



Isotopic study of the rates of hydrogen provision vs. methanol synthesis from CO₂ over Cu–Ga–Zr catalysts



Esteban L. Fornero, Adrian L. Bonivardi, Miguel A. Baltanás*

INTEC (Instituto de Desarrollo Tecnológico para la Industria Química – UNL/CONICET), Güemes 3450, S3000GLN Santa Fe, Argentina

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ABSTRACT

Cu/ZrO₂ and Ga₂O₃-promoted Cu/ZrO₂, with the same copper loading (2.6 wt.%), were evaluated in a Carberry-type batch-operated microreactor for methanol synthesis using a H₂/CO₂/He mixture (75/22/3 v/v) at 1.6 MPa and 498 K. The gallia-promoted catalyst was 5-fold more active to methanol production (per catalyst specific surface) than Cu/ZrO₂. In addition, after the incorporation of Ga₂O₃ the selectivity to the alcohol was enhanced by a factor of three.

To discern whether different degrees of hydrogen provision were responsible for the dissimilar performances observed, thus affecting the overall reaction rate to methanol ($R_{\text{CH}_3\text{OH}}$), the ability to activate H₂ of the catalysts was assessed – in the same microreactor – by a combination of H₂/D₂ isotopic equilibration (H₂/D₂/Ar = 37.5/37.5/25 v/v) and H/D isotopic exchange (D₂/Ar = 10/90 v/v) reactions at 0.1 MPa, between 353 and 393 K.

The equilibration rate (R_{equil}) was far higher than $R_{\text{CH}_3\text{OH}}$ on both, Cu/ZrO₂ and Ga₂O₃-promoted Cu/ZrO₂. In agreement with the property of gallia to dissociate H₂, Ga₂O₃ increased further R_{equil} in the ternary catalyst. Vis-à-vis, the isotopic-exchange reaction rates (R_{exchg}) were considerably lower than the R_{equil} for each catalyst, more so for the gallium containing one. However, the extrapolation of those R_{exchg} values to the temperature of methanol synthesis gave always much higher rates than $R_{\text{CH}_3\text{OH}}$, thus allowing to conclude that the supply of ‘active’ hydrogen is fully secured on these copper-supported (gallium-promoted) catalysts.

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1. Introduction

Hydrogen migration on the surface of bifunctional heterogeneous catalysts may involve one or more steps, such as surface diffusion and/or the transfer across a phase boundary usually known as ‘spillover’. Sometimes, in several commercially important catalytic processes such as the water gas shift reaction, Fischer–Tropsch synthesis or numerous hydrogenation reactions, these steps have been found rate determining [1–7].

In the synthesis of methanol, the catalyst must be able to dissociate molecular hydrogen and – in the case of metal catalysts supported onto oxides – the dissociated hydrogen (H) must be transferred to the carbonaceous species chemisorbed onto the support to carry out the hydrogenation. With commercial Cu/ZnO/Al₂O₃ methanol synthesis catalysts, it was reported that hydrogen spillover can proceed from Cu to ZnO or vice versa depending on whether CO or CO₂ is the carbon source, the specific catalyst used and/or experimental conditions employed [8,9].

In novel supported catalysts it is generally postulated that hydrogen migrates from the metal surface to the oxides. Such is the case of Cu/ZrO₂/SiO₂, for which all the carbonaceous species are associated with the ZrO₂ surface: CO₂ adsorbs as carbonate and/or bicarbonate, which then reacts with atomic hydrogen to give formate species and – later – methoxide species, all of them chemisorbed on the zirconia. The presence of Cu greatly accelerates these transformations, as well as the reductive elimination (or hydrogenation) of methoxide species to methanol [10]. Likewise, on zirconia-promoted Cu–ZnO catalysts, Arena et al. substantiated the occurrence of a dual-site (bifunctional) mechanism in the methanol synthesis via CO₂ hydrogenation [11]. On Ga₂O₃–Pd/SiO₂ catalysts using H₂/CO₂ mixtures, carbon dioxide adsorbs onto Ga₂O₃ and then undergoes stepwise hydrogenation to formate, dioxymethylene, methoxide and methanol, with atomic hydrogen supplied by spillover from bimetallic PdGa particles that are generated in situ [12–14]. Recent studies indicate that reverse spillover can also take place on these catalysts [15].

As per Martin and Duprez’s suggestion [16], detailed analyses regarding the “availability of hydrogen atoms” on the surface of a supported metal catalyst can be achieved by means of

* Corresponding author. Fax: +54 (342) 455 0944.

E-mail address: tderliq@santafe-conicet.gov.ar (M.A. Baltanás).

equilibration and isotopic exchange reactions (Fig. 1 a and b, resp.) between hydrogen and deuterium. These reactions allow the identification of several steps of the process, namely: (1) D_2 dissociation on the metal, (2) D transfer from one surface to the other (i.e., spillover [4]) and (3) diffusion onto the support. These species can next undergo the following process: (4) exchange, (5) desorption from the support, or migration (-4 , -3 , -2) and (-1) desorption from the metal. Although controversy still remains about the actual existence of spillover in non-reducible oxides [7,17], and other mechanisms for the exchange reaction have been put forward [17], the joint analysis of hydrogen isotopic equilibration and exchange in supported metal catalysts is a revealing indicator of the availability of activated hydrogen on the entire surface of these materials [18].

Isotopic exchange studies on monoclinic ZrO_2 (exposed to O_2 at 804 K and then evacuated at 773 K) indicated that deuterium adsorbs dissociatively, and then ‘the D atoms migrate’ onto the hydroxylated oxide surface and are exchanged, being migration the rate determining step (*rds*) of the process at 373–473 K [19].

With regard to composite materials consisting of copper and zirconia, Jung and Bell [10] analyzed the dynamics of H/D exchange of hydroxyl groups in the Cu/ZrO_2 catalyst (ZrO_2 : 20 m^2/g ; 5.7 Cu wt.%) and in the pure support by means of in situ infrared spectroscopy. They found that the *rds* was the exchange on the support surface and concluded that on this catalyst the rate of hydrogen spillover from Cu was not a limiting step in the methanol synthesis [10]. Later on Bell analyzed, on the basis of former work by his team, the performance of zirconia-supported copper (5–15 wt.% loading) using supports with different morphologies (viz., monoclinic or tetragonal) and specific surface areas. He observed that, even though some catalysts had up to 9-fold higher CO_2 adsorption capacity the reaction rate did not increase in the same proportion, suggesting then that H spillover from the disperse Cu was insufficient to raise the synthesis rate accordingly [20].

This work analyzes the hydrogen-supplying ability of two catalysts: Cu/ZrO_2 and $Ga_2O_3/Cu/ZrO_2$ prepared with low Cu loading and low metal dispersion which, even then, showed good performance for methanol synthesis from binary and ternary

$H_2/CO_2/CO$ reaction mixtures at 3 MPa, 523 K. In particular, the gallia-promoted catalyst exhibited better stability and selectivity to methanol [21]. Their ability to dissociate H_2 and the availability of the activated hydrogen on the support of both catalysts are evaluated by means of hydrogen isotopic equilibration and exchange. The main goal of this work was to analyze whether the H/D reaction is affected by the presence of gallia on the ternary catalyst and to determine, for both materials, whether the copper loading was enough so as to guarantee sufficient provision of activated hydrogen for the methanol synthesis. If so, further effort should rather focus on the remaining reaction steps of the synthesis so as to unravel the underlying causes for the observed activity, and selectivity differences.

2. Experimental

Zirconia was synthesized by hydrolysis of Zr(IV) *n*-propoxide in 1-propanol (70 wt.%) at ambient temperature, using a sol-gel technique and deliberately avoiding precursor salts that might include any other cation. Inert Nalgene® vessels were employed instead of glass. After drying and calcining (383 and 673 K, respectively), the BET specific surface area of ZrO_2 was 35 m^2/g .

Copper was incorporated to the zirconia by ion exchange (IE), using high purity copper nitrate (99% Cu) at pH = 11. The support was put in contact with an aqueous solution of ammonia complexes of copper (mostly $[Cu(NH_3)_4]^{2+}$ at this pH) for 2 h, under stirring, using a liquid to solid ratio of 200 ml/g. The suspension was then filtered and washed (two times, 15 min/ea.) with $NH_4OH(aq.)$, also at pH 11. The IE material was dried (323 K, 18 h, and then 383 K, 4 h) and calcined (673 K, 2 h). The metal loading in the binary Cu/ZrO_2 catalyst was 2.6 wt.% and the specific surface area was 29 m^2/g . The metal dispersion of the reduced catalyst, measured by reactive frontal chromatography [22], was 5.4%.

Gallium was added to an aliquot of this material by incipient wetness (IW) impregnation, using an aqueous solution of $Ga(NO_3)_3 \cdot 8H_2O$ (99.999% Ga), so as to obtain a Ga/Cu atomic ratio = 1/1 (Ga_2O_3 loading = 3.8 wt.%). The specific surface area of the dried (383 K, 4 h) and calcined (673 K, 2 h) ternary catalyst was 9 m^2/g with a metal dispersion (in the reduced catalyst) of 2%. No incorporation of Ga^{3+} ions into the structural network of the zirconia was observed by XRD [21]. A dedicated characterization of these Cu–Ga–Zr catalysts by TPR and XPS aimed to analyzing the copper–gallia interaction was recently presented by some of us [23].

For comparison purposes gallium oxide ($S_{BET} = 90 m^2/g$) was prepared as well, by precipitating gallium nitrate with $NH_4OH(aq.)$ in ethanol. Likewise, a well-characterized sample of Ga_2O_3/ZrO_2 , kindly provided by P. Sanguineti (6.3 wt.% Ga_2O_3 , $\theta_{Ga/Zr} = 0.3$, $S_{BET} = 70 m^2/g$), prepared by incipient wetness impregnation of gallium nitrate on zirconia, was employed. Further details on the preparation methods of these supports can be found elsewhere [21,24,25].

The dried and calcined materials were crushed and sieved to +60/–80 Tyler mesh particles. Afterward, each of them was pelletized into cylindrical wafers of approx. 0.25 mm thickness and 1 cm diameter. The pellets were gently crushed and sieved to obtain coarse grains (+20/–30 Tyler mesh, 0.5–0.8 mm), which were then stored to conduct the different reactivity studies.

All reactivity studies were carried out using a novel catalytic reaction device featuring a Carberry-type, well-mixed microreactor built inside a medium pressure leak valve, in which carefully controlled temperature (± 0.2 K) and pressure (up to 3 MPa) conditions could be achieved [26]. The reaction system was operated in the batch (transient) mode. Continuous sampling of the reacting mixture allowed instantaneous evaluation of the gas phase

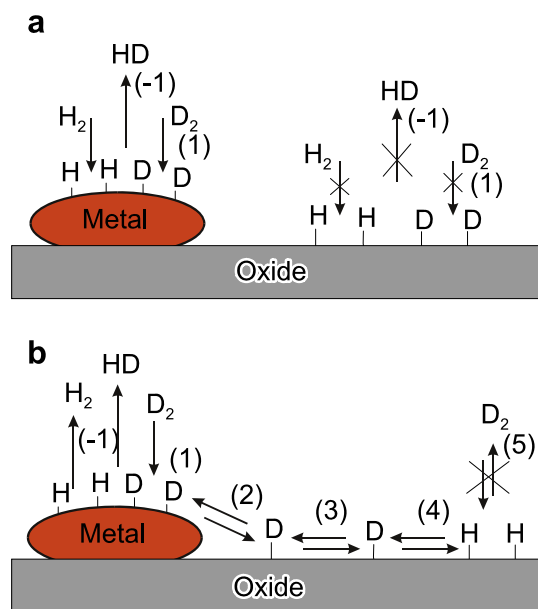


Fig. 1. Schematic representation of hydrogen isotopic equilibration (a) and exchange (b) for a supported metal catalyst whenever the support is inactive for dissociating molecular hydrogen (adapted from Martin and Duprez [16], see text).

composition. Due to the continuous gas sampling to the mass spectrometer via the leak valve there was always a small, intrinsic pressure drop in the microreactor ($\Delta P = 0.1$ MPa/h).

Two identical, small volume cylindrical compartments (~ 37 cm³ ea.) made of 316 stainless steel, enclosed in an thermostated oven and interconnected by a high rating (high purity, high pressure-high vacuum, high temperature) bellows valve, constitute the core of the reaction device. For the batch operating mode the first compartment acts as a premixer/homogenizer of the reaction mixtures. The composition of said mixtures could be adjusted by means of a dosing manifold, as detailed and exemplified elsewhere [26].

Each compartment accommodates a small, removable, magnetically stirred spinning basket that can be filled with the crushed and sieved catalysts. The complete device was gold-plated to ensure inertness. Its performance was validated by comparing methanol synthesis reaction rates obtained under transient conditions using said microreactor with steady-state kinetic rate expressions obtained with a conventional plug-flow catalytic microreactor employing the same Pd–GaO_x/SiO₂ catalyst, using H₂/CO₂ mixtures, and an excellent agreement was found [26].

2.1. Catalytic activity measurements (methanol synthesis)

Aliquots of the Cu/ZrO₂ and Ga₂O₃/Cu/ZrO₂ catalysts (approx. 1 g/ea.) were loaded into the microreactor baskets and then reduced under H₂ flow (50 cm³/min; heating ramp = 2 K/min) from room temperature to 523 K, maintaining this last temperature for 2 h. Afterward, the reactor was cooled down to the chosen reaction temperature (498 K, the maximum admissible to ensure long-term tightness of the device), under H₂ flow. The reactor was next evacuated (600 Pa) for 20 min. The catalyst performance was evaluated at 1.6 MPa, in the batch mode, using a certified H₂/CO₂/He = 75/22/3 mixture. The reacting mixture was previously loaded in the premixer at 3.2 MPa and allowed into the reactor by opening the interconnecting valve. Blanks with the empty reactor baskets, and loaded with either zirconia or gallia were also run and under these reaction conditions no catalytic activity was observed.

A 64-channel mass spectrometer (Residual gas analyzer Balzers QMS 421, 0–300 AMU range), with a QMH 400–5 quadrupole and SEM and Faraday cup detectors was employed to measure continuously the gas composition inside the microreactor. Two daily calibrations were performed to correlate the signal intensities in the mass spectrometer with the respective molar fraction of each component inside the microreactor. The first calibration was made using a blank run and to calibrate the signals of the reaction products, a gas mixture with the thermodynamic equilibrium composition at same temperature and pressure was used instead. For the geometric dimension of the catalysts particles and the initial reaction rates that were measured, the system always operated within the kinetic regime [26].

Ultra high purity gases were used (H₂, He and Ar INDURA, grade 5; H₂/CO₂/He, INDURA certified mixture; CO₂ and CO, 99.99% pure). Silica gel was used to eliminate water traces in both H₂ and the H₂/CO₂/He gas mixtures; CO was purified using crushed quartz (–20/+30 Tyler mesh) at 473 K, to decompose metal carbonyls.

2.2. Hydrogen isotopic equilibration and isotopic exchange measurements

Both isotopic studies were performed using the Carberry microreactor in the batch mode, using fresh aliquots (approx. 1 g) of each material.

For these catalysts, isotopic equilibration was reached in less than 30 min within the experimental temperature range that was

chosen (vide infra). As in the catalytic hydrogenation study, the materials were prereduced (523 K) and cooled down to 498 K under H₂ flow. The reactor was next evacuated (600 Pa) for 20 min, pressurized with pure Ar (0.1 MPa) and cooled down further to the first isotopic equilibration temperature chosen (353 K). The reactor was again evacuated (600 Pa) for 20 min, after which the equilibration mixture (H₂/D₂/Ar = 37.5/37.5/25; approx. 0.1 MPa) was introduced. Continuous sampling of the gas composition during 40 min was done, using the inert gas (Ar) as internal standard. A second equilibration experiment was then performed, starting with a new evacuation (600 Pa; 20 min), followed by Ar pressurization (0.1 MPa) and temperature rise, to 393 K. After complete temperature stabilization of the device, the reactor was once more evacuated (600 Pa) and the equilibration mixture was again admitted for another 40 min, with continuous sampling to the mass spectrometer. The deuterium used in these experiments was Scott CP grade, 99.7%, used as received. The calibration of the HD molar fraction was done using as the response factor the signal intensity of the molecule measured for the already equilibrated H₂/D₂ stoichiometric mixture, at 393 K.

Hydrogen isotopic exchange was performed following the same pretreatment protocol used in the equilibration experiments. This time, instead, the first dose of reactants introduced at 353 K was a deuterium/argon mixture (D₂/Ar = 10/90; approx. at 0.1 MPa). The gas composition was continuously sampled for 40 min, after which the reactor was evacuated and the catalyst sample was re-reduced in pure H₂ (50 cm³/min, heating to 498 K @ 2 K/min) to restore all the exchanged H atoms on the material. After a new evacuation (600 Pa; 20 min; 498 K) Ar was added (0.1 MPa) and the device was cooled down to perform hydrogen exchange at another temperature (373 K), using the D₂/Ar = 10/90 mixture. Identical steps were used to perform a third exchange at 393 K.

3. Results and discussion

3.1. Catalytic activity

The catalytic activity of Cu/ZrO₂ and Ga₂O₃/Cu/ZrO₂ for carbon dioxide hydrogenation at 1.6 MPa and 498 K (H₂/CO₂/He = 75/22/3) under differential, transient conditions is shown in Figs. 2 and 3. The complete records for the 2 h reaction time are given in Supplementary Information (Figs. S.1 and S.2). In both cases, a steady increase of the CH₃OH and CO molar fractions with

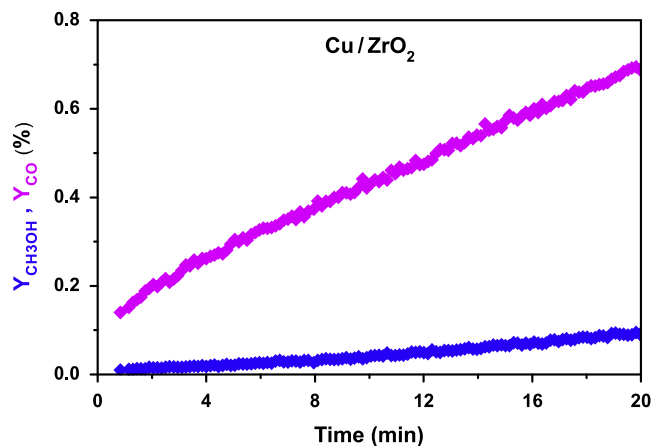


Fig. 2. Time evolution of the percent molar fractions of the reaction products in the methanol synthesis for the Cu/ZrO₂ catalyst (reaction mixture: H₂/CO₂/He = 75/22/3 v/v; 1.6 MPa; 498 K). Blue: CH₃OH. Magenta: CO. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

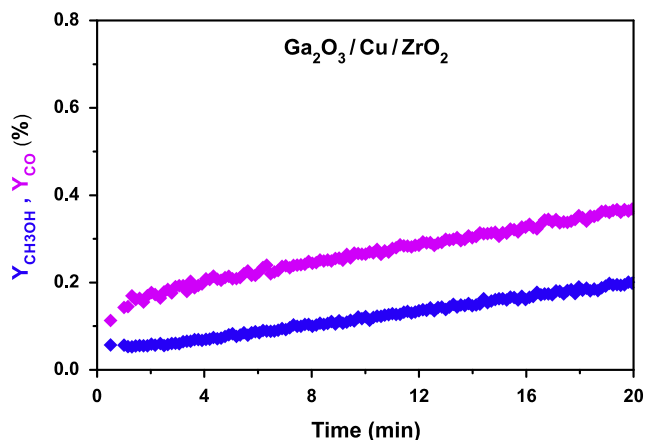
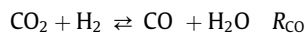
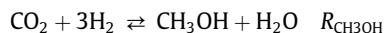


Fig. 3. Time evolution of the percent molar fractions of the reaction products in the methanol synthesis for the $\text{Ga}_2\text{O}_3/\text{Cu}/\text{ZrO}_2$ catalyst (reaction mixture: $\text{H}_2/\text{CO}_2/\text{He} = 75/22/3$ v/v; 1.6 MPa; 498 K). Blue: CH_3OH . Magenta: CO . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

time was observed, both related to the synthesis and the reverse water gas shift (RWGS) reactions:



After 2 h of reaction the molar fractions of dimethyl ether (DME) and methane (CH_4) were less than 0.01% and 0.05%, respectively, indicating no significant impact of either different support acidity or C–O bond scission. Because the synthesis reaction features a change in the number of moles, Δv , the equilibrium molar fractions in the reacting system are pressure-dependent. Therefore, *initial* reaction rates were estimated using only the experimental data taken during the first 20 min, where the equilibrium molar fraction of methanol only decreases by approx. 3% (see Figs. S.1 and S.2 in Supplementary information).

The initial delay and shift of the recorded molar fractions of CH_3OH and CO during the first minute of reaction of the $\text{H}_2/\text{CO}_2/\text{He}$ gas mixture are related to the sudden, profound changes taking place on the supported metal catalyst from the H_2 -reduced state, after which only hydroxyl and dissociated (atomic) hydrogen species are left on the catalyst surface, to a new state in which carbonaceous (intermediate) species and chemisorbed products coexist. The exposure to CO_2 partially oxidizes copper [27,28] while, at the same time, reservoirs of reaction intermediates build-up on the support surface. Said reservoirs of reaction intermediates lead then to the observed reaction products in the gas phase.

Nonetheless, after this brief interval the CH_3OH and CO molar fractions grew linearly and, therefore, the initial reaction rates, $R_{\text{CH}_3\text{OH}}$ and R_{CO} , were calculated for both catalysts using the composition data (viz., the slopes of the straight lines of $Y_{\text{CH}_3\text{OH}}$ and Y_{CO}) taken under differential conditions, between 3 and 20 min (see Appendix A).

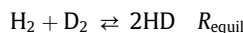
Table 1 shows the initial reaction rate and turnover frequency (TOF) values for Cu/ZrO_2 and $\text{Ga}_2\text{O}_3/\text{Cu}/\text{ZrO}_2$ at 498 K, and each percent selectivity to methanol ($S_{\text{CH}_3\text{OH}}$ %). It is apparent that the gallia-promoted catalyst was far more selective to methanol than Cu/ZrO_2 . Under these experimental conditions the supports were unreactive.

These results are entirely consistent with our previous steady-state, isoconversion data ($X_{\text{CO}_2} = 1.8\%$, $P = 3$ MPa, $T = 523$ K, $\text{H}_2/\text{CO}_2/\text{He} = 75/22/3$) [21]. At this point it is also important to compare the methanol synthesis activity of our Cu/ZrO_2 catalysts

with those of the Bell's group [20], who tested two 5 wt.% Cu/ZrO_2 catalysts (on tetragonal and monoclinic zirconia phases, both with a specific surface of approximately equal to $20 \text{ m}^2/\text{g}$) for CO_2 hydrogenation reaction under steady state conditions at 0.65 MPa and 548 K with a H_2/CO_2 mixture (3/1 M ratio) [20]. Their $\text{TOF}_{\text{CH}_3\text{OH}}$ values were estimated at 1.6 MPa and 498 K (our experimental conditions) using the stoichiometric coefficients of the methanol synthesis as reaction orders and an activation energy equal to 13.1 kcal/mol [29], obtaining $1.4 \times 10^{-4} \text{ s}^{-1}$ and $5.0 \times 10^{-4} \text{ s}^{-1}$ for the tetragonal and monoclinic ZrO_2 supported catalyst, which are in close agreement with our $\text{TOF}_{\text{CH}_3\text{OH}}$ value for the 2.6 wt.% Cu/ZrO_2 catalyst. Nevertheless, it is important to note that TOF values calculated for the catalysts considering the copper as the active and limiting sites become meaningless whenever the copper loading and/or dispersion is enough so as to secure sufficient provision of activated hydrogen for the reactions (see below).

3.2. Hydrogen isotopic equilibration

The reaction of isotopic equilibration of hydrogen, which is pressure-indifferent,



allows for the assessment of the ability to dissociate molecular H_2 and D_2 (Fig. 1a, step 1) as well as of the recombination–desorption of HD (step 2) of a given catalyst. Generally speaking, some metals have better capacity than oxides to dissociate hydrogen. Nonetheless, to fully understand the isotopic exchange of hydrogen on supported metal catalysts it is necessary to establish the reaction conditions under which hydrogen isotopic equilibration proceeds mostly – or entirely – over the metal surface and not on the support (see Fig. 1a, [16]).

As an example, Figs. 4 and 5 show the isotopic equilibration results for Cu/ZrO_2 and $\text{Ga}_2\text{O}_3/\text{Cu}/\text{ZrO}_2$ at 393 K, respectively (the experimental results at 353 K are given in Supplementary Information, Figs. S.3 and S.4). As expected, the molar fractions of H_2 and D_2 (red and green traces, resp.) immediately decreased with reaction time, and the HD molar fraction (black trace) increased, until near equilibrium values were reached: $\text{H}_2/\text{D}_2/\text{HD}/\text{Ar} = 19.5/19.5/36/25$ (these values are very similar at 353 K, [30]).

The experimental value of the H_2 molar fraction that was recorded after reaching thermodynamic equilibration was always slightly higher than the theoretical value (19.5%), due to the presence of atomic hydrogen onto the catalysts surface caused by the reduction pretreatment and to some isotopic exchange that also occurs at these temperatures. As shown below, however, the exchange reaction is far slower. Fig. 4 also shows the Y_{HD} % values measured using the empty reactor and the pure zirconia. The isotopic equilibration rate on this support was much lower than those of the copper-containing catalysts, thus indicating that on Cu/ZrO_2 the equilibration reaction proceeds mostly on the metal surface.

Table 2 details the hydrogen isotopic equilibration rates, R_{equil} , and turnover frequencies per Cu surface atom (whenever appropriate) for the complete set of materials tested (0.1 MPa; 353 and 393 K). Said rates were calculated using the time interval elapsed from the beginning of each experiment until the measured value of Y_{HD} % was 50% of the equilibrium value (approx. 18%), and subtracting the contribution of the empty reactor.

As it can be readily appreciated, R_{equil} and TOF were higher for the ternary catalyst, $\text{Ga}_2\text{O}_3/\text{Cu}/\text{ZrO}_2$. Yet, because the copper loading in both catalysts was the same, and the metal dispersion is higher in the binary catalyst, a question then arose about the possible contribution of the gallia promoter to the isotopic equilibration on the ternary catalyst under our experimental conditions,

Table 1
Initial reaction rates for methanol synthesis ($R_{\text{CH}_3\text{OH}}$) and carbon monoxide generation via the RWGS reaction (R_{CO}), turnover frequencies, and percent selectivity to methanol ($S_{\text{CH}_3\text{OH}}$ %) on Cu/ZrO₂ and Ga₂O₃/Cu/ZrO₂. Experimental conditions: H₂/CO₂/He = 75/22/3 v/v; P = 1.6 MPa; T = 498 K.^a

Catalyst	$R_{\text{CH}_3\text{OH}} \times 10^8$ (mol/g _{cat} s) ^{b,c}	TOF _{CH₃OH} (s ⁻¹) ^d	$R_{\text{CO}} \times 10^8$ (mol/g _{cat} s) ^{c,e}	TOF _{CO} (s ⁻¹) ^d	$S_{\text{CH}_3\text{OH}}$ (%) ^f
Cu/ZrO ₂	1.11 (0.04) ^g	5.0×10^{-4}	6.42 (0.22) ^g	2.9×10^{-3}	15
Ga ₂ O ₃ /Cu/ZrO ₂	1.92 (0.21) ^g	2.4×10^{-3}	2.46 (0.27) ^g	3.1×10^{-3}	44

^a The time course of the reaction is given in Figs. S.1 and S.2 (Supplementary information).

^b $R_{\text{CH}_3\text{OH}}$: $\text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O}$.

^c The coefficient of determination values of each linear regression for ΔY_i % vs. Δt (i = CH₃OH or CO) within the 3–20 min time interval (see Appendix A) was between 0.980 and 0.998.

^d Turnover frequencies expressed as molecules of product (CH₃OH or CO) per copper surface atom per second.

^e R_{CO} : $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$ (RWGS).

^f $S_{\text{CH}_3\text{OH}}$ (%) = $R_{\text{CH}_3\text{OH}} / (R_{\text{CH}_3\text{OH}} + R_{\text{CO}}) \times 100$.

^g Parentheses: Surface-normalized rates, $R \times 10^8$ (mol/m_{cat}² s).

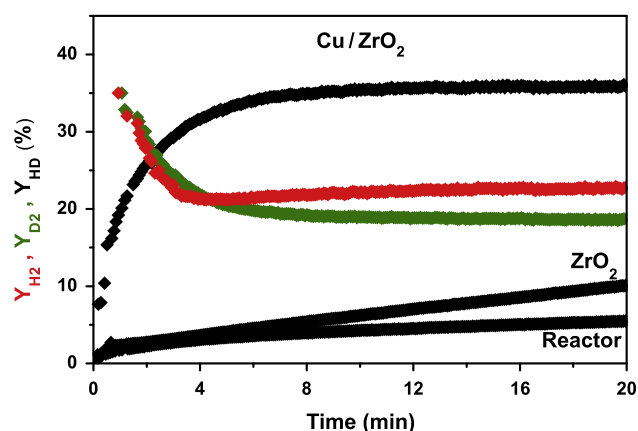


Fig. 4. H₂/D₂ isotopic equilibration on Cu/ZrO₂ (feed mixture: H₂/D₂/Ar = 37.5/37.5/25 v/v) at 393 K and 0.1 MPa. Red: H₂. Green: D₂. Black: HD. The responses for the empty reactor and the pure ZrO₂ support (Y_{HD} % traces) are included as well. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

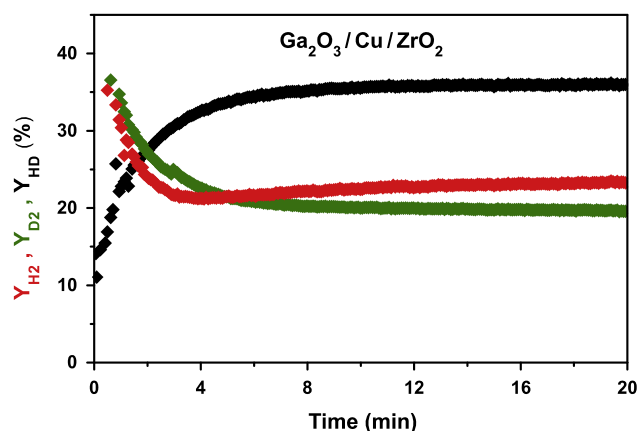


Fig. 5. H₂/D₂ isotopic equilibration on Ga₂O₃/Cu/ZrO₂ (feed mixture: H₂/D₂/Ar = 37.5/37.5/25 v/v) at 393 K and 0.1 MPa. Red: H₂. Green: D₂. Black: HD. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

as it is well known that Ga₂O₃ shows some ability to dissociate hydrogen (and therefore to equilibrate H₂/D₂ mixtures) [24].

At 393 K, R_{equil} for pure gallia was 97×10^{-8} mol HD/s g_{cat} (the experimental details are shown in Supplementary Information, Fig. S.5). Normalized by catalyst mass, this equilibration rate is 20-fold higher than for ZrO₂, and approx. 7-fold higher per catalyst specific surface (1.08×10^{-8} vs. 0.13×10^{-8} mol HD/s m²). Therefore, the presence of Ga₂O₃ ‘patches’ on the surface on the

Table 2
Initial reaction rates and turnover frequencies (TOF) of H₂/D₂ isotopic equilibration, R_{equil} , on the oxides and catalysts. Experimental conditions: H₂/D₂/Ar = 37.5/37.5/25 v/v; P = 0.1 MPa.^a

Catalyst or support	$R_{\text{equil}} \times 10^8$ (mol HD/g _{cat} s) ^b		TOF (s ⁻¹) ^d	
	Temperature (K)		Temperature (K)	
	353	393	353	393
ZrO ₂	–	4.5 (0.13) ^c		
Ga ₂ O ₃	–	97.0 (1.08)		
Ga ₂ O ₃ /ZrO ₂	–	95.0 (1.36)		
Cu/Ga ₂ O ₃	–	228.7 (2.57)		0.23
Cu/ZrO ₂	65.1 (2.24)	367.7 (12.7)	0.03	0.17
Ga ₂ O ₃ /Cu/ZrO ₂	82.5 (9.17)	541.6 (60.2)	0.10	0.68

^a The time course of the reaction is given in the text and in Figs. S.3–S.7 (Supplementary information).

^b R_{equil} : $\text{H}_2 + \text{D}_2 \rightleftharpoons 2\text{HD}$.

^c Parentheses: Surface-normalized rates, $R_{\text{equil}} \times 10^8$ (mol HD/m_{cat}² s).

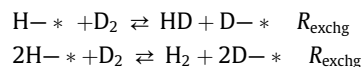
^d Turnover frequencies (TOF) expressed as molecules of HD per copper surface atom per second.

ternary Ga₂O₃/Cu/ZrO₂ catalyst might be thought to be contributing to increase the observed isotopic equilibration rate.

Yet, although the presence of Ga₂O₃ ‘patches’ on the surface on the ternary Ga₂O₃/Cu/ZrO₂ catalyst might certainly contribute to increase the observed isotopic equilibration rate, the surface-normalized data (between parentheses in Table 2) clearly show that R_{equil} is far higher for the ternary catalyst than for gallia. Moreover, even though gallia can activate/dissociate hydrogen above 500 K, this support was unable to hydrogenate carbon dioxide at 523 K and 3 MPa (that is, for much higher temperature and pressure than in this work) [21].

3.3. Hydrogen isotopic exchange

The isotopic exchange of hydrogen (Fig. 1b), which can be written as follows:



allows to evaluate the migration ability of atomic H(D) surface species from the metal to the support and vice versa (steps 2, 3 and 4) provided that the support is inactive for hydrogen dissociation (step 5, see Fig. 1b) under the experimental conditions employed.

Figs. 6 and 7 show the time course of the H/D exchange upon introducing the D₂/Ar = 10/90 gas mixture into the microreactor, at 393 K and 0.1 MPa, for Cu/ZrO₂ and Ga₂O₃/Cu/ZrO₂, respectively (the H/D exchange time courses at 353 and 373 K are shown in Supplementary Information, Figs. S.8–S.11). As the D₂ molar fraction progressively decreased (green trace), the HD and H₂ molar fractions increased (black and red traces, resp.), indicating that

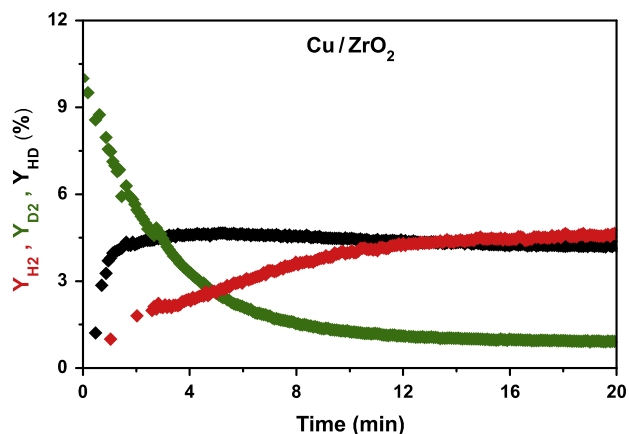


Fig. 6. Hydrogen/deuterium (H/D) isotopic exchange on Cu/ZrO₂ (feed mixture: D₂/Ar = 10/90 v/v) at 393 K and 0.1 MPa. Green: D₂. Black: HD. Red: H₂. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

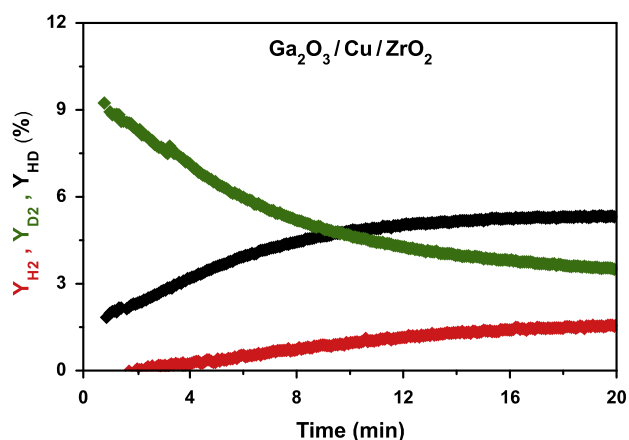


Fig. 7. Hydrogen/deuterium (H/D) isotopic exchange on Ga₂O₃/Cu/ZrO₂ (feed mixture: D₂/Ar = 10/90 v/v) at 393 K and 0.1 MPa. Green: D₂. Black: HD. Red: H₂. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

the H species on the zirconia support, as well as those on the gallia promoter in the case of the ternary catalyst – vide infra – was being exchanged with the D atoms, mostly originated (see Table 2, last column) from D₂ dissociation on the metal crystallites.

Table 3 shows the initial rates of H/D isotopic exchange, R_{exchg} , for the oxides and the two zirconia-based catalysts, at three different temperatures. These rates were estimated by considering the time consumption of deuterium atoms, $\Delta D/\Delta t$, using the observable change of the molar fractions of D₂ and HD in the gas phase measured in the initial exchange period, when said change was quasi-linear (see Appendix A and Supplementary Information, Figs. S.12 and S.13). As it can be appreciated by comparing Tables 2 and 3, the H₂/D₂ equilibration rates were substantially higher than the exchange rates, which shows that the H₂(D₂) adsorption and dissociation steps of molecular hydrogen are not rate limiting of the hydrogen isotopic exchange reaction. These results indicate that the metallic particles are efficiently acting as ‘gateways’ for the dissociation of H₂(D₂).

Even though hydrogen equilibration was faster on the ternary catalyst, Ga₂O₃/Cu/ZrO₂, the H/D exchange reaction was faster, instead, in the binary one (Cu/ZrO₂), in which the gallia promoter was absent. This suggested that either the presence of gallium

Table 3

Initial reaction rates of hydrogen/deuterium isotopic exchange, R_{exchg} , on the oxides and catalysts. Experimental conditions: D₂/Ar = 10/90 v/v; P = 0.1 MPa (see text).^a

Catalyst or support	$R_{\text{exchg}} \times 10^8$ (mol D/g _{cat} s) ^{b,c}		
	Temperature (K)		
	353	373	393
ZrO ₂	0.05 (0.00143) ^d	–	0.2 (0.0057)
Ga ₂ O ₃	–	–	7.1 (0.080)
Ga ₂ O ₃ /ZrO ₂	–	–	6.2 (0.088)
Cu/Ga ₂ O ₃	–	–	36.4 (0.51)
Cu/ZrO ₂	14.2 (0.49)	32.3 (1.11)	60.8 (2.09)
Ga ₂ O ₃ /Cu/ZrO ₂	3.9 (0.43)	10.1 (1.12)	15.2 (1.69)

^a The time course of the reaction is given in the text, and in Figs. S.8–S.11 and S.14–S.16 (Supplementary information).

^b R_{exchg} : H–* + D₂ ⇌ HD + D–* and R_{exchg} : 2H–* + D₂ ⇌ H₂ + 2D–*.

^c The correlation coefficients of the linear fits of $\Delta D/\Delta t$ vs. Δt were between 0.936 and 0.994 (see Appendix A).

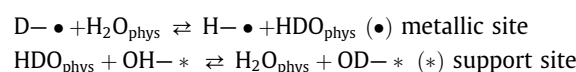
^d Parentheses: Surface-normalized rates, $R_{\text{exchg}} \times 10^8$ (mol D/m₂cat s).

oxide next to or in intimate contact with the metal particles (‘metal-oxide junction’) or the presence of Ga₂O₃ onto the zirconia support might constitute a barrier for the H/D exchange. These hypotheses were tested by performing the exchange at 393 K on Cu/Ga₂O₃ ($S_{\text{BET}} = 89$ m²/g, 2 wt.%Cu [21]), as shown in Supplementary Information, Fig. S.16. At such temperature, a lower exchange rate than that for Cu/ZrO₂ was observed (Table 3) which means that migration through the interface copper/gallia or the surface diffusion on gallia is lower compared to zirconium.

An explanation to these different rates of isotopic exchange might be found after considering the different acidity of gallia as compared to zirconia. However, there are still several viewpoints in regard to the impact of the acidity of oxidic supports on isotopic exchange rates. Some authors have suggested that the strength of the Brønsted acidity of different materials can be directly linked to the H/D exchange kinetics [31,32], while others (e.g., Ref. [16]) state that there is no correlation between (atomic) hydrogen mobility and surface acidity of the oxides. The latter postulated that just very weak acidity is sufficient to promote hydrogen migration and, moreover, they actually observed larger migration rates on basic supports, such as ceria and magnesia. More recently, a lack of a correlation between Lewis acidity and H/D exchange was observed by Schimming et al. [33] after re-plotting the density of exchangeable H atoms vs. the surface acidity concentration of their ceria–zirconia mixed oxides. It seems reasonable to conclude, then, that a more careful consideration of not only the type and density but also the strength of the acid sites, is still needed to arrive to a more accurate correlation (if any) between acidity and H/D exchange rate.

3.4. Comparison between H/D exchange and methanol synthesis rates

According to Martin and Duprez, the R_{exchg} determined from isotopic exchange experiments can be envisaged as spillover rates, or surface diffusion rates, depending on which of these steps are rate limiting [16]. A different point of view was presented by Prins in a recent review paper [17], who stated that “hydrogen spillover onto the surface of a defect-free nonreducible support is energetically improbable and that H/D exchange of OH groups on such a support provides no proof of spillover”. He postulated, rather, that on these catalysts: “First, a D atom on the metal particle exchanges with the H atom of an OH group on the support at the perimeter of the metal particle. A water molecule speeds up this step, via:



The H atom of an OH group on a support is not a hydrogen atom, but rather a proton. Thus, a D⁺ cation (deuteron), not a D atom, diffuses over the support by OH–OD exchange between the OD groups around the metal particles and OH groups on the support. In this H/D exchange, H atoms do not move from the metal particle to the support surface, and thus spillover does not occur”.

In addition, Prins sustains that no scientific work has ever shown any correlation between H/D exchange and hydrogenation reactions [17]. Nonetheless, in a recent paper about the hydrogenating properties of silica-supported silver catalysts, Claus and co-workers sustained that “the rate of HD exchange of OH groups of the silica support in the presence of silver in comparison with the exchange of the pure support is an indicator for the availability of activated hydrogen on the entire support surface” [18].

Borrowing this last concept, and regardless of the current controversy, a comparison between the H/D exchange rate, R_{exch} , and the methanol synthesis rate, $R_{\text{CH}_3\text{OH}}$, for the same catalyst can be of help in identifying whether the provision of activated hydrogen is enough to guarantee the synthesis demand. So, for instance, considering for each catalyst 1/6 of R_{exch} measured at 393 K (using the stoichiometric number concept [34], because six H atoms are involved in the synthesis of methanol), and comparing these values with those of $R_{\text{CH}_3\text{OH}}$ obtained at 498 K (Table 1) it is readily appreciated that, even for these dissimilar temperatures (1/6) $R_{\text{exch}} > R_{\text{CH}_3\text{OH}}$ in each case. In other words, because at 498 K every R_{exch} must certainly be higher than at 393 K, it can be safely inferred that the provision of hydrogen was not rate limiting for the methanol synthesis on our catalysts.

Similarly, if CO was only produced via a bifunctional pathway (i.e., from carbonaceous species associated with the ZrO₂ surface, reacting with atomic hydrogen supplied from the metal surface by dissociation followed by spillover/migration [35]) (1/2) $R_{\text{exch}} > R_{\text{CO}}$ would suffice to attend the demand of active hydrogen for this reaction. In any event, the observed values for R_{CO} in our catalyst (even if, instead, CO was produced by consecutive decomposition onto the metal crystallites [11]) were always noticeably smaller than those for R_{exch} .

More rigorous analyses could be done if $R_{\text{CH}_3\text{OH}}$ was compared with R_{exch} extrapolated to 498 K, and several additional factors such as the presence of water and/or adsorbed carbonaceous species onto the catalysts' surface (which may modify the dynamics of the H/D exchange) were taken into account [10]. However, a problem arises regarding a correct or appropriate extrapolation, because the temperature dependence of diffusional processes (such as that of the one illustrated by step 3, Fig. 1b) differs from that of ‘intrinsically chemical’ reaction steps (i.e., those associated with steps 2 and/or 4).

Because it is not known a priori which step (2, or 3–4 – Fig. 1b) is rate-controlling in the H/D exchange reaction, we decided to extrapolate R_{exch} to 498 K taking either of them as rate limiting. So, using the experimental R_{exch} values given in Table 3 and considering Arrhenius-type functional dependency, a first extrapolation was made. Table 4 shows the obtained H/D exchange rate values at 498 K, together with the respective values of the apparent

Table 4

Apparent activation energy, E_{act} , of hydrogen isotopic exchange and estimated hydrogen isotopic exchange rate, R_{exch} , for Cu/ZrO₂ and Ga₂O₃/Cu/ZrO₂ at 498 K, assuming that the exchange reaction is ‘a chemical process’.

Catalyst	E_{act} (kJ/mol) ^a	$R_{\text{exch}} \times 10^8$ (mol D/g _{cat} s)
Cu/ZrO ₂	42.0	840 (29.0) ^b
Ga ₂ O ₃ /Cu/ZrO ₂	39.7	200 (22.2) ^b

^a The estimations were made using data taken from Table 3, considering Arrhenius-like rate behavior.

^b Parentheses: Surface-normalized rates, $R_{\text{exch}} \times 10^8$ (mol D/m_{cat}² s).

overall activation energy, E_{act} , for Cu/ZrO₂ and Ga₂O₃/Cu/ZrO₂. Using again the stoichiometric number concept, it can be readily appreciated that these reaction rates are higher than the ones for the methanol synthesis and/or the RWGS reaction at 498 K. Note, however, that these calculated E_{act} are approx. 10 kcal/mol, truly closer to the lower limit of any chemical process but, nevertheless, similar to the ones reported for Cu/ZrO₂ ($S_{\text{BET}} = 20 \text{ m}^2/\text{g}$ and 5.7 wt.% Cu) by other workers [10].

If, rather, it were considered that the rate limiting step of the hydrogen exchange process was surface diffusion (step 3), the amount of deuterium (hydrogen) diffusing over the support would be given by [36]:

$$N_e = \frac{2}{\sqrt{\pi}} C_D I_0 \sqrt{D_S t} \quad (1)$$

where N_e stands for the number of atoms exchanged (this amount is equal to ΔD), C_D is the surface concentration of D on the metal particles at time = 0, I_0 is the length of the metal-support interface, D_S is the surface diffusion coefficient and t is time [36].

The slope of the relationship between the number of exchanged atoms and the square root of time allows estimating the surface diffusion coefficients:

$$D_S = \frac{\pi}{4} \left(\frac{S_1}{C_D I_0} \right)^2 \quad \text{with} \quad S_1 = \left(\frac{dN_e}{d\sqrt{t}} \right) \quad (2)$$

Table 5 shows the calculated values of the surface diffusion coefficients for atomic H(D) at 353, 373 and 393 K for Cu/ZrO₂ and Ga₂O₃/Cu/ZrO₂. The C_D value was assumed to be 1.46×10^{19} atoms per square meter for copper [37], while the I_0 values were estimated from the metal dispersion measured for both materials, assuming semi-spherical particles of copper in contact with the support. It is worth mentioning that the obtained values for D_S are similar to the ones found by Martin and Duprez for ZrO₂ [16], albeit they are considered rather low values for this support [10]. Furthermore, the total number of exchanged H/D atoms (that is, the values corresponding to the asymptotes of Figs. S.12 and S.13 – which were approximately the same for the different reaction temperatures tested after 40 min) was 3.3 at/nm² for Cu/ZrO₂ and 5 at/nm² for Ga₂O₃/Cu/ZrO₂, very close for the binary catalyst to the value reported in the literature for Rh/ZrO₂ (3 at/nm²) using same vacuum treatment temperature [16].

Because the functional relationship of surface diffusion coefficients with temperature is also of Arrhenius-type (i.e., because it is an activated process, [38]), its value at 498 K can then be estimated as well (Table 5). So, using Eq. (1), and assuming that the *rd*s of the isotopic exchange process was surface diffusion, the estimated values of the H/D exchange rates for Cu/ZrO₂ and Ga₂O₃/Cu/ZrO₂ at 498 K would be 5200 and 2300×10^{-8} mol D/s g_{cat} respectively, which are far larger than those of the methanol synthesis. These high values strongly suggest that diffusional phenomena (step 3) were not rate limiting in our H/D exchange experiments.

It is necessary to analyze, finally, the impact of the presence of adsorbed water and/or carbonaceous species onto the catalysts on

Table 5

Surface diffusion coefficient for H(D) on Cu/ZrO₂ and Ga₂O₃/Cu/ZrO₂ at different temperatures.^a

Catalyst	$D_S \times 10^{12}$ (cm ² /s)			
	Temperature (K)			
	353	373	393	498
Cu/ZrO ₂	0.05	0.1	0.2	4.1
Ga ₂ O ₃ /Cu/ZrO ₂	0.3	1.1	1.6	47.5

^a Calculated with Eq. (2) (see text).

the dynamics of the H/D exchange. Isotope exchange (and equilibration) experiments performed in the presence of water can differ from those made without it, because water can inhibit dissociation of H₂ (D₂) on pure ZrO₂ but not on the Cu surface [10]. Then, water can catalyze the direct exchange between OH and H(D) on the catalyst – that is, the isotopic exchange between the metal and the support [8,10,17]. Under these premises, the movement of adsorbed atomic H (or D) from the metal particles to the oxide(s) surface – and vice versa – would be enhanced during methanol synthesis, due to the presence of water formed in both the main ($R_{\text{CH}_3\text{OH}}$) and the (R_{RWGS}) reactions, in comparison with the observed in the hydrogen isotopic experiments performed here. In our experiments, the moderate evacuation down to 600 Pa after CuO reduction left only traces of water whereby, comparatively, the rate of hydrogen provision to the carbonaceous species adsorbed onto the support would result even much higher during the alcohol synthesis.

As for the presence of carbonaceous species on the catalysts surface, Conner and Falconer put forward that such species, together with neighbor hydroxyls facilitate the spillover and/or exchange of atomic species [8]. However, Jung and Bell [10] showed that formates on zirconia inhibit H/D exchange, suggesting instead that what is affected is surface transport (not spillover) of the adsorbed H(D) species. So, it is possible to think that under process conditions this formate species could affect methanol synthesis rate if the reductive elimination of methoxide species adsorbed onto the entire surface of the zirconia support was predominant, because in the case that those formates were adsorbed at the metal-oxide junction the hydrogenation would be always ensured. Even so, assuming that owing to the presence of formates the exchange rate would decrease down to an order of magnitude, and the apparent activation energy, E_{act} , was then approx. 40% higher [10], the estimated R_{exch} at 498 K would be 50×10^{-8} mol D/s g_{cat} for the Ga₂O₃/Cu/ZrO₂ catalyst. That is, even for the most disadvantageous situation derived from the presence of adsorbed formates and the absence of water, the H/D exchange rate would still be higher than the methanol synthesis and RWGS rates (2×10^{-8} mol CH₃OH/s g_{cat} and 2.5×10^{-8} mol CO/s g_{cat} , Table 1) and, thus, not rate-controlling.

4. Conclusions

The study of the capacity of H₂ dissociation (isotopic equilibration experiments) at 353–393 K on Cu/ZrO₂ and Ga₂O₃/Cu/ZrO₂ suggested that Cu metal crystallites host the main sites for molecular hydrogen dissociation.

Since the contribution of the support was negligible for the H₂/D₂ equilibration reaction (at least 50-fold smaller), the H/D exchanged reaction yielded unmasked diffusion (and/or spillover rates) for both Cu-supported catalysts in said temperature range. It was also found that the addition of gallia produced a detrimental effect on the rate of isotopic exchange (2.09 vs. 1.69×10^{-8} mol D/m_{cat}² s for Cu/ZrO₂ vs. Ga₂O₃/Cu/ZrO₂, respectively).

Then, the assumptions of a diffusional (step 3), or intrinsically chemical (steps 2 and 4) processes as *rd*s of the H/D exchange reaction were used to evaluate whether the provision of activated hydrogen was enough to successfully accomplish the observed methanol synthesis rate. The estimated exchange rates, which were noticeably higher for either of both processes (either 2 or 3 order of magnitude) than the rate of methanol production on our low copper loaded catalysts at 498 K, clearly indicated that the provision of activated hydrogen is sufficient to ensure the hydrogenation of CO₂ to methanol (and CO) under typical synthesis conditions. That is, spillover or surface diffusion is not *rd*s and, therefore, not responsible for methanol selectivity.

Acknowledgments

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Appendix A

A.1. Ancillary calculations

A.1.1. Initial reaction rates, $R_{\text{CH}_3\text{OH}}$ and R_{CO}

Each rate was calculated using the slopes of the $Y_{\text{CH}_3\text{OH}}$ % and Y_{CO} % traces vs. time, $\Delta Y/\Delta t$, within the linear region (3–20 min reaction time, Figs. 2 and 3), the total amount of moles loaded into the microreactor at the given pressure and temperature (1.6 MPa and 498 K) and the mass of catalyst:

$$\text{Rate} \left[\frac{\text{mol}_{\text{CH}_3\text{OH}}}{\text{s } g_{\text{cat}}} \right] = \text{Slope} \left[\frac{\text{mol}_{\text{CH}_3\text{OH}}}{\text{mol}_{\text{tot}} \text{ s}} \right] \cdot \text{Moles reactor} [\text{mol}_{\text{tot}}] \frac{1}{\text{Weight cat} [g_{\text{cat}}]} \quad (\text{A.1})$$

A.1.2. Initial rate of hydrogen isotopic exchange, R_{exch}

Said rate was calculated through the following intermediate steps:

- Calculation of the instant change in the percent molar fraction of deuterium with time, ΔY_{D_2} %, considering its initial value at time zero ($Y_{\text{D}_2}^0$ % = 10) [16]:

$$\Delta Y_{\text{D}_2} \% = 10\% - \left(Y_{\text{D}_2} \% + \frac{1}{2} Y_{\text{HD}} \% \right) \quad (\text{A.2})$$

- Measurement of the total amount of moles loaded into the microreactor at the given pressure and temperature, and the mass of catalyst used.
- Calculation of the instant exchanged moles of deuterium with time, $\Delta D/\Delta t$:

$$\Delta D [\text{mol}_\text{D}] = \Delta Y_{\text{D}_2} \% \left[\frac{\text{mol}_{\text{D}_2}}{\text{mol}_{\text{tot}}} \right] \cdot \text{Moles reactor} [\text{mol}_{\text{tot}}] \cdot 2 \left[\frac{\text{mol}_\text{D}}{\text{mol}_{\text{D}_2}} \right] \quad (\text{A.3})$$

$$\text{Rate} \left[\frac{\text{mol}_\text{D}}{\text{s } g_{\text{cat}}} \right] = \text{Slope } \Delta D \left[\frac{\text{mol}_\text{D}}{\text{s}} \right] \cdot \frac{1}{\text{Weight cat} [g_{\text{cat}}]} \quad (\text{A.4})$$

Appendix B. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jcat.2015.07.025>.

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