions.

The absence of a substantial KIE for RWGS and CO hydrogenation and the presence of as strong inverse KIE for methanol formation from CO₂ rules out that the CO₂-to-methanol reaction proceeds through a consecutive mechanism of RWGS followed by CO hydrogenation on Cu/ZnO/Al₂O₃. In addition, the differences in total hydrogenation rates of CO and CO₂ (13.6 and 168.0 $\mu\text{mol min}^{-1} \text{g}_{\text{cat}}^{-1}$ at 483 K in hydrogen from CO and CO₂, respectively) also suggests that CO₂ is the direct source of methanol on Cu-based in agreement with recent ¹³C- [25] and the earlier ¹⁴C- [38] tracer studies of methanol synthesis near industrial conditions.

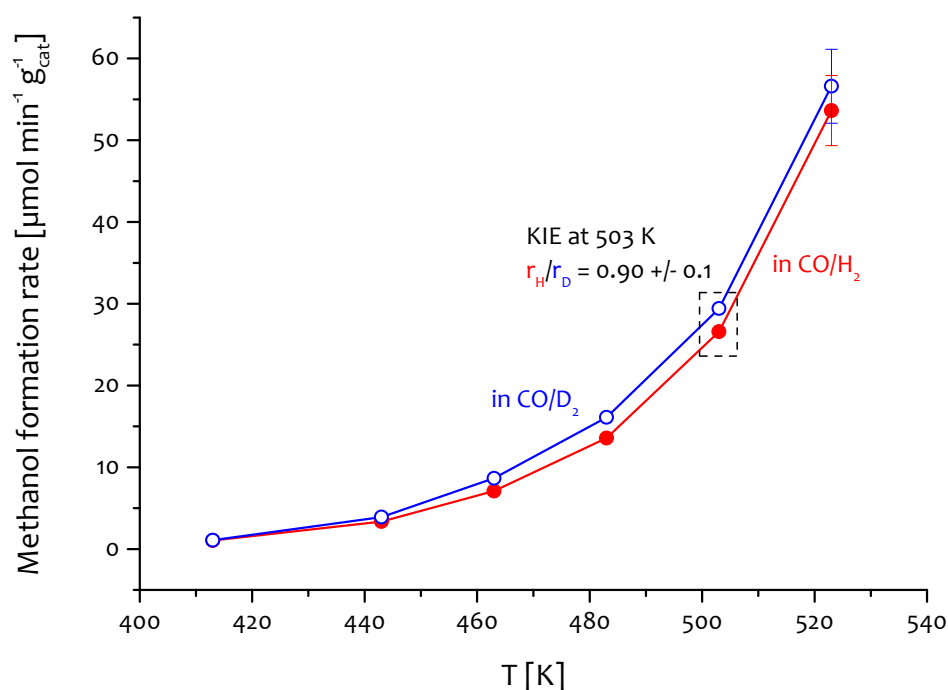


Fig. 3: Methanol formation rates in a CO/H₂ (red, filled circles) and CO/D₂ (blue, open circles) feed (1:3) at 30 bar and a flow of 100 ml/min. The KIE at 503 K is indicated. The error was assumed to be 8% at 523 K.

Inverse secondary KIEs of H/D substitution have been previously reported for FTS due to H-assisted C-O cleavage [21, 39], but also for other organic reactions if the RDS includes the transition of a sp²- to an sp³-hybridized carbon atom [16, 40]. It is noted that such a transition is present in the hydrogenation of formate (HCOO* + H ⇌ H₂COO*) or formic acid (HCOOH + H* ⇌ H₂COOH*) and not in possible subsequent steps like dioxomethylene conversion to methoxy (H₂COO* + H* ⇌ H₃CO* + O*). This suggests one of the former steps to be the RDS of methanol synthesis [6, 13, 32]. An analogous effect was reported by Gnanamiani et al. for the hydrogenation of butanoic acid and butyraldehyde to butanol on Co/Al₂O₃ [40]. The authors observed an inverse KIE (R_H/R_D = 0.54) for the hydrogenation of the acid group (CO₂ analogue), while the rate of aldehyde hydrogenation (CO analogue) was not affected by H/D substitution.

Altogether, the present results provide support for a methanol synthesis mechanism that was proposed already in the 1990s [32, 33] with formate being the relevant intermediate. The experimental data presented here for CO₂ hydrogenation are consistent with the recently published model of methanol synthesis from CO/CO₂/H₂ that includes the synergetic effect of Zn [25]. According to this picture, RWGS and methanol synthesis follow parallel mechanisms and the higher sensitivity of the latter toward product inhibition by water furthermore suggests that different active surface sites are responsible for each reaction. This is consistent with the observation that Cs-doping of Cu catalysts can promote WGS [41] and at the same time poison methanol formation in favor of RWGS [42], thus allowing an independent tuning of both reactions. This observation holds promises with regard to the development of an effective CO₂ hydrogenation catalyst based on Cu/ZnO/Al₂O₃, on which RWGS is an undesired side reaction that should be suppressed.

Substantial WGS activity is desired in industrial methanol synthesis and required to moderate product inhibition by water scavenge, which provides CO₂ as new precursor molecules for methanol and cleans the surface from chemisorbed water [43]. This situation is markedly different for CO₂/H₂ feeds envisioned for carbon capture and utilization (CCU) applications, where the shift chemistry is harmful for the methanol yield due to RWGS. The industrial Cu/ZnO/Al₂O₃ catalyst due to its shift activity is thus *per se* not an optimal CO₂ hydrogenation catalyst, although CO₂ hydrogenation is the relevant step also in the industrial process. However, the industrial catalyst is a promising starting point that requires modification to suppress RWGS and improve its sensitivity toward product inhibition.

There is ample evidence that an effective methanol synthesis in industrial catalysts is due to the presence of Zn [37, 44, 45], while its effect on RWGS is less important [37, 44]. An optimized CO₂ hydrogenation catalyst might thus require an increase in the Zn-promoted Cu sites active in methanol formation at the expense of the unpromoted clean Cu sites that likely form CO [30, 46]. However, it seems that the former have unique and very special structural properties as represented for instance by the fully Zn covered surface step, which can be used as model for the active site capable of explaining the “Cu-Zn synergy” [14, 25]. Such synergistic sites are likely present only as a minority of total surface sites in real catalysts. Creating them in excess of clean or partially Zn-covered Cu steps will be difficult and finding a selective poison for only the latter sites is a major challenge for catalyst design. A promising way to modify state-of-the-art methanol synthesis catalyst appears to be an optimization of Zn-promotion through the dynamic SMSI [14, 37, 47-51] to favor the Zn-decoration of the Cu surface and thus the formation of methanol synthesis sites in highest possible amounts. Recent progress in catalyst synthesis suggests that variations in the industrial synthesis recipe [37], optimized promotion by adding refractory oxides to Cu/ZnO [12, 15, 26, 45, 52] or completely new classes of catalysts [53] can be effective in this respect. However, the exact mechanisms, the structural details and the stability of the relevant SMSI chemistry in real catalysts remain an open question for the truly rational design of these types of synergetic catalysts. Alternatively, reaction engineering approaches can help to increase the overall selectivity toward methanol [10, 54].

Conclusion

The H/D substitution experiments on an industrial-like Cu/ZnO/Al₂O₃ catalyst have shown that methanol synthesis and RWGS display a strong thermodynamic isotope effect. In the kinetic regime of CO₂ hydrogenation, an inverse kinetic isotope effect of H/D substitution was observed, which is much stronger for methanol than for CO formation suggesting that the two reactions do not share a common intermediate in the RDS. These observations were also made on other catalysts like Cu/MgO, Cu/SiO₂ and Pd/SiO₂. In contrast to the CO₂ hydrogenation, the CO hydrogenation on Cu/ZnO/Al₂O₃ did not show a strong inverse kinetic isotope effect indicating that methanol formation from CO₂ does not proceed via consecutive RWGS and CO hydrogenation steps. By the analogy to acid and aldehyde hydrogenation, the inverse effect is consistent with formate hydrogenation being the RDS of methanol synthesis from CO₂. The independent pathways of RWGS and methanol synthesis on Cu/ZnO/Al₂O₃ make this catalyst a promising candidate for modifications to increase the methanol yield in a CO₂ hydrogenation application. Such modifications should improve the suppression of RWGS-active sites and the robustness against product inhibition on the methanol synthesis sites.

Acknowledgements

We thank the staff at the Department of Inorganic Chemistry of the FHI for the support of the experiments. Stefan Zander is acknowledged for synthesizing the Cu/MgO catalyst. E.L.K., R.S. and M.B. acknowledge the Deutsche Forschungsgemeinschaft (DFG, BE4767/1-1), who funded a part of this work. F.S. and F.A.P. gratefully acknowledge the support from the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences to the SUNCAT Center for Interface Science and Catalysis.

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Supporting information

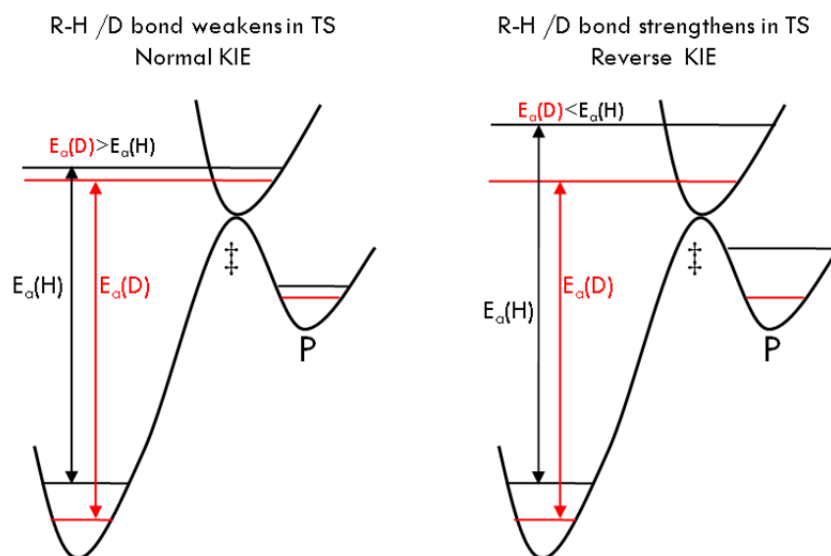


Fig. S1: Schematic representation of the normal and inverse secondary KIE.

TIE measurements:

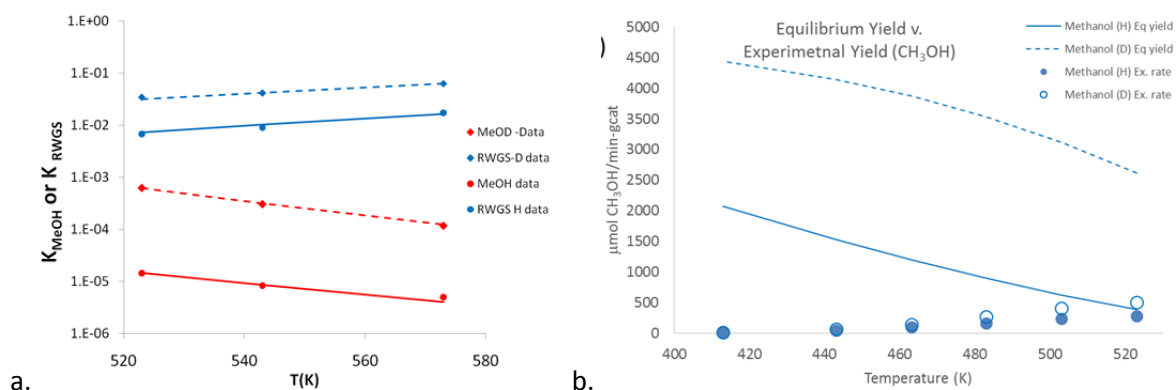


Fig. S2: Temperature-dependence of the equilibrium constants K for $\text{CO}_2 + 3 \text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O}$ (K_{MeOH}) and $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$ (K_{RWGS}) measured at 30 bar in a conventional syngas mixture for industrial methanol synthesis. Data obtained in the deuterated feed are shown as diamonds with broken lines (a). Calculated Equilibrium yields of methanol and the rate data measured in the kinetic regime as shown in Fig. 1a of the main article.

In the TIE study, the synthesis gas feed rate was varied between 100 and 50 ml/min at each temperature. The lack of significant change in composition at the reactor outlet during this flow variation confirmed that the reaction was in equilibrium. The extent of the thermodynamic effect is governed by the differences in zero point energies between H-H/D-D bonds in the reactants and the O-H/D and C-H/D bonds in the products for deuterated vs. hydrogenated species. From the slopes of the linearized temperature dependences of the equilibrium constants shown in Figure S2, we have calculated that methanol synthesis and RWGS reactions become 30.4 and 17.4 kJ/mol respectively more exothermic upon H/D substitution. The increased exothermicity results from the fact that more bonds to hydrogen or deuterium are formed in the products than are broken in the reactants, making the net zero-point energy difference higher on the products side. For methanol synthesis three net bonds to hydrogen are formed, whereas only one net bond is formed in the case of RWGS.

Tab. S1 reports the differences in methanol yield between hydrogen- and deuterium-containing syngas.

Tab.S1: Measured values for the equilibrium methanol yield in presence of hydrogen or deuterium in the syngas feed at 30 bar.

Temp (K)	H ₂	D ₂
523	18.1%	52.7%
543	10.4%	40.6%
573	4.0%	20.4%

KIEs during reaction parameter variation:

During the measurements in the kinetic regime, the closest approach to equilibrium was attained at the two higher temperature measurements during the CO₂ hydrogenation study using H₂. Figure S2b shows the equilibrium yields for both methanol synthesis and RWGS alongside the measured rates. To obtain an estimate of the equilibrium yields in the case of D₂, $\Delta H(\text{CH}_3\text{OH})$ was taken to be -82 kJ/mol and constant with reaction temperature, similarly $\Delta H(\text{CO})$ was taken to be 30.05 kJ/mol. The equilibrium isotope effect magnitudes differ vastly from those observed in the kinetic regime. This is also confirmed a more accurate representation of the proximity of both reactions to equilibrium obtained from the ratio of the reaction quotients to the equilibrium constants (Q/K). These ratios are lower than 10% for all temperatures below 503 K in the case of H₂ and D₂. Data points deemed to be too close to equilibrium at T = 523 in H₂ K (Q/K(CH₃OH) = 49% and Q/K(CO) = 61%) and at T = 503 K in H₂ (Q/K(CH₃OH) = 12 % and Q/K(CO) = 20 %) were not included in the determination of the activation energy (see below). The Q/K value in D₂ were orders of magnitude lower than those in H₂, and not as affected by equilibrium. Due to lower yields and a significantly higher equilibrium constant for CO hydrogenation at comparable conditions, the CO hydrogenation rates that appear in this work can also be considered free of thermodynamic artifacts. Figure S3 shows the evolution of the formation rates and the KIE with parameter variation in the CO₂/H₂-D₂ feeds.

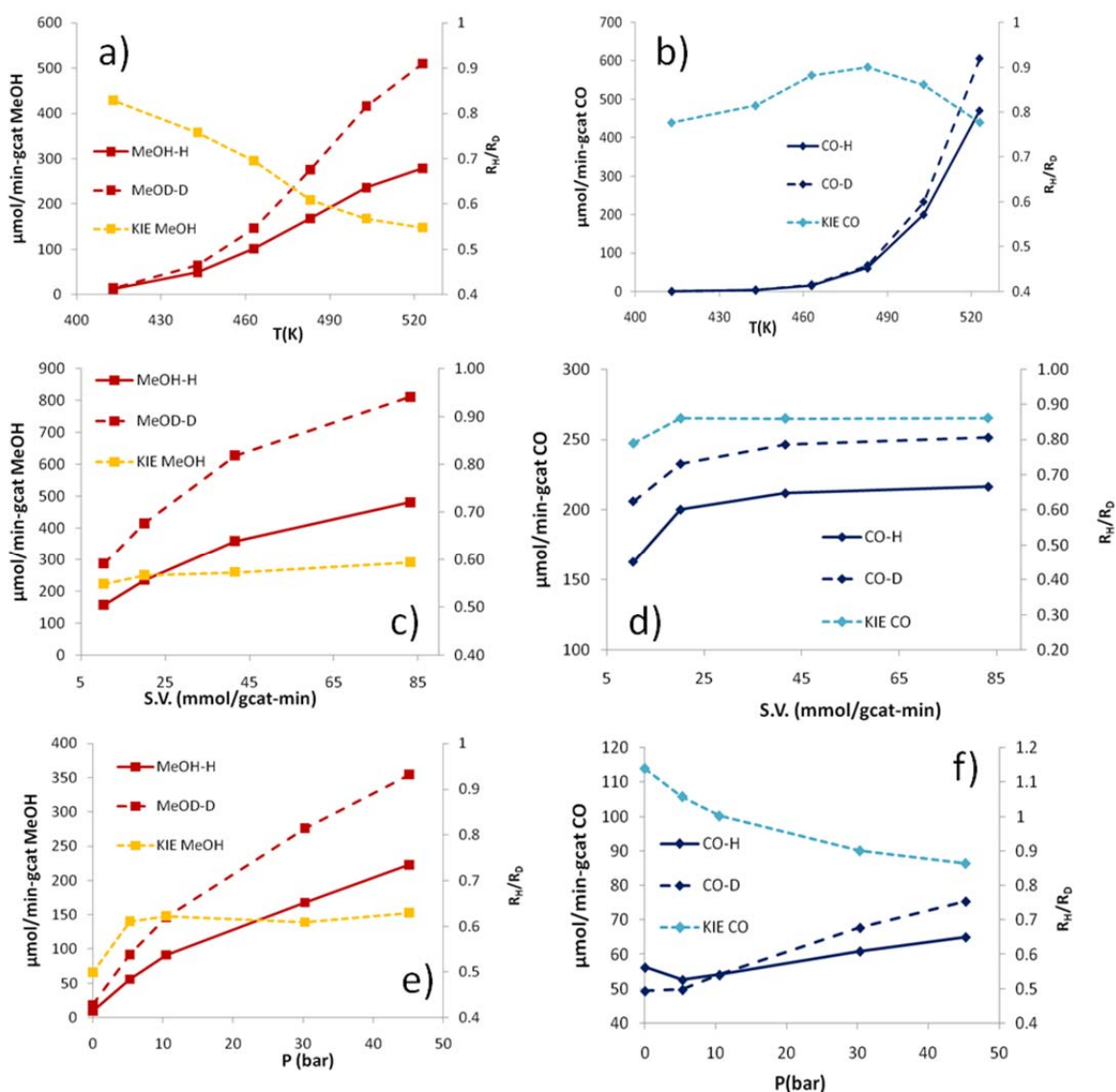


Fig. S3: Formation rates of methanol (dark red) and CO (dark blue) and their ratio R_H/R_D (yellow and light blue, respectively) on a Cu/ZnO/Al₂O₃ catalyst in a 1:3 CO₂/H₂ (full lines) and CO₂/D₂ (broken lines) feed, respectively, as a function of temperature (a,b; at 30 bar and 100 ml/min), space velocity (c,d; at 30 bar and 503 K) and pressure (e,f; at 100 ml/min and 493 K).

A monotonous increase in the extent of inverse KIE with temperature was observed for methanol formation (Fig. S3a). No such clear trend and a weaker inverse KIE is present in the case of RWGS (Fig. S3b). The KIEs for methanol synthesis and the RWGS reaction as a function of space velocity remain rather constant, while it is stronger in the former reaction (approx. 0.6) compared to the latter reaction (approx. 0.9), where it is much closer to unity for almost the entire range.

The monotonic increase in the rate of methanol synthesis from CO₂ with increasing space velocity (Fig. S3c) was also observed by Sahibzada et al. [S1] and attributed, in the absence of external mass transfer limitations, to product inhibition by water. We have ruled out external mass transfer limitations by obtaining equal reaction rates from measurements at the same space velocity, conducted with different amounts of catalyst. Furthermore, a change in CO₂ conversion from 13.7% to 3.7% when measured with hydrogen over the entire space velocity range corresponds to an almost quadruple decrease in the outlet concentrations of water and methanol when comparing

rates measured at the lowest and the highest space velocity respectively. To that end, the product inhibition is less significant for CO formation and an effect on the rates is only observed at very low flows (Fig. 3d).

Variation of pressure (Fig. S3e,f) again revealed a stable inverse KIE for methanol synthesis ($R_H/R_D=0.6$) with an exception for the measurement at atmospheric pressure ($r_H/r_D=0.5$, Fig. 2e). At these conditions the methanol production is approaching equilibrium and the isotope effect is likely controlled by thermodynamics. In case of RWGS, the KIE decreases with increasing pressure, but is always found in a regime near unity (Fig. 3f).

Temperature variation at 1 bar (Fig. S4) showed a further decrease in the isotope effect of methanol formation with temperature while the formation rates went through a maximum indicating that this decrease corresponds to a thermodynamic effect (Fig. S4a). The temperature variation at 1 bar showed that KIE in RWGS at atmospheric pressure is negligible (Fig. S4b).

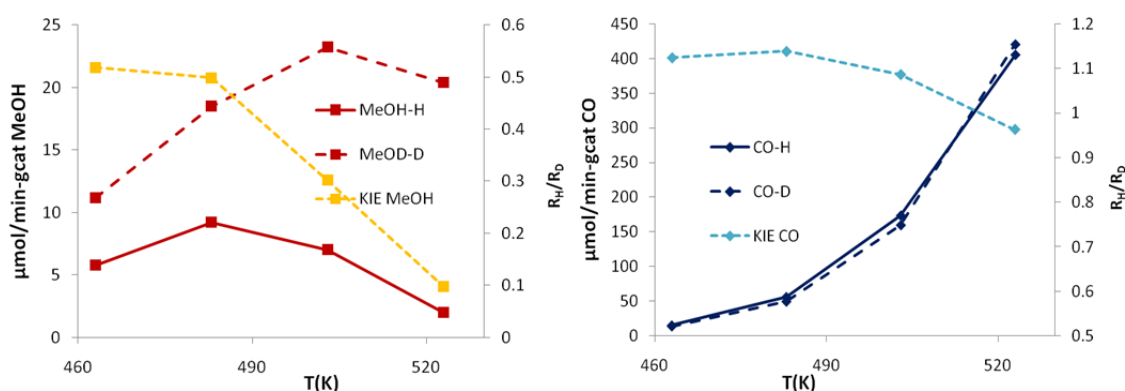


Fig. S4: Methanol formation rates measured at 1 bar. The maximum in the rates indicate the approach to equilibrium and that the isotope effect is rather related to thermodynamic than to kinetic effects under these conditions (30 bar, 100 ml/min, 200 mg catalyst). CO formation rates due to RWGS measured at 1 bar.

From the temperature variation data shown in Figure 1 and S3a,b, the apparent activation energies (E_A) were determined (Fig. S5). A minor effect of H/D-exchange on the E_A of methanol synthesis was observed. $E_A = 70.3$ kJ/mol were found for CO₂ hydrogenation with D₂, while $E_A = 63.7$ kJ/mol – slightly lower than reported for polycrystalline Cu (77 kJ/mol [S2]) – was observed for H₂. No significant change in the activation energy was detected for RWGS ($E_A = 116.7$ kJ/mol in H₂ and $E_A = 115.9$ kJ/mol in D₂), which is again lower than reported for a polycrystalline Cu model catalyst (135 kJ/mol [S2]).

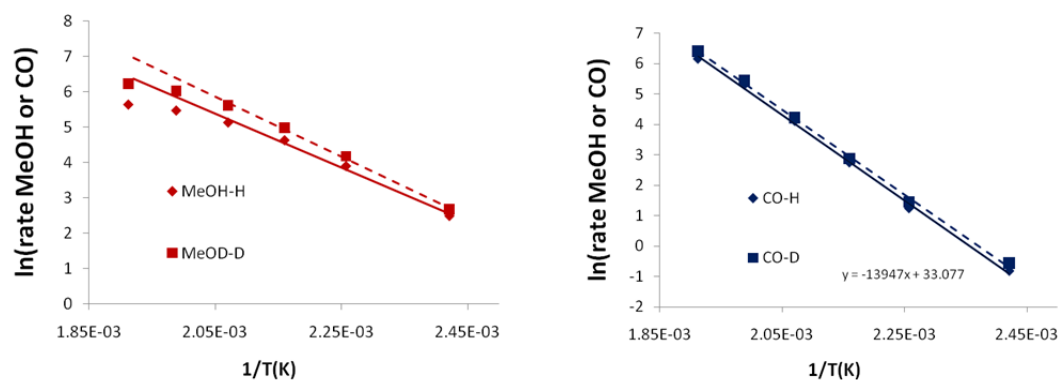


Fig S5: The Arrhenius plot for methanol synthesis revealed that the reaction showed a significant approach to equilibrium for the two highest temperatures. Thus, these data points were excluded from the linear regression fitting.

In a feed gas composition variation study at the lowest temperature employed in this work, at 413 K, the effect of the CO:CO₂ ratio was investigated. The low temperature assures that the methanol synthesis reaction far from its equilibrium. The tests were done at a flow of 100 ml/min and the CO_x:H₂/D₂ composition was 1:3 (200 mg catalyst at 30 bar). The quasi-differential regime of this measurement is confirmed by the linear dependence of the methanol formation on the CO₂ content [S1]. In agreement with Fig. 3, no significant KIE was observed for CO hydrogenation, while the presence of CO₂ led to occurrence of a KIE as discussed in the main article.

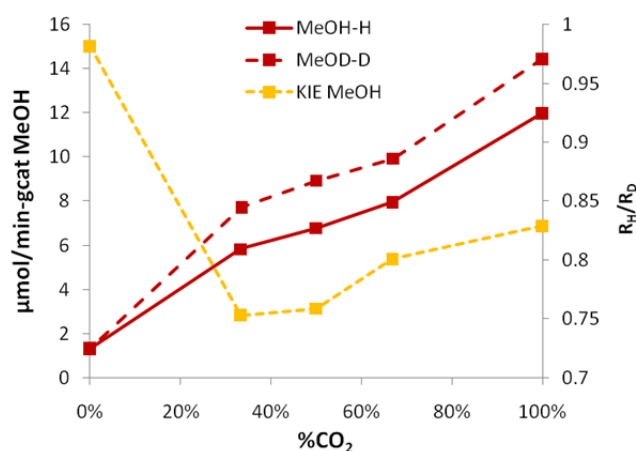


Fig. S6: Dependence of the KIE and the methanol formation rates on the feed gas composition.

Tab. S2: Change in ZPE upon deuterium substitution.^[a]

Intermediate	$\Delta ZPE(H)-ZPE(D)$	$\Delta S(H)-S(D)$	$\Delta T^{500K} \Delta S(H)-S(D)$	$\Delta ZPE-\Delta T \Delta S$
H ₂ (g)	0.057	0.0000000	0.000	0.057
MeOH(g)	0.366	-0.0000602	-0.030	0.397
H ₂ O(g)	0.162	-0.0000024	-0.001	0.163
H*	0.046	-0.0000038	-0.019	0.065
HCOO*	0.086	-0.0000250	-0.013	0.099
HCOOH*	0.172	-0.0000521	-0.026	0.198
H ₂ COOH*	0.273	-0.0000694	-0.035	0.308
H ₂ CO*	0.163	-0.0000458	-0.023	0.186
OH*	0.084	-0.0000398	-0.020	0.104
OCH ₃ *	0.260	-0.0000761	-0.038	0.298
HCO*	0.076	-0.0000315	-0.016	0.092

Transition-state	$\Delta ZPE(H)-ZPE(D)$	$\Delta S(H)-S(D)$	$\Delta T^{500K} \Delta S(H)-S(D)$	$\Delta ZPE-\Delta T \Delta S$
H-H	0.076	-0.0000759	-0.038	0.114
H-COO	0.041	-0.0000373	-0.019	0.060
HCOO-H	0.108	-0.0000468	-0.023	0.131
H-HCOOH	0.212	-0.0000846	-0.042	0.254
H ₂ CO-OH	0.247	-0.0000857	-0.043	0.290
H-H ₂ CO	0.206	-0.0000760	-0.038	0.244
H-OCH ₃	0.285	-0.0001096	-0.055	0.340
H-OH	0.103	-0.0000770	-0.039	0.142
H-CO	0.037	-0.0000310	-0.016	0.053
H-HCO	0.121	-0.0000480	-0.024	0.145

[a] All energies are in eV

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