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Effect of alkali cations on the $CuZnOAl_2O_3$ low temperature water gas-shift catalyst

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ABSTRACT

Low temperature water gas-shift catalysts containing 1.0% by weight of alkali elements (Li, K, Rb and Cs) were prepared by impregnation of a ternary $Cu/ZnO/Al_2O_3$ (CZA) base catalyst. The calcined precursors were characterized by different physical and chemical techniques such as X-ray diffraction, X-ray fluorescence, N_2O chemisorption, N_2 adsorption at low temperature and X-ray photoelectron spectroscopy. Then these precursors were activated and tested in the low temperature water gas-shift reaction (LT-WGS). It was shown that the K-containing CZA catalyst exhibited the highest CO conversion level at reaction temperature within the range 450–530 K. In addition, the alkali promoters were found to prevent methanol production at temperatures higher than 480 K.

1. Introduction

The copper–zinc–alumina (CZA) low temperature water gas-shift (LT-WGS) catalyst is employed in the industry since the years 1960s for methanol synthesis from syngas and also for the conversion of CO-containing streams into additional hydrogen. As copper is the active component in both LT-WGS and methanol synthesis catalysts, by-products such as methanol, acetaldehyde and amines, have been found in the effluent of LT-WGS reactors in hydrogen and ammonia plants [1]. This indicates that the catalyst is not selective enough to prevent the formation of methanol and other compounds derived therefrom, which decrease the hydrogen yield; contaminate the CO_2 stream, limiting its use in food and fine chemistry industries, and may impact the environment [2,3].

Thus, reducing the formation of oxygenates in the LT-WGS reactor remains a subject of investigation [4,5]. The positive alkali-doping effects have been described for different reactions, such as the synthesis of ammonia, oxidation of sulfur dioxide to sulfur trioxide and the dehydrogenation of ethylbenzene to styrene [6]. The use of alkali metal cations as promoters to avoid the formation of methanol is related to the nucleophilic activation of CO:

$$OH^- + CO \leftrightarrow HOCO^- \tag{1}$$

$$HOCO^- \leftrightarrow HCOO^- \tag{2}$$

These reactions are accelerated in the presence of alkali metal cations which can render more reactive OH^-, $HCOO^-$ and $HOCO^-$ counter ions than the primary components of the CZA catalyst. Then, the decomposition of surface hydroxyl groups and of $HOCO^-$ and $HCOO^-$ to CO_2 would be expected in the next step of the water gas shift reaction mechanism [7]. Klier et al. [7,8] found that reaction (1) is not activated but reaction (2) occurs with an activation energy barrier and, therefore, the isomerization (2) may be influenced by the nature of the alkali metal cations. It is also established that on Cu based catalysts the LT-WGS reaction occurs exclusively through a redox cycle [9–11]:

$$2Cu_{(s)} + H_2O_{(g)} \leftrightarrow Cu_2O_{(s)} + H_{2(g)} \tag{3}$$

$$Cu_2O_{(s)} + CO_{(g)} \leftrightarrow 2Cu_{(s)} + CO_{2(g)} \tag{4}$$

Thus, the rates of the reactions (3) and (4) may be only indirectly influenced by the presence of alkali metals [12].

The reverse water gas-shift (RWGS) reaction was studied over Cu/SiO_2 catalysts, with and without potassium promoters [13]. Hydrogen was dissociatively adsorbed on Cu and could spill over K_2O to associate with CO_2, rendering formate species for CO production. In addition, Pt/ZrO_2 doped with alkali cations, such as Li, Na, and K were studied using combinatorial methods. A positive effect was found on the low temperature water gas shift rate [11]. In this investigation, DRIFTS results indicated that the alkali cation significantly shifted the formate C–H band positions toward lower wave numbers and the overall intensities of these bands were found to be higher with the addition of alkali promoters. These results

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suggest a new direction in water gas shift catalyst design. Ternary Cu/M/Zn catalysts (M = alkaline earth metal: Mg, Ca, Sr and Ba) were prepared by homogeneous precipitation using urea hydrolysis [14]. The structure and water gas shift activity of these catalysts were compared to those of catalysts prepared by coprecipitation. The highest activity was found over Cu/Mg/Zn catalysts containing an actual amount of Mg less than 1.0 at%.

In this work, CZA catalysts containing 1.0% by weight of Li, K, Rb and Cs were prepared and characterized by XRD, XRF, N_2O chemisorption, N_2 physisorption isotherms and XPS, in order to study the influence of the alkali metal cations on the LT-WGS reaction, preventing the by-production of methanol.

2. Experimental

2.1. Catalysts preparation

A CZA catalyst, of nominal atomic composition Cu:Zn:Al = 45:50:5, was prepared by simultaneous precipitation of the cations. The precipitate was then dried at 363 K for 12 h and finally calcined at 633 K for 4 h [14,15]. Alkali cations (1% by weight) were incorporated to the CZA catalyst by impregnation using acetate solutions of Li^+, K^+, Rb^+ and Cs^+. The solids were dried overnight at 383 K and then calcined at 633 K for 4 h. These catalyst precursors were coded as CZA-M, where M = Li, K, Rb and Cs.

2.2. Catalysts characterization

The chemical composition of the calcined precursors was determined by X-ray fluorescence using a XRF-1800 Shimadzu X-ray analyzer. The specific surface area was calculated by applying the BET method to nitrogen adsorption isotherms, recorded at 77 K, in a Micromeritics ASAP-2000A equipment. A DRX 6000 Shimadzu diffractometer was used to determine the crystalline phases and crystallinity of the samples. The exposed metallic area of copper was determined by N_2O reactive chemisorption. Typically, 0.30 g of catalyst was previously reduced 493 K for 1 h in a 50 mL/min flow of 1.5% H_2/Ar. Thereafter, the reactor was purged with a 50 mL/min Ar flow and the temperature lowered to room temperature. The copper area was evaluated by re-oxidation of the reduced surface at 353 K for 1 h, in a 50 mL/min flow of 5% N_2O/Ar. Once this re-oxidation process was achieved, a second reduction was performed according to the above methodology. The Cu/N_2O stoichiometric coefficient was considered to be equal to 2 [16].

Photoelectron spectra (XPS) were obtained with a VG Escalab 200R spectrometer equipped with a hemispherical electron analyser (pass energy of 50 eV) and an MgKα ($h\nu$ = 1254.6 eV) X-ray source, powered at 120 W. The area of the peaks was estimated by calculating the integral of each peak after smoothing and subtraction of an S-shaped background and fitting of the experimental curve to a combination of Lorentzian and Gaussian lines (10%L–90%G). All binding energies (BE) were referenced to the C 1s signal at 284.9 eV from carbon contamination of the samples to correct the charging effects. This reference gave BE values within an accuracy of ±0.2 eV. Quantification of the atomic fractions on the sample surface was obtained by integration of the peaks with appropriate corrections for sensitivity factors [17]. Prior to analysis the samples were degassed for 0.5 h under a residual pressure of ca. 8.5×10^{-9} mbar. Then they were reduced at 493 K in a flow of H_2 under atmospheric pressure for 0.5 h.

2.3. Activity measurements

Activity tests were carried out to establish the influence of the alkali cation promoters on the CO conversion (X_{CO}%) and CH_3OH selectivity (%S_{CH3OH}) under the LT-WGS reaction conditions. A fixed-bed tubular stainless-steel reactor was operated at atmospheric pressure. Steam was supplied to reactor from a saturator containing distilled water, under rigorous temperature control, in order to allow an accurate variation of the steam/gas (S/G) molar ratio. The space velocity was 4500 h^{-1} during the reaction tests. A model synthesis gas consisting of 0.25% CH_4, 16.5% CO_2, 3.2% CO, 0.23% Ar, 20.5% N_2 and 59.3% H_2 was employed. The catalysts were reduced *in situ* under 1.5% H_2/Ar, at 493 K, for 1 h at a heating rate of 4 K/min. Reagents and products were analyzed on a Thermo Quest Analytical Trace GC model chromatograph equipped with TCD and FID detectors, using Porapak Q and 13X Molecular Sieve columns.

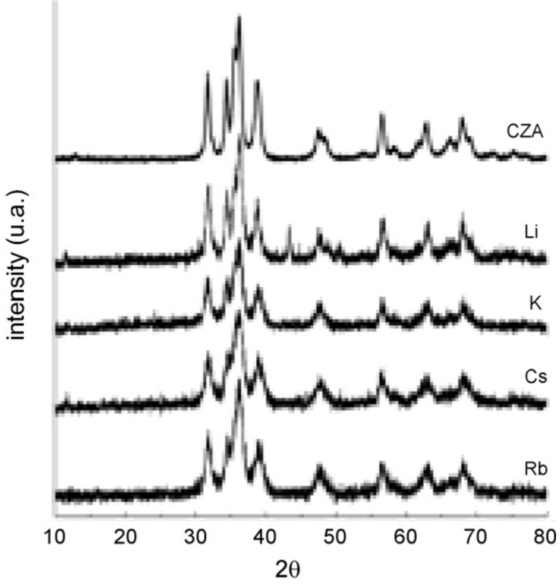

Fig. 1. X-ray diffraction patterns of CZA and CZA-M (M = Li, K, Rb, Cs) catalysts.

Table 1
Chemical composition of calcined precursors and metallic area of copper of the H_2-reduced catalysts.

Catalyst	Cu (%)	Zn (%)	Al (%)	M (%)	S_{Cu} ($m^2 g^{-1}$)
CZA[a]	42.00	53.00	5.00	–	–
CZA	41.02	53.70	5.28	–	25.61
CZA_{Li}	42.36	51.42	5.31	0.91	8.40
CZA_K	43.06	50.9	5.02	1.02	16.33
CZA_{Rb}	41.52	52.21	5.32	0.95	18.97
CZA_{Cs}	41.78	52.17	5.08	0.97	21.14

[a] Nominal composition.

3. Results and discussion

Calcination of the precursors at 623 K produces metal oxides, after removal of carbon dioxide and water. Thus, a broad peak refers to CuO tenorite (34.5°, 36.6° and 38.5°) and ZnO (31.8°, 34.3° and 38.9°) are observed in the diffraction pattern shown in Fig. 1, indicating a poor crystallinity of the calcined CZA precursors. A low intensity, broad peak belonging to the α-Al_2O_3 is observed but any of the diffraction lines of a $CuAl_2O_4$ phase could not be detected [13]. The X-ray diffraction patterns of calcined CZA precursors containing 1.0% of alkali promoters (CZA-M) are also shown in Fig. 1. More intense peaks assigned to CuO and ZnO were found for CZA-Li but no significant changes were found comparing the diffraction patterns collected for CZA and CZA-M (M = K, Rb and Cs) catalyst precursors.

The experimental chemical compositions of the catalyst precursors, determined by XRF, are collected in Table 1. The nominal bulk

Table 2
Binding energy (eV) of the most intense lines of samples calcined degassed and H_2-reduced.

Catalyst	Cu $2p_{3/2}$	Zn $2p_{3/2}$	Al 2p	M
CZA, vac	933.7(43)935.1(57)	1022.2	74.6	–
CZA, H_2	932.5(81)934.1(19)	1022.3	74.7	–
CZA$_K$ O_2, 623	933.7(46)935.3(54)	1022.3	74.6	–
CZA$_{Li}$, vac	934.0	1022.1	74.7	Li 1s = 64.2
CZA$_{Li}$, H_2	932.7	1022.2	74.7	Li 1s = 64.2
CZA$_K$, vac	934.2	1022.2	74.7	K 2p = 294.1
CZA$_K$, H_2	932.7	1022.2	74.7	K 2p = 294.0
CZARb, vac	933.9	1022.2	74.8	Rb 3d = 111.3
CZA$_{Rb}$, H_2	932.7	1022.1	74.6	Rb 3d = 111.3
CZACs, vac	934.5	1022.2	74.8	Cs 3d = 725.5
CZA$_{Cs}$, H_2	932.7	1022.1	74.8	Cs 3d = 725.3

Vacuum (vac) or reduction (H_2) pretreatment; CZA oxidized catalyst at 623 K was also included for comparison.

Cu/Zn and Al/Zn atomic ratios for CZA are 0.816 and 0.228 while the experimental values are 0.787 and 0.238, respectively. On the hand, the bulk Cu/Zn and Cu/Al atomic ratios for the CZA-M catalysts are quite similar to those determined for CZA, regardless the alkaline metal. This observation indicates that no metal loses have been produced along the preparation steps.

The specific BET surface area of the calcined CZA precursors was 46.6 $m^2 g^{-1}$ and this value was apparently not affected by the impregnation of the alkali promoters (Table 1). The exposed metallic area of copper of the calcined CZA catalyst was 25.6 $m^2 g^{-1}$ and this value decreases slightly upon incorporation of the alkali promoter (Table 1). For the CZA-Li catalyst the drop in the exposed metallic area of copper is much more marked. This is due to the fact that the atomic weight of Li is very low and hence the catalyst incorporates a higher number of Li mmoles for the same metal loading, i.e. the Li-loaded catalysts incorporates about three times higher mmoles than its Na counterpart.

The chemical state of copper and the relative abundance of the elements in CZA-M catalyst precursors subjected at different pretreatments have been determined by photoelectron spectroscopy. The binding energy of the most intense Cu $2p_{3/2}$ peak of the Cu 2p doublet of the representative CZA-K catalyst is shown in Fig. 2. The Cu $2p_{3/2}$ main peak appears at 934.0 eV is wide and asymmetric. The value of this binding energy and the appearance of a satellite structure at a binding energy somewhere around 943 eV are indicative of the presence of Cu(II) species. For all the samples, the binding energies (BE) of core electrons of the most abundant elements of the catalysts have been measured and they are collected in Table 2.

These binding energies were recorded for each catalyst subjected to different pretreatments: vacuum and H_2-reduction *in situ* at 493 K. The binding energies (BE) of Al 2p, Zn 2p and those of the alkali metals (Li 1s, K $2p_{3/2}$, Rb $3d_{5/2}$ and Cs $3d_{5/2}$) remained practically constant, even after different pretreatments. As shown in Fig. 2, the Cu 2p line profile of H_2-reduced catalyst is completely different from that of the calcined counterpart: not only the binding energy of Cu $2p_{3/2}$ peak shifted to lower value but also the satellite peaks disappeared. Both facts are indicative of the reduction of Cu^{2+} ions into metallic copper.

The X/Zn (X = Cu, Al, K, Li, Cs and Rb) surface atomic ratios were calculated and are presented in Table 3 for the vacuum treated and reduced catalysts. In all cases, the Cu/Zn surface atomic ratios were lower than the Cu/Zn bulk atomic ratio. The experimental Cu/Zn surface atomic ratios in catalysts CZA-M changed depending on the nature of the alkali precursor. After a vacuum treatment, the experimental Cu/Zn surface ratio increased in the order: Li < K < Rb < Cs. These results are consistent with the values of metallic area of copper summarized in Table 1. However, the alkali promoter seemed to stabilize the surface Cu/Zn ratio in the reduced catalysts and this effect was more important for catalysts containing higher atomic number alkali promoters, namely, Rb and Cs. Thus, the calculated Cu/Zn surface ratios were 0.720 and 0.290, for the vacuum

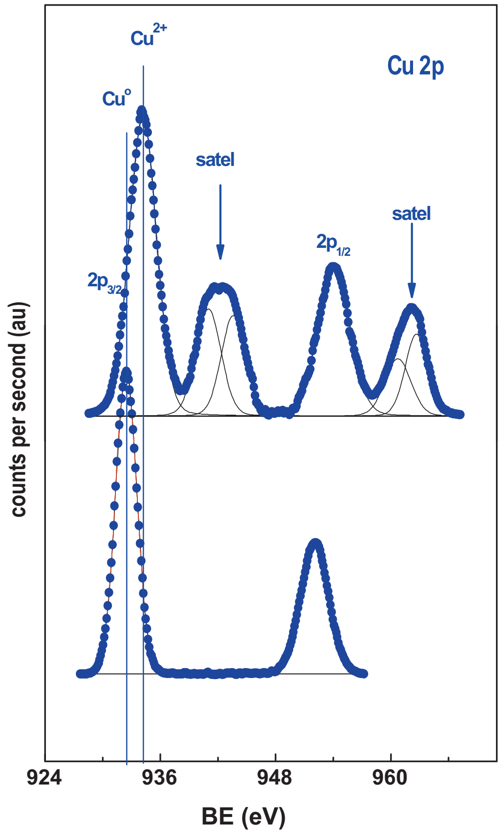

Fig. 2. Cu 2p core level spectra of the representative CZA-K catalyst precursor: calcined (top), and H_2-reduced at 493 K for 0.5 h (bottom). Arrows indicate the position of the satellite peaks of the principal (Cu $2p_{3/2}$ and Cu $2p_{1/2}$) lines.

Table 3
Surface atomic ratios of calcined, degassed and H_2-reduced samples relative to Zn.

Catalyst	Cu/Zn	Al/Zn	M/Zn
CZA, vac	0.72	0.70	–
CZA, H_2	0.29	0.58	–
CZA, O_2	0.49	0.63	–
CZA$_{Li}$, vac	0.253	0.351	0.742
CZA$_{Li}$, H_2	0.208	0.332	0.770
CZA$_K$, vac	0.571	0.294	0.171
CZA$_K$, H_2	0.503	0.274	0.187
CZA$_{Rb}$, vac	0.670	0.265	0.063
CZA$_{Rb}$, H_2	0.644	0.277	0.068
CZA$_{Cs}$, vac	0.701	0.219	0.033
CZA$_{Cs}$, H_2	0.643	0.288	0.035

Vacuum (vac) or reduction (H_2) pretreatment.

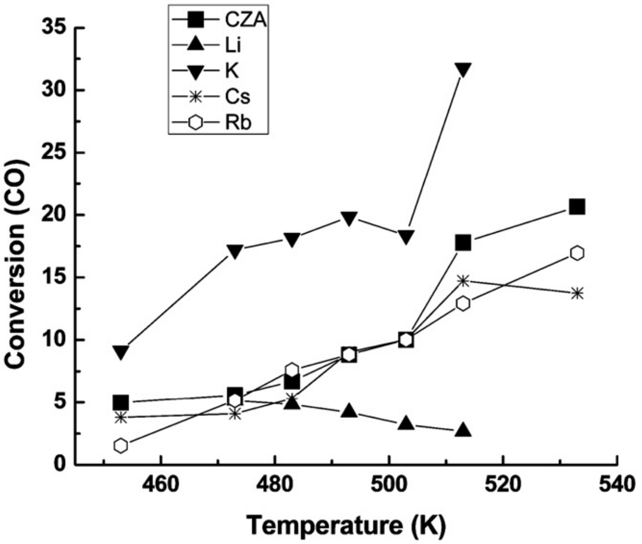

Fig. 3. CO conversion as a function of the reaction temperature for CZA and CZA-M catalysts: (■) CZA; (▲) CZA-Li; (▼) CZA-K; (✳) CZA-Cs; (○) CZA-Rb. Reaction conditions are given in Section 2.

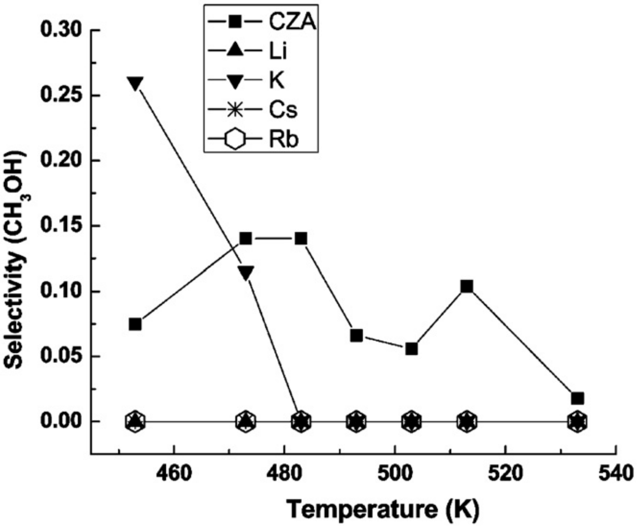

Fig. 4. Methanol selectivity as a function of the reaction temperature for CZA and CZA-M catalysts: (■) CZA; (▲) CZA-Li; (▼) CZA-K; (✳) CZA-Cs; (○) CZA-Rb. Reaction conditions are given in Section 2.

treated and hydrogen reduced CZA catalyst, respectively. For the vacuum treated and reduced CZA-Rb catalyst, Cu/Zn = 0.670 and 0.644, respectively. The Al/Zn surface atomic ratio was apparently less affected by presence of the alkali promoters, either in oxidized or in reduced catalysts. The Al/Zn ratio decreases for the reduced CZA-Li and CZA-K samples but follows an opposite trend for CZ-Cs and CZA-Rb catalysts suggesting an Al-enrichment. The X/Zn surface atomic ratio is practically not affected by the pre-treatment of the sample. The comparison of surface X/Zn ratios with the bulk ones indicates that the alkali promoters are essentially deposited on the outer surface of the catalyst, which is consistent with the impregnation methodology employed in this work.

CO conversion and methanol selectivity results are shown in Figs. 3 and 4, respectively, as a function of the reaction temperature. The conversion of CO increased with the increase of reaction temperature over the ternary CZA and CZA-M catalysts, with the only exception of the CZA-Li one. On the other hand, it is observed that the CO conversion is much higher over CZA-K catalyst than over the reference alkali-free CZA one and much lower over CZA-Li, but no significant effect on CO conversion is detected on CZA-Rb and CZA-Cs catalysts. In addition, in Fig. 4 it is shown that the alkali promoters are very efficient in preventing methanol production at temperatures higher than 480 K. This behavior seems to be independent either of the metallic surface area of copper; Cu/Zn atomic surface ratio or the nature of the alkali cation. In the range of 450–530 K, the selectivity toward H_2 was higher than 96%, over the investigated catalysts.

Both methanol synthesis and water gas shift reactions can occur in a system with five gaseous components (H_2, CO, CO_2, CH_4 and H_2O). These reactions may occur via a common intermediate or through a pathway that is entirely independent of methanol synthesis. It is hypothesized that the paths for both reactions proceed via nucleophilic activation of CO molecule and hence they will be accelerated in the presence of alkali metals which will render the counterions OH^-, HCO^- and $HCOO^-$ more reactive than the native components of the Cu/Zn catalyst. These reactions proceed over Cu-based catalysts exclusively according to a redox cycle involving copper and surface oxide, and the rates of reaction may indirectly influenced by the presence of alkaline metals [18,11,19]. In addition, it is possible to alter the amount of methanol produced across LTS catalysts by increasing the steam/gas (S/G) ratio to the reactor, which reduces the average operating temperature of converter, reducing the partial pressure of H_2 and CO and increasing the amount of process condensate downstream of the reactor. Reducing the partial pressure of H_2 and CO will decrease methanol produced. If extra steam is added, the amount of CO inlet the reactor will be lower. This helps reduce methanol make by reducing the CO partial pressure and average operation temperature of the LTS reactor [19–21].

As shown in a previous paper [22], high metallic copper surface areas were observed when Cu^{2+} and Zn^{2+} ions were simultaneously coprecipitated and a remarkable low temperature WGS activity was found to be related to the catalyst ability to restore the copper surface dispersion in a redox cycle. Notwithstanding the "wetting" of copper particles by the alkali hydroxide produced (melting points of the hydroxides are: 722 K for LiOH; 633 K for KOH; 545 K for CsOH; and 574 K for RbOH) under the reaction conditions is suggested to play a major role in both activation of CO molecule and/or desorption of CO_2 at the promoter-Cu interface. With the exception of CZA-Li catalyst, the other alkali promoted CZA-M catalysts form liquid alkali hydroxides which are in close contact with copper crystallites where the Activation of CO and the reactivity of formate (–OOCH) intermediate is altered, i.e. by weakening the formate C–H bond [23,24], thus facilitating CO_2 desorption instead to be hydrogenated to methoxide.

4. Conclusions

Alkali cations (1% by weight) have proved to be useful promoters for the CZA low temperature water gas-shift catalyst. The addition of alkali promoters (Li, K, Rb and Cs) by impregnation of the ternary CZA catalyst affects to some extent the exposed metallic area of copper but not the main phases and crystallinity determined by X-ray diffraction. However, no clear trend could be found relating the metallic surface area of copper to CO conversion, under the reaction conditions selected in this work. With the exception of CZA-Li catalyst, the other CZA-M catalysts tend to form liquid alkali hydroxides which are in close contact with Cu crystallites where the reactivity of formate (–OOCH) intermediate is altered, i.e. by weakening the formate C–H bond, thus facilitating CO_2 desorption instead to be hydrogenated to methoxide. Specifically, the CZA-K catalyst showed an increase in CO conversion with respect the

K-free CZA one and simultaneously it increased H_2 selectivity by inhibiting methanol production at temperatures higher than 480 K.

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