and formaldehyde, but in inverted relation. To use just mass fragments 29 amu, 30 amu, or 31 amu is less reliable than using the ratio, because all of them are also observed when only methanol is present. To exclude an influence of other species, mass fragments like 75 amu (for dimethoxymethane) or the ratio of 44 and 45 amu to 46 amu (for formic acid or DME) are also considered. When only the ratio of mass fragments 29 amu/31 amu changes, the production of formaldehyde is detected. Different y axes are chosen for best visualization of the yields of methyl formate and formaldehyde, but no conclusion of the produced amounts of formaldehyde compared to methyl formate is possible because of the lacking absolute calibration.

It has to be pointed out that the yields of methyl formate or formaldehyde of different measurements can be compared, because the y axes are kept the same for all figures. The maximum yield of methyl formate over 0.9 wt.% Au/ZnO is obtained at 425 K. At 495 K, traces of formaldehyde become maximum. At the highest investigated temperatures, small

và formaldehyde, nhưng theo hệ thức nghịch đảo. Việc chỉ sử dụng các mảnh lớn amu 29, 30 amu, hoặc 31 amu ít tin cậy hơn dùng tỉ số, bởi vì tất cả chúng xuất hiện khi methanol hiện diện. Để loại trừ ảnh hưởng của các chất khác, các mảnh lớn như 75 amu (đối với dimethoxymethane) hoặc tỷ lệ 44 và 45 amu đến 46 amu (axit formic hoặc DME) cũng được xem xét. Khi chỉ có tỷ lệ các mảnh lớn 29 amu/31 amu thay đổi, sự tạo formaldehyde được phát hiện. Các trục y khác nhau được chọn để hình dung tốt nhất sản lượng methyl formate và formaldehyde, nhưng không có kết luận về lượng formaldehyde được tạo ra so với methyl formate có thể do thiếu hiệu chuẩn tuyệt đối.

Người ta chỉ ra rằng sản lượng methyl formate hoặc formaldehyde của các phép đo khác nhau có thể được so sánh, bởi vì các trục y được giữ giống nhau cho tất cả các hình. Năng suất tối đa của methyl formate trên 0,9 wt.% Au / ZnO thu được tại

yields of H2 are achieved additionally. CO is also produced, but maximum yields at 523 K are as low as 4%. Obtaining the same yields during heating and subsequent cooling of the catalyst with a slow rate (0.5 Kmin-1) indicates that the yields correspond to the yields at steady state and can therefore be regarded as pseudo steady-state yields. Fig. 3C and D shows the subsequently performed repeated measurement of methanol oxidation without any further pretreatment. Results equal the first run of methanol oxidation and, therefore, underline that yields are obtained at pseudo steady state and that no deactivation or activation occurs.

When the 0.9 wt.% Au/ZnO sample was pretreated at the higher temperature of 723 K, catalytic activity in methanol combustion is decreased (Fig. 4), and comparable yields are achieved at higher temperatures. During heating, the yield of methyl formate is lower

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425 K. Tại 495 K, các vết của formaldehyde trở thành cực đại. Ở nhiệt độ khảo sát cao nhất, sản lượng nhỏ H2 đạt được bổ sung vào. CO cũng được tạo ra, nhưng năng suất cực đại ở 523 K thấp cỡ 4%. Thu được cùng một sản lượng trong quá trình nung nóng và sau đó làm lạnh chất xúc tác với tốc độ chậm (0,5 Kmin-1) cho thấy rằng sản lượng tương ứng với sản lượng ở trạng thái ổn định và do đó có thể được coi như sản lượng ở trạng thái gần ổn định (giả ổn định). Hình 3C và D cho thấy các phép đo lặp đi lặp lại sau đó được thực hiện cho quá trình oxy hóa methanol mà không có bất kỳ quá trình xử lý trước nào. Kết quả tương đương với lần oxy hóa đầu tiên và, do đó, nhấn mạnh rằng sản lượng thu được ở trạng thái gần ổn định và không có sự khử hoạt tính hoặc kích hoạt xảy ra.

Fig. 4. Yields during methanol oxidation over 0.9 wt.% Au/ZnO after O2 pretreatment at 723 K. Yields of(A) (o) H2O, (□) CO2, (m) H2 and (B) ({) CHOOCH3 and (v) CH2O are shown. Traces with full symbols were obtained during heating, traces with open symbols during cooling of the catalyst.

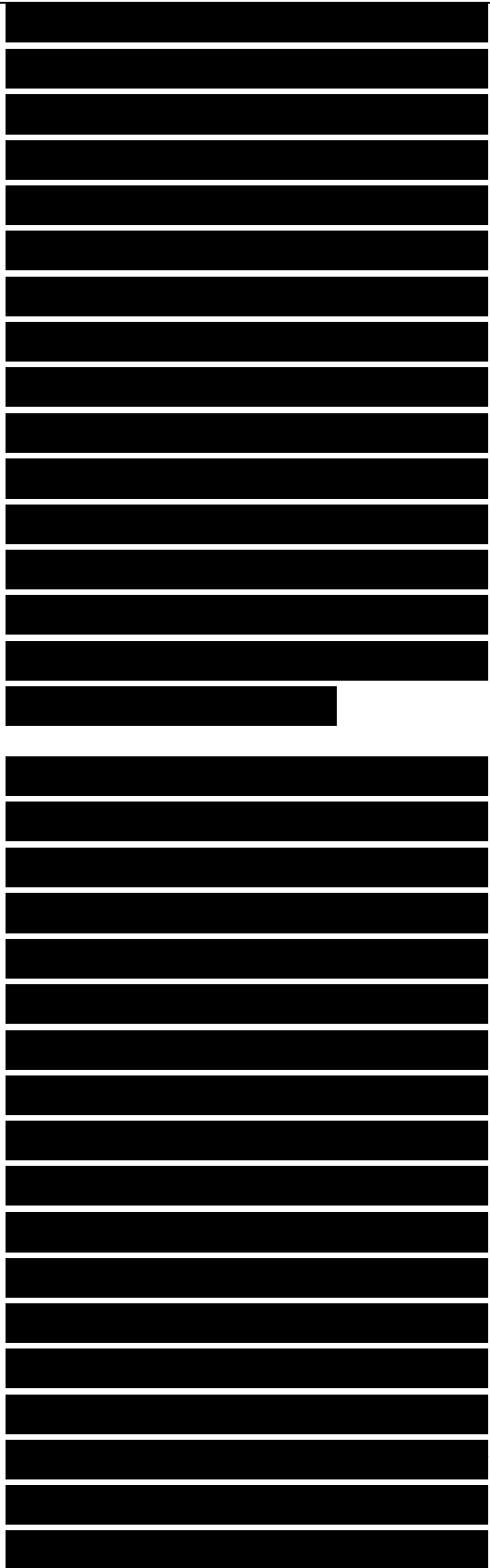…………………………………………………
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Fig. 5. Yields during methanol oxidation over 0.6 wt.% Au/ZnO after O2 pretreatment at 523 K. Yields of (A) (o) H2O, (□) CO2, (m) H2 and (B) ({) CHOOCH3 and (v) CH2O are shown. Traces with full symbols were obtained during heating, traces with open symbols during cooling of the catalyst.

and the maximum is shifted to a higher temperature compared to the same sample pretreated at 523 K, whereas the yield of formaldehyde increases. The H2O yield passes through a maximum at 560 K. CO2 production runs through a point of inflection and reaches almost 100% at 613 K coincidentally with full conversion

of CH3OH. H2 yield is at the maximum again at the highest temperature, and CO was only produced in traces (yield 6 4%) with a maximum at 515 K (not shown). During cooling, the yields differ slightly from the heating branch indicating a minor modification of the catalyst. The overall activity for methanol combustion is somewhat higher, the temperature at the maximum yield of methyl formate is decreased coincidentally with an increase in selectivity, and selectivity toward formaldehyde is decreased.

Figs. 5 and 6 show the yields of methanol oxidation using 0.29% CH3OH/0.29% O2/He at temperatures between 323 and 523 K over 0.6 and 1.9 wt.% Au/ZnO catalysts. The activity depends on the Au loading: the higher the loading, the more active is the catalyst. Also the selectivities to the products of the selective oxidation of methanol depend on the Au loading. The more Au is deposited on ZnO, the more methyl formate is produced coincidentally with a higher activity of the sample in methanol combustion. Inversely, the formaldehyde selectivity is decreased with increasing activity in methanol combustion.

For the 1.9 wt.% Au/ZnO sample, an additional experiment is performed, where the temperature is changed stepwise. After heating to 373, 423, 473, and 523 K with 0.5 K min-1, the temperature is held constant for 90 min to ensure steady-state conditions. After ……………………………………………… ……


Fig. 6. Yields during methanol oxidation over 1.9 wt.% Au/ZnO after O2 pretreatment at 523 K. Yields of (A) (o) H2O, (□) CO2, (m) H2 and (B) (}) CHOOCH3 and (v) CH2O are shown. Traces with full symbols were obtained during heating, traces with open symbols during cooling of the catalyst.

reaching 523 K, the temperature is again stepwise decreased to verify that steady state was achieved. The yields in the stepwise performed experiment of CO2, H2O and H2 are added to Fig. 6 as grey symbols at the dashed lines. They also demonstrate that the yields in the transient experiments correspond to the yields at steady state.
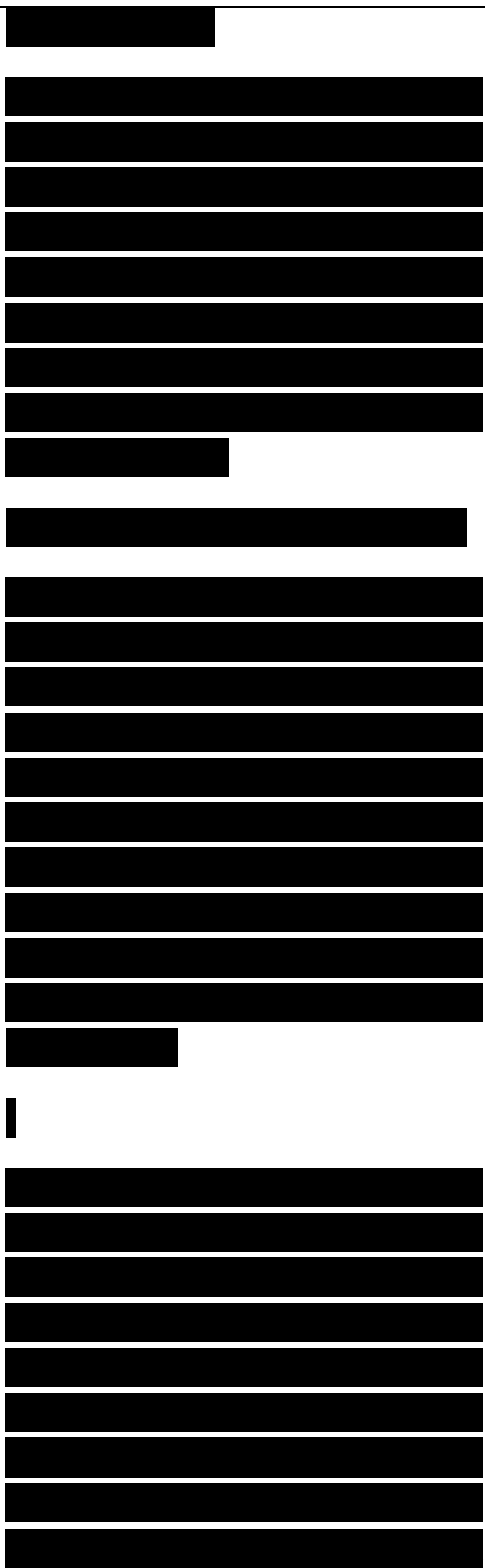
To investigate the effect of the oxide support, measurements are also performed with Au/TiO2 samples shown in Figs. 7 and 8. In the first run after pretreatment in 10% O2/He, the heating branch differs significantly from the cooling branch indicated by the hysteresis in Fig. 7A and B as well as in Fig. 8A and B. No steady-state conditions can be assumed. The catalyst changes dramatically during the first heating in CH3OH/O2/He, and when the measurement is repeated directly after cooling in the reaction gas mixture without further treatment, the activities of both heating and cooling branches match the activity during cooling of the first run. The methyl formate yields are again depending on the overall activity in methanol combustion, but selectivity is much lower compared to Au/ZnO samples (multiplied by a factor of 5 in the figures).

During the first heating, almost no formaldehyde is produced. Upon decreasing activity in the following runs, traces of formaldehyde can be detected.
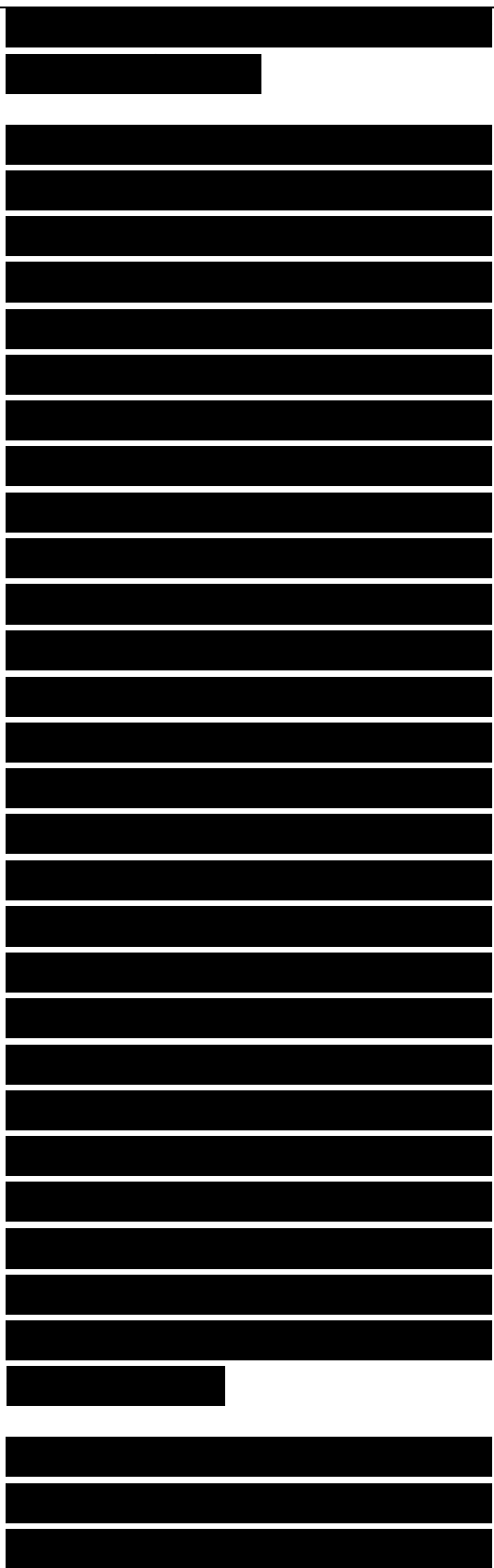
Therefore, formaldehyde selectivity is reciprocally depending on the overall activity similar to the Au/ZnO samples. Again, traces of CO are detected at the highest investigated temperatures (not shown). Contrary to Au/ZnO, a very weak signal of the mass fragment of 75 amu is detected during cooling in the first run and the following runs (not shown) indicating the production of dimethoxymethane. Its maximum is at 464 and 481 K for 0.7 and 0.9 wt.% Au/TiO2, respectively. Comparing the activities of the two Au/TiO2 samples with slightly different Au content, the activity is scaling with the Au loading.

Pretreatment at the higher temperature of 723 K has less influence on the activity compared to Au/ ZnO, but again the activity was lower after this pretreatment. The temperatures at 50% O2 conversion $(T(XO2 = 50\%))$ in the first cooling branch of the methanol oxidation experiments of the different catalysts are summarized in Table 2 helping to compare the activities at steady-state conditions.
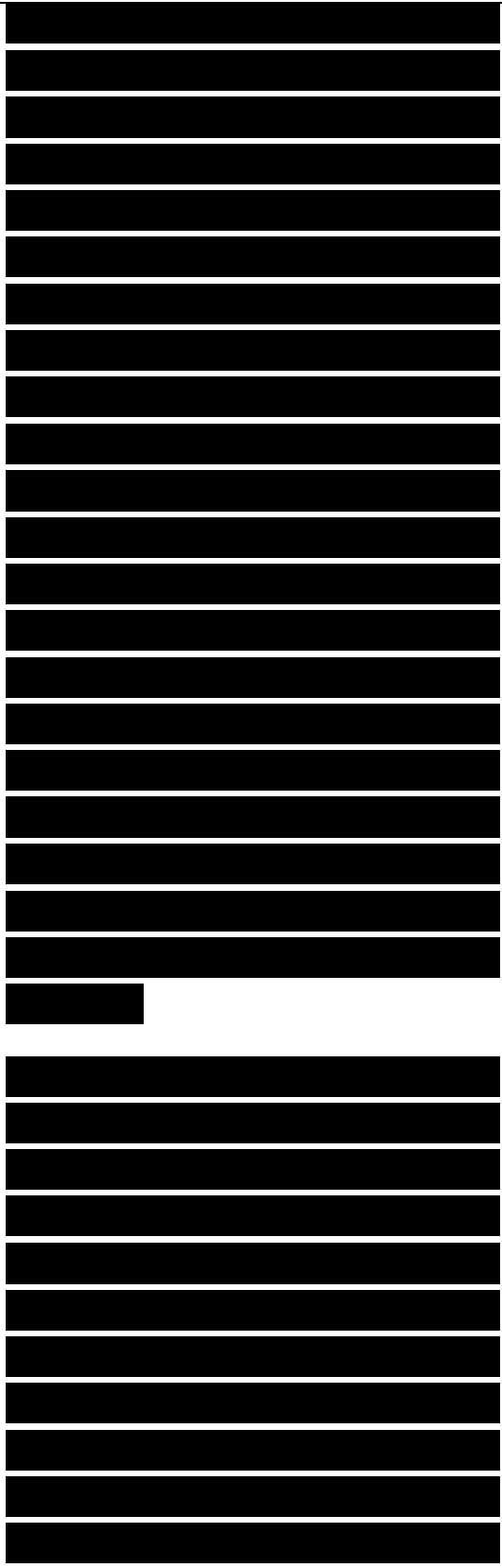
The presence of the hysteresis indicates a deactivation of the catalysts. To gain deeper insight in the nature of the hysteresis, measurements were conducted after different pretreatment procedures. With a reducing procedure like hydrogen exposure or CO exposure, the extent of the hysteresis is only slightly decreased. To prove that no continuous deactivation is the reason for the slight decrease in the hysteresis, a repeated measurement after an O2 pretreatment is performed over the same sample and the initial hysteresis is restored. Fig. 9 shows the temperature at 50% O2 conversion during heating and cooling in the first run of methanol oxidation after different pretreatments serving as a measure of the dimension of the hysteresis. Using CH3OH during the pretreatment results in a disappearance of the hysteresis (Fig. 9B). Moreover, the activity is lower compared to the cooling branch after the abovementioned treatments.

Cooling in 4% CO2/He is also decreasing the hysteresis (Fig. 9C), but it is more significantly decreased after exposure to 0.24% HCOOH/He at 323 K (Fig. 9D). After formic acid exposure, the activity during heating in the first run is almost as
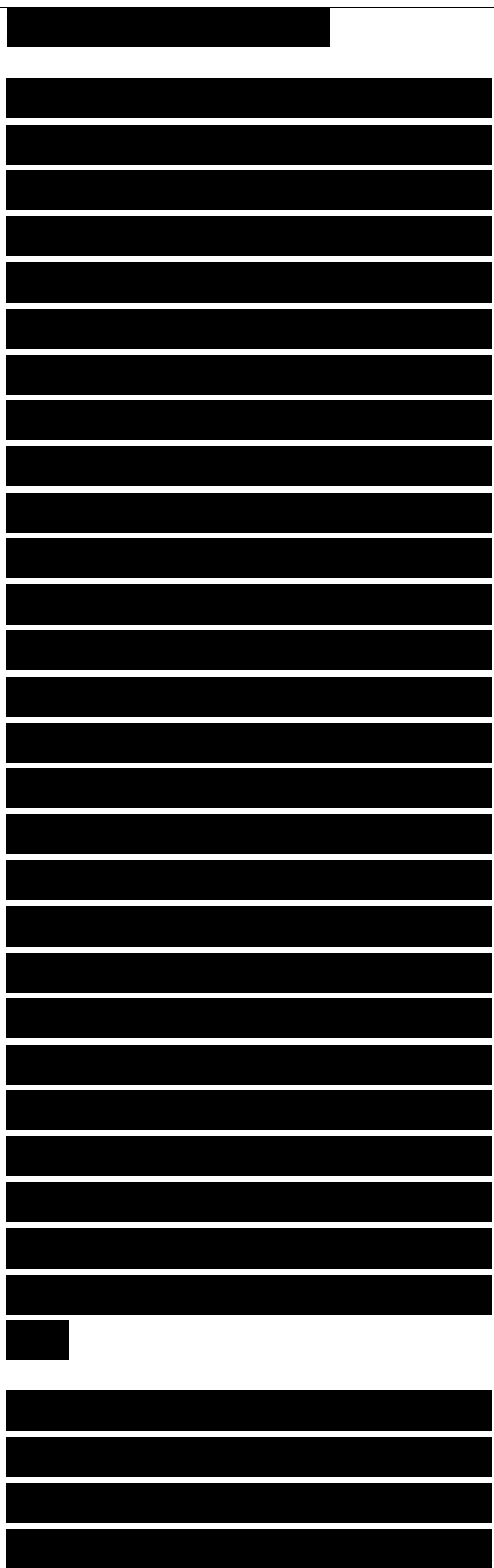
low as during cooling.

3.3. Infrared spectroscopy

Fig. 10 shows the in situ DRIFT spectra of the 0.6 wt.% Au/ZnO catalyst after pretreatment at 523 K. Bands at 1558, 1510, 1438, and 1332 cm-1 as well as bands in the region between 3000 and 2800 cm-1 are due to organic impurities, residues of the PVA protecting shell, and carbonate-like species after the pretreatment. Heating to higher temperatures results in a complete removal of