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Catalysis Today 100 (2005) 269–274

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Activation of carbon dioxide on Fe-catalysts

Marita Niemelä*, Milja Nokkosmäki

VTT Processes, P.O. Box 1602, FI-02044 VTT, Finland

Available online 20 January 2005

Abstract

Development and evaluation of novel catalysts capable of activating CO_2 especially in CO_2 hydrogenation have been investigated. Several catalysts have been prepared, and characterized by CO_2 TPD. Their performance has been evaluated at 300 °C and 10 bar. All catalysts were active in CO_2 hydrogenation reaction with conversions of approximately 15–30% at 24 h time on stream. Potassium was found to enhance chain growth and to decrease the formation of methane. Ru promoter did not provide any benefit in activity or selectivity. Zr-promoted catalyst materials exhibited enhanced CO_2 adsorption and improved hydrocarbon yields.

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Keywords: Iron catalysts; CO_2; TPR; Adsorption; TPD; Hydrogenation

1. Introduction

The need for greenhouse gas emission reduction has increased the interest also in chemical fixation and utilization of carbon dioxide [1]. Yet, to be able to reduce CO_2 emissions, all operations must have zero CO_2 release. In addition, the anticipated utilization processes require use of catalytic materials, which activate CO_2 at low or moderate temperatures and convert it to useful products such as olefins, alcohols or hydrocarbons in high yield.

An on-going Finnish research project is considering catalytic means for the activation of CO_2. The catalysts have been evaluated in dry reforming [2], methanol synthesis [3] and FT synthesis reaction. Hydrogenation via Fischer–Tropsch synthesis using $CO_2 + H_2$ as the feed has recently been studied by Lee and coworkers [4–6], Ando et al. [7,8] and by the research groups of Schaub [1,9] and Davis and coworkers [10]. Utilization of gasification gas originating from biomass or waste materials for methanol or FT synthesis has also gained attention [11].

FT reaction utilizing CO_2 proceeds in two steps: first a reverse water gas shift (RWGS) reaction takes place ($CO_2 + H_2 \rightarrow CO + H_2O$) and then the CO formed is consumed in the Fischer–Tropsch reaction ($CO + H_2 \rightarrow$ products) [9]. The reaction can be used as a challenging and industrially relevant model system for understanding the activation of carbon dioxide on heterogeneous catalysts and its role in FT synthesis. Iron is typically used as the active metal on the catalyst, and K and Cu are important promoters.

In this work, the effect of Ru and Zr promoters on iron catalysed CO_2 hydrogenation were tested. Three different preparation methods were applied and the temperature-programmed catalyst characterisation results were compared to the CO_2 hydrogenation activity. A widely studied Fe-Cu-Al-K catalyst [12] was used as a reference catalyst.

2. Experimental

The reference catalyst, comprising Fe-Cu-Al-K was coprecipitated from Al, Fe and Cu nitrates at 80 °C at pH of 7.0 using ammonia (aq) [12]. The precipitate was washed with water and dried at 110 °C for 12 h. Potassium was added by aqueous impregnation of K_2CO_3 followed by drying at 110 °C for 12 h and calcination at 450 °C for 6 h. Fe-Cu-Al-K-Ru was prepared by aqueous impregnation of ruthenium(III) chloride hydrate on Fe-Cu-Al-K (ref). The catalyst was dried at 110 °C for 12 h and calcined at 450 °C for 6 h.

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* Corresponding author. Tel.: +358 9 456 5935; fax: +358 9 456 7026.
E-mail address: marita.niemela@vtt.fi (M. Niemelä).

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doi:10.1016/j.cattod.2004.09.061

The second set, Fe-Zn-Cu, was prepared by coprecipitating Fe, Zn and Cu nitrates at 80 °C at pH of 7.0 using ammonium hydrogen carbonate [13]. The precipitate was washed with water, dried at 110 °C and calcined at 350 °C for 1 h. Potassium promoter was added as explained above to obtain Fe-Zn-Cu-K(3) and Fe-Zn-Cu-K(6), where the number in brackets refers to the potassium content of the catalyst. The Ru promoted sample was prepared by coimpregnation of K_2CO_3 and $RuCl_3$ using equilibration of 6 h, drying overnight at 110 °C and calcination at 400 °C for 4 h. The Zr- and K-promoted sample was prepared by impregnating the Fe-Zn-Cu first with a zirconium propoxide solution [14] and then with K_2CO_3 as explained above.

The third set of catalysts was prepared by using the solvent replacement (SR) method [13]. Thus, Fe-Zn-Cu (SR) differed from the second set only in the washing step where the precipitate was washed with alcohol instead of water. The promoted Fe-Zn-Cu-K (SR) and Fe-Zn-Cu-Zr-K (SR) samples were prepared by impregnation as explained above.

The BET-surface areas and the pore volumes of the calcined catalysts were measured with Micromeritics TriStar equipment. The metal contents were determined by wavelength-dispersive X-ray fluorescence spectrometry (XRF).

The dynamic CO_2 chemisorption and desorption studies were carried out with a quartz microreactor connected to a Balzers quadrupole mass spectrometer (MS). Ground and sieved catalyst samples (0.3–0.4 mm) of 0.6 g were dried in He (3 °C/min, 200 °C 2 h) and reduced by 3% H_2 in Ar (3 °C/min, 400 °C overnight) in situ (TPR). The samples were flushed with helium at 400 °C for 0.5 h and cooled to 30 °C. The CO_2 adsorption capacity at 30 °C was evaluated with ten pulses (1 ml) of CO_2 using He as a carrier gas (50 ml/min). Then the temperature was raised from 30 to 400 °C (20 °C/min) under He flow of 100 ml/min (TPD). Calibration was performed by pulses of a known volume of CO_2, CO or H_2, and by calculating the corresponding area for the intensity response versus time. The measured mass intensity of CO(28) was corrected in the presence of CO_2(44) by substracting the percentage of the 28-mass fragment of CO_2.

The fixed bed reactor and the activity test method for the CO_2 hydrogenation reaction has been desribed in more detail in a previous publication [15]. In experimental runs, 1 g of catalyst was reduced in situ at 400 °C for 10 h. The temperature was decreased to 300 °C, the reactor was pressurized with hydrogen, and the reaction was commenced at 300 °C and 10 bar using a flow rate of 2 l/h of a gas mixture CO_2:H_2:Ar in ratio 60:30:10.

3. Results and discussion

3.1. Temperature-programmed reduction

The catalysts were evaluated by TPR (see Fig. 1). Hydrogen consumption occurs mainly at 150–400 °C and is due to the simultaneous reduction of $CuO \rightarrow Cu$ (shoulder) and $Fe_2O_3 \rightarrow Fe_3O_4$. The reduction of iron catalysts by hydrogen is known to be a two or three-staged process [16–19]. That is, Fe_2O_3 is first reduced at 397 °C to Fe_3O_4, which is then reduced to metallic iron at 702 °C [17]. The data in Fig. 1 shows that the maximum temperature of reduction increased with potassium and the initial temperature of reduction decreased with addition of ruthenium. Nevertheless, in all tested catalysts, iron oxides were reduced to Fe_3O_4 and probably partly also to oxygen-deficient Fe_3O_4 species during the TPR to 400 °C. According to Iglesia and coworkers [20] the initial removal of only a very small amount of lattice oxygen from Fe_2O_3 facilitates the formation of the active sites during the FTS reaction.

3.2. CO_2 adsorption and desorption

CO_2 adsorption at 30 °C and subsequent desorption were measured for all samples. Typically, adsorption took place during the first pulses and simultaneously the temperature of the catalyst bed increased by some degrees centigrade. The determined CO_2 uptakes are shown for all catalysts in Table 1. The presence of Ru decreased the amount of CO_2 adsorption, while potassium significantly increased the CO_2 adsorption capacity—a result in accordance with literature findings [21]. Highest CO_2 uptake was achieved with the reference catalyst, Fe-Cu-Al-K (ref), which also exhibited the highest BET-surface area of 110 m^2/g. It should also be noted that the adsorption uptake measured by Yan et al. [21] for a precipitated Fe-Cu-Al-K (100:6.6:15.7:6) catalyst was higher (443 $\mu mol/g_{cat}$) than ours (304 $\mu mol/g_{cat}$). This was due to the higher BET-surface area (165 m^2/g) of their catalyst.

For the Fe-Zn-Cu-K(3) and Fe-Zn-Cu-K (SR) catalysts the CO_2 adsorption capacities were significantly lower than for the Fe-Cu-Al-K catalyst, but so were also the surface areas. Accordingly, the CO_2 uptake/m^2_{cat} was fairly similar for Fe-Cu-Al-K and Fe-Zn-Cu-K(3), and lower for Fe-Zn-Cu-K (SR), see Table 1. Previously Nam et al. [22] have suggested that addition of Zn to iron increases the amount of CO_2 chemisorbed on the catalyst. In our experiments, the CO_2 uptake/m^2_{cat} was either slightly higher or lower in the presence of Zn.

Adsorption of CO_2, which is an acidic gas, takes place on basic sites. With this view, a fairly recent paper has introduced a superbase material, a zirconia-supported potassium nitrate, with enhanced CO_2 uptake [23]. It has also been argued that activation of CO_2 takes place on the Zr atom [24]. The present results also indicated that addition of Zr clearly improved the adsorption capacity of CO_2. That is, the zirconium and potassium promoted Fe-Zn-Cu-Zr-K (SR) exhibited a significantly higher uptake (150 $\mu mol/g_{cat}$) than did the potassium promoted Fe-Zn-Cu-K (SR) catalyst (58 $\mu mol/g_{cat}$). This data from our experiments and the results on the FT catalysts such as Fe/ZrO_2 and $Fe/K/ZrO_2$

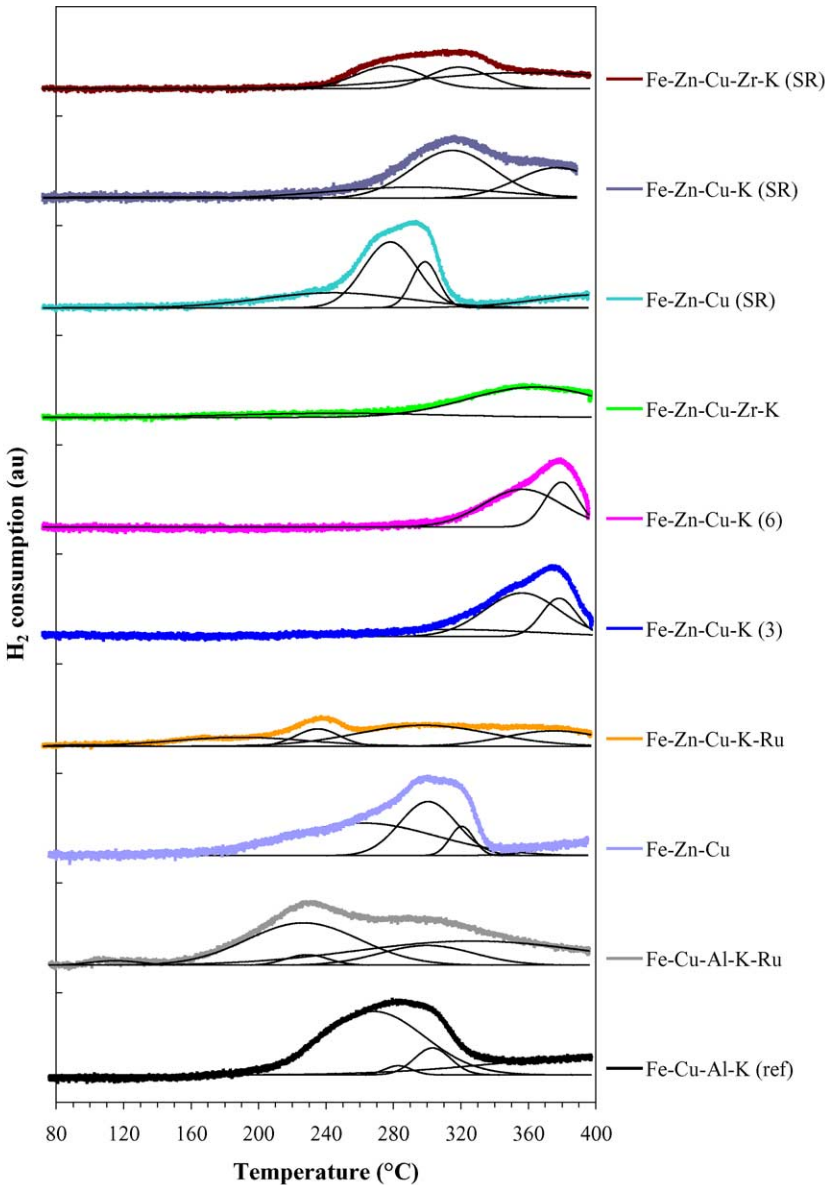

Fig. 1. Hydrogen consumption and Gaussian deconvolution of bands for the Fe-catalysts during TPR.

Table 1
Metal contents, BET-surface areas and pore volumes and CO_2 adsorption capacities at 30°C of catalyst materials

Catalyst	Fe (%)	M (%)	Cu (%)	K (%)	BET (m^2/g)	PV BHJ (cm^3/g)	CO_2 uptake ($\mu mol/g_{cat}$)	CO_2 uptake ($\mu mol/m^2_{cat}$)
Fe-Cu-Al-K (ref)	53	7 Al	3	3	110	0.17	304	2.8
Fe-Cu-Al-K-Ru	53	7 Al 1 Ru	3	2	94	0.17	186	2.0
Fe-Zn-Cu	63	5 Zn	0.5		32	0.18	17	0.5
Fe-Zn-Cu-K(3)	60	5 Zn	0.5	3	22	0.15	63	2.9
Fe-Zn-Cu-K(6)	58	5 Zn	0.5	6	10	0.12	46	4.6
Fe-Zn-Cu-K-Ru	60	5 Zn 1 Ru	0.5	2	23	0.17	7	0.3
Fe-Zn-Cu-Zr-K	55	5 Zn 6 Zr	0.4	5	5	0.06	55	–
Fe-Zn-Cu (SR)	62	7 Zn	0.7		78	0.19	49	0.6
Fe-Zn-Cu-K (SR)	59	7 Zn	0.7	3	58	0.15	58	1.0
Fe-Zn-Cu-Zr-K (SR)	57	7 Zn 4 Zr	0.6	3	58	0.14	150	2.6

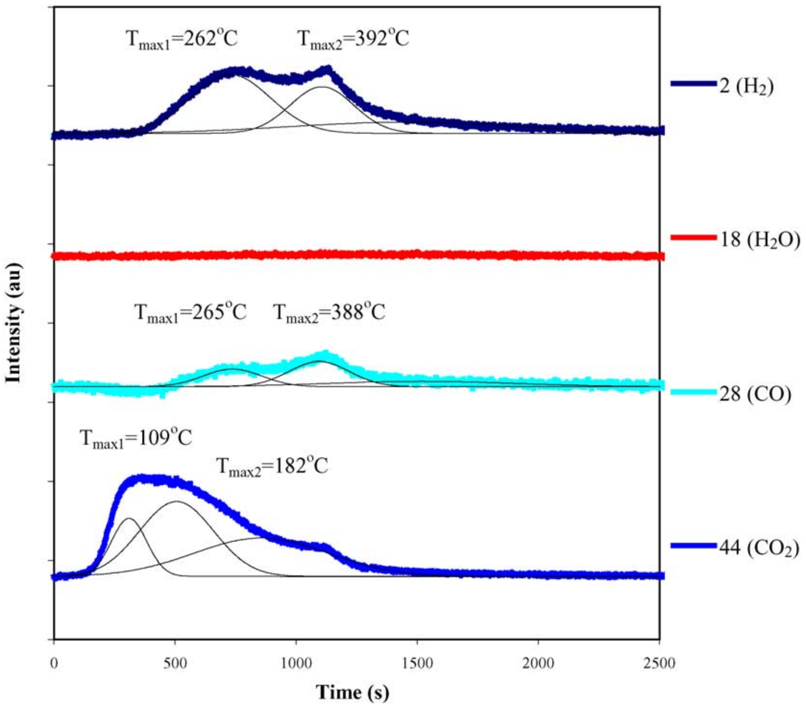

Fig. 2. TPD results after CO_2 pulsing at 30 °C for Fe-Cu-Al-K (ref).

[25] suggest that Zr may well be a suitable component for activation of CO_2 in the two-staged FT reaction.

During the TPD, carbon dioxide, carbon monoxide and hydrogen were desorbed from the catalysts. With the reference catalyst Fe-Cu-Al-K (ref) the peak maxima temperatures determined by Gaussian deconvolution were 109 °C and 182 °C for CO_2. And, CO and H_2 were desorbed simultaneously at temperatures of approximately 260 and 390 °C (see Fig. 2). The lower simultaneous desorption of CO and H_2 at 260 °C may be ascribed to the presence of surface species such as formate [26] or carbonate [27]. Values very similar to ours have been observed by Zhang et al. [28] who measured TPD after CO_2 adsorption at room temperature by TCD (RT-20 °C/min-800 °C). They observed a molecular CO_2 desorption peak at 182 °C and a CO peak at 337 °C. They also noted that the decomposition of carbon dioxide into carbon on oxygen-deficient magnetite ($Fe_3O_{4-\delta}$, $\delta > 0$) occurs in two steps: $CO_2 \rightarrow CO + O^{2-}$ and $CO \rightarrow C + O^{2-}$, and simultaneously, $Fe_3O_{4-\delta}$ captures the oxygen released by CO_2 and converts itself into stoichiometric Fe_2O_3. The deactivated magnetite could easily be regenerated by H_2 reduction (formation of water) [28]. In our TPD experiment, no formation of water was observed although hydrogen was detected (see Fig. 2).

TPD data on the desorbed amounts of CO_2, CO and H_2, and the calculated amounts of carbon on the surface of the catalysts are shown for all samples in Fig. 3. This figure shows that CO_2 was at least partly dissociated on the

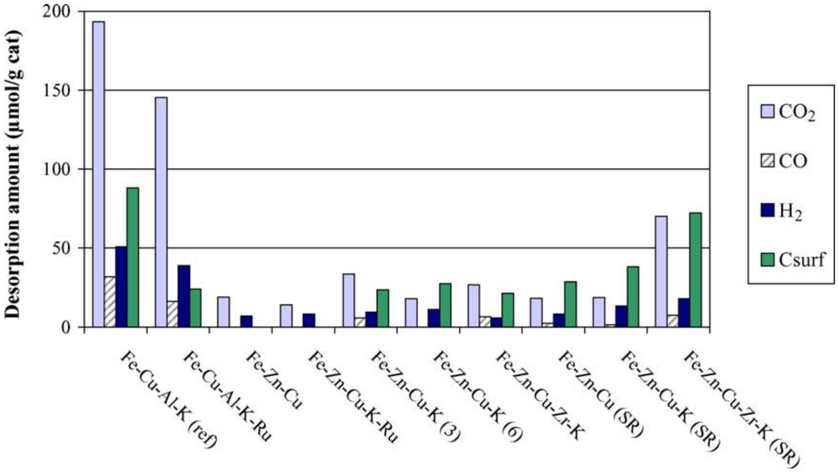

Fig. 3. Desorption amounts of various compounds after CO_2 pulsing for all catalysts. Carbon on the surface (C_{surf}) is calculated by subtraction.

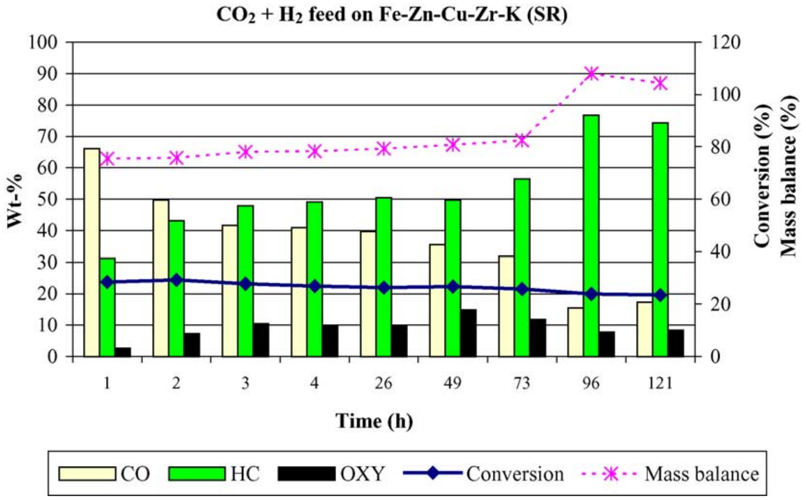

Fig. 4. An illustrative example of CO_2 hydrogenation data for catalyst Fe-Zn-Cu-Zr-K. CO = carbon monoxide, HC = hydrocarbons, OXY = oxygenated compounds.

catalysts and in part decomposed further to carbon. Therefore, the amount of carbon on the surface of the catalyst (C_{surf}) may be considered as an indication of the dissociative adsorption of CO_2. The amount of C_{surf} was highest for the Fe-Cu-Al-K (ref) and the Fe-Zn-Cu-K-Zr (SR) catalysts. The percentage of C_{surf} of the adsorbed CO_2 were 28% and 48%, and the desorbed amounts of CO were 10% and 5%, respectively. Therefore, the propensity for CO_2 decomposition was highest for the zirconium containing catalyst Fe-Zn-Cu-K-Zr (SR).

3.3. CO_2 hydrogenation

In CO_2 hydrogenation, the catalysts reached a fairly constant level of conversion of approximately 15–30% in about 24 h. The data quotations refer to 100 h of time on stream. The products comprising of CO, hydrocarbons and oxygenates have been normalized to 100% [15] as illustrated in Fig. 4.

In general, the K-promoted catalysts exhibited a higher conversion than did the unpromoted ones in accordance with the findings of Lee and coworkers [21] at 265 °C and Luo et al. [29] at 230 °C. Yet, the effect of K-promotion was more notable than that observed by Lee and coworkers [21]. For example, the conversion obtained for Fe-Zn-Cu was 18% compared to 27% for Fe-Zn-Cu-K(6). The products formed on all of the K-promoted catalysts were highly olefinic and the product distribution obeyed the Schulz–Flory polymerization law as also observed previously [9]. For example, the probability of chain growth, alpha (calculated from C_3 to C_8)

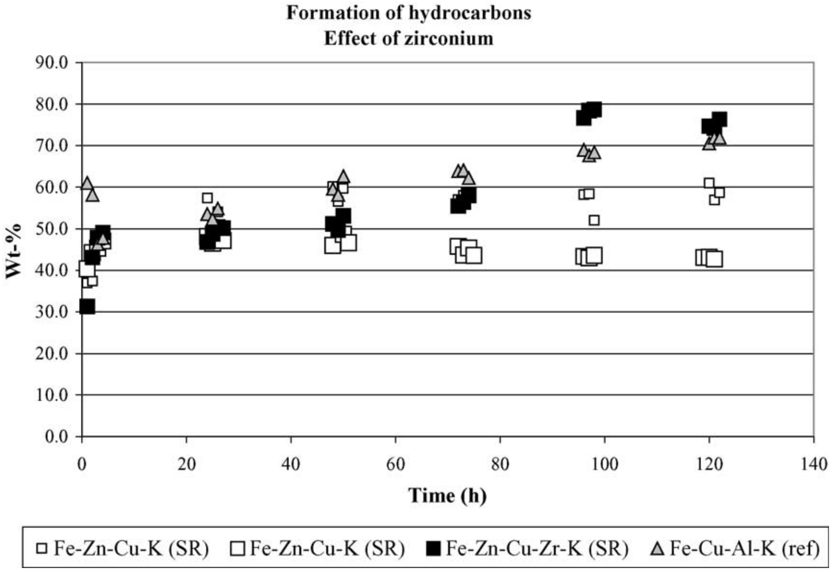

Fig. 5. The effect of zirconium promotion on the amount of hydrocarbons in the product as a function of reaction time.

was 0,42 for Fe-Zn-Cu and 0,65 for Fe-Zn-Cu-K(6). In addition, K-promoted catalysts produced a lower amount of methane and a higher amount of oxygenated products than did the unpromoted ones. That is, Fe-Zn-Cu gave approximately 30 wt.% methane and 1 wt.% oxygenates, whereas Fe-Zn-Cu-K(6) produced approximately 7 wt.% methane and 10 wt.% oxygenates. These changes in selectivity also resemble those obtained before by others [21,29].

In our work, the catalysts containing a Ru promoter showed a slightly lower activity than the nonpromoted ones in contrast to the literature findings in classical FT synthesis utilizing $CO + H_2$ [30]. In case of our Ru-containing catalysts, the selectivity to methane was higher, the overall selectivity to hydrocarbons was lower and surprisingly the alpha-values were lower than for the unpromoted catalysts. The effects were more pronounced in the presence of zinc. For example, conversion for Fe-Zn-Cu-Ru-K was 20% compared to 25% for Fe-Zn-Cu-K, and selectivity to methane was 15% compared to 4%, respectively. Thus, the addition of Ru promoter did not give any benefit in activity or selectivity, rather vice versa. This result is contradictory to the recent findings of Lee et al. [31].

Considering Zr-promotion, the activity of Fe-Zn-Cu-K was similar to Fe-Zn-Cu-Zr-K, and no selectivity benefit was observed. Similarly, in case of Fe-Zn-Cu-K (SR) and Fe-Zn-Cu-Zr-K (SR) the activity was similar, but an interesting change in selectivity was observed (see Fig. 5). The data indicate that with increasing time on stream the selectivity to hydrocarbons increases rapidly. Apparently, the hydrocarbons formed during the synthesis reaction start to flow as "droplets" into the analysis system thus changing the proportion of different products in the product stream. It is evident that the formation of these heavier hydrocarbon products is clearly enhanced in the presence of Zr.

4. Conclusions

All catalysts studied in this work were active in CO_2 hydrogenation with conversions of approximately 15–30% at 24 h of time on stream. Potassium was found to enhance the chain growth of hydrocarbons and to decrease formation of methane. On our catalysts Ru promoter did not provide any benefit in activity or selectivity. Our Zr-promoted catalyst materials exhibited enhanced CO_2 adsorption and improved hydrocarbon yields.

Acknowledgements

The financial support from VTT Clean World Theme, TEKES National Technology Agency of Finland, Fortum Oil, and Conox is greatly appreciated. The authors thank the project group members from Helsinki University of Technology and University of Oulu for co-operation. The personnel of VTT Processes, especially Dr. M. Reinikainen, Ms. Päivi Jokimies, MSc., K. Karinto, Mr. T. Klasila, and Ms. P. Launiainen are acknowledged for the technical and analytical assistance.

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