

## TPR AND INFRARED MEASUREMENTS WITH Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> BASED CATALYSTS FOR THE SYNTHESIS OF METHANOL AND HIGHER ALCOHOLS FROM CO + H<sub>2</sub>

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### SUMMARY

The influence of different promoters (CeO<sub>2</sub>, MnO<sub>x</sub>, K<sub>2</sub>CO<sub>3</sub>) on various properties of a standard coprecipitated Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst has been examined. The catalysts prepared were characterized by Cu surface area, FTIR and TPR measurements. It was found that addition of K<sub>2</sub>CO<sub>3</sub> reduced the Cu surface area by about 30%, whereas the Cu surface area did not decrease with addition of the other promoters. The reduction behaviour was affected by the addition of K<sub>2</sub>CO<sub>3</sub> as well as by MnO<sub>x</sub>, but not by CeO<sub>2</sub>. The cause of these effects is possibly an electronic interaction between the promoter and Cu ions. The effect of the different promoters on the activity and selectivity has also been studied. The K<sub>2</sub>CO<sub>3</sub> promoted catalyst has an optimum selectivity to higher alcohols at 280 °C; addition of Mn made the catalyst more selective towards methanol. At 300 °C, the Ce promoted catalyst had a high selectivity to methanol and iso-butanol. The promoting effect of the additives may be caused by stabilization of the surface intermediates leading to alcohols. Infrared measurements of adsorbed CO or adsorbed methanol on materials with and without K did not, however, provide any evidence for a difference in reaction mechanism.

### INTRODUCTION

Pure methanol may, in the future, become a replacement for lead-free fuels. However, until that occurs, it may also be blended with petrol to increase octane number. In order to overcome problems of phase separation of the petrol and methanol, caused by the inevitable presence of water, a quantity of higher alcohols must be added. These higher alcohols, especially those with branched chains such as iso-butanol, have a further advantage: they give a further increase in the octane number of the resultant fuel mixture.

Methanol is produced industrially from synthesis gas using Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst [1]. It has been found that promotion of this type of catalyst with an alkali metal ion changes the selectivity such that mixtures of methanol with a small percentage of higher alcohols can be produced [2]. Promoters other than the alkali metals have also been mentioned in the literature; for example, the addition of MnO<sub>x</sub>, Cr<sub>2</sub>O<sub>3</sub> or ThO<sub>2</sub> has been reported in the open literature and also patented by Kochloefl et al. [3,4,5]. The use of lanthanides as promoters, in combination with the alkali metals, cobalt and manganese, has also been mentioned in the patent literature [6]. The reaction mechanisms described in the literature for this type of catalyst are all based on the assumption that consecutive reaction steps occur and that methanol is the primary product. The addition of small methanol- and ethanol-like species [2,7,8] or of CO [9] to a growing chain then leads to the formation of the higher alcohols.

We have previously reported [10] the results of experiments in which the effect of residence time and other parameters on the product distribution was examined for a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst promoted by K<sub>2</sub>CO<sub>3</sub>, MnO<sub>x</sub>, or CeO<sub>2</sub>; these results were in agreement with the type of reaction mechanism outlined above. We also described the effect of the different promoters on the structural and physical properties of the catalyst. This paper gives a brief summary of some of the previously work [10] and then presents the results of experiments aimed at characterizing the catalyst systems used and giving more information on the reaction mechanism; temperature programmed reduction (TPR) was used to examine the interaction between the promoter and the copper, while in-situ Fourier Transform Infrared (FTIR) spectroscopy was used to investigate the nature of the surface species resulting from adsorption of CO or methanol or during the reaction of CO with hydrogen at pressures of about three atmospheres. As copper-containing catalysts turn black on reduction, infrared experiments of this type described in the literature for Cu-containing catalysts have up to now only used methods in which an infrared-transparent support such as SiO<sub>2</sub> was used [11] or the catalyst was diluted considerably [12,13]. We have been able to surmount the difficulties of non-transparent samples by using diffuse reflectance (DRIFT) techniques; we believe that the work presented here represent the first investigations using such samples to have been reported.

## EXPERIMENTAL

### Catalyst Preparation

A standard Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts with a Cu:Zn:Al molar ratio of 9:9:2 was prepared by coprecipitation from a solution of the metal nitrates using a solution of K<sub>2</sub>CO<sub>3</sub>; the temperature and pH were kept constant during precipitation. In order to remove all the residual potassium, the resultant material was washed twice with water; it was then dried at 80° C and calcined overnight at 350° C. Two of the promoted samples examined (promoter CeO<sub>2</sub> or MnO<sub>x</sub>) were coprecipitated in the same way by adding the appropriate nitrate to the solution of Cu, Zn and Al nitrates; the promoters concentrations were either 4 or 6 mole% Mn and 4 mole% Ce with respect to the metal ions. In the case of the potassium-promoted catalysts, pore-volume impregnation of the calcined material (which had been shaped into pellets after calcination) was carried out using a K<sub>2</sub>CO<sub>3</sub> solution. The impregnated pellets were calcined at 350° C in air. For comparison purposes, impregnation by K<sub>2</sub>CO<sub>3</sub> was also carried out using a commercial methanol-synthesis catalyst (BASF S3/85). The composition of this catalyst, before adding the potassium, was comparable to that of the unpromoted catalyst prepared by the method described above.

### Catalyst Characterization

Copper metal surface areas were measured using the N<sub>2</sub>O decomposition method ("Reactive Frontal Chromatography") described by Chinchén et al. [14]. Prior to these measurements, the catalyst was reduced in-situ at temperatures up to 240 °C in a 10%H<sub>2</sub>/Ar mixture, using a heating rate of 1 K min<sup>-1</sup>. The progress of this temperature programmed reduction (TPR) treatment was monitored by a thermal conductivity detector (TCD).

Infrared measurements were carried out with a Nicolet 20 SXB FT Infrared Spectrometer fitted with a Barnes diffuse-reflectance cell and incorporating a controlled-environmental chamber. Adsorption of CO and of methanol on a BASF catalyst both with 0.5 wt%  $K_2CO_3$  and without  $K_2CO_3$  were studied in this equipment, as well as *in situ* reactions of  $H_2 + CO$  at a pressure of 300 kPa. Reduction was carried out *in situ*, before either the adsorption measurements or reaction, at 170 °C in a 2%  $H_2/N_2$  mixture; the hydrogen content was then stepwise increased up to 100%, after which the temperature was increased to 240 °C.

#### Measurement of Activity and Selectivity

The activities and selectivities of the catalysts were measured in a tubular reactor operating at pressures up to 7 MPa. The feed gas consisted of CO and  $H_2$  (molar ratio = 1). The products were analyzed using a Varian 3300 gas chromatograph equipment with a Chrompack Hayesep R column. Prior to the reaction the catalyst was reduced *in-situ* in a mixture of 2%  $H_2$  in nitrogen at a pressure of about 200 kPa at temperatures rising to 240 °C, with a heating rate of 0.7 K  $min^{-1}$ ; when the temperature had reached 240 °C, the gas flow was changed to pure hydrogen for one hour prior to the start of the experiment. The conditions used in the comparative experiments with catalysts promoted in the different ways described here were as follows: P = 40 Bar; T = 240-300 °C;  $H_2/CO = 1$ ; catalyst weight = 1 g.; and flow rate = 1.92 l  $h^{-1}$ . Any deviation from the conditions given above are stated where appropriate.

## RESULTS AND DISCUSSION

### Copper Surface Areas

The results of measurements of the copper surface area have been reported elsewhere [10] and will thus only be summarized here. The copper surface area of an un-promoted BASF catalyst was found to have an average value of 23.1  $m^2g^{-1}$  catalyst. Addition of potassium caused an initial sharp decrease (30%) in the copper surface area; however, at higher values of potassium content, the Cu surface area had become more or less constant [10]. It was concluded that potassium has its greatest effect at the surface of the copper.

In contrast to what was found with potassium additions, the copper surface area increased slightly as a result of the addition of Mn. The materials with Ce additions (2-4 mole%) had slightly lower copper surface areas than the unpromoted catalyst. It would thus appear that partial coverage of the Cu surface by the promoter ions is not so likely to occur in those samples in which the promoters were added by coprecipitation.

### Reduction Behaviour

Fig. 1 shows TPR data for the reduction of the standard catalyst and of samples to which different amounts of  $K_2CO_3$  had been added. Each profile was in the form of a peak with a distinct shoulder which occurred at either higher or lower temperatures. As the concentration of potassium was increased, the shoulder at lower temperatures grew until it was the major component; with the sample containing 0.69 wt%  $K_2CO_3$ , the two constituent peaks had about the same magnitude. Furthermore, the temperature required for total reduction shifted to higher values with increasing potassium content. These results seem to be indicative of copper in two

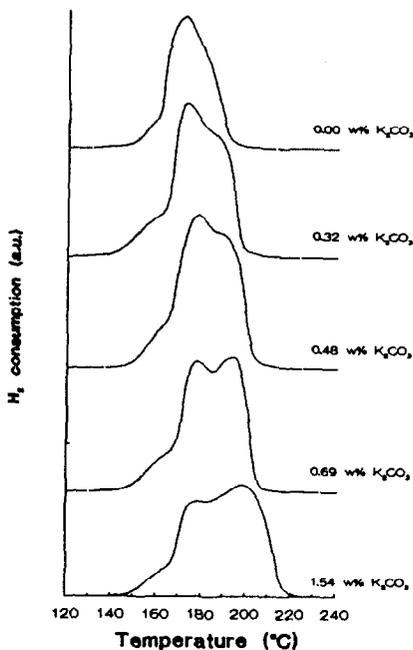


Fig. 1. TPR profiles of Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst impregnated with different amounts of K<sub>2</sub>CO<sub>3</sub>. The y-axis is shifted for the different profiles.

different environments. A similar behaviour was found as a result of the addition of Mn [10]. Addition of cerium (up to 4 wt%), however, had no influence upon the reduction behaviour. The total amount of CuO that could be reduced at the uppermost temperature was not affected by the presence of the promoter in any of the cases studied.

The increase in the temperature required to bring about reduction when potassium was added (Figure 1) can possibly be explained by the occurrence of partial coverage of the surface by promoter-compounds, as was suggested in the preceding paragraph (Cu surface areas). In the case of the addition of Mn, however, there is no reason to suggest that coverage of the surface occurred, as the copper surface area increased rather than decreased. Hence, the corresponding shift of TPR peaks to higher temperatures must be related to some other phenomenon, for example, to an electronic interaction between the Mn and Cu ions, resulting in a strengthening of the Cu-O bond.

#### Infrared Measurements

Figures 2 and 3 show FTIR results for adsorption of CO on an unpromoted and a K-promoted Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> catalyst, and Figure 4 shows equivalent results for the adsorption of methanol. The adsorption of CO was carried out at room temperature and also at higher

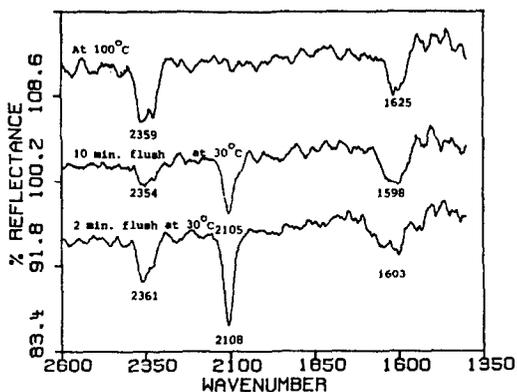


Fig. 2. Infrared spectra of CO adsorbed on a reduced and subsequently reoxidised Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst surface, during flushing with nitrogen after adsorption.

temperatures, using a stream of pure CO at atmospheric pressure which was passed over the catalyst for 30 minutes. For the methanol adsorption experiments, a stream of nitrogen saturated with methanol at 30° C was used. The catalyst samples used were either a freshly (in-situ) reduced material or one which had been reduced and then partially reoxidized with N<sub>2</sub>O; the latter was assumed to have a surface layer consisting of Cu<sub>2</sub>O, this being roughly equivalent to the oxygen coverage of the surface during methanol synthesis with CO<sub>2</sub> is present in the feed gas [15].

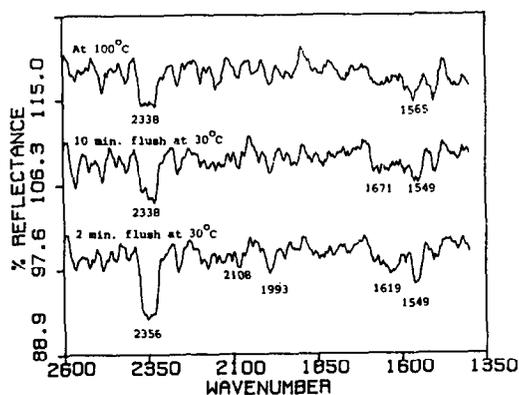


Fig. 3. Infrared spectra of CO adsorbed on a K-Promoted Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst during flushing with nitrogen. Pretreatment of the catalyst was as for the sample used for Fig. 2.

Under the present experimental circumstances, there was no evidence that CO was adsorbed to any appreciable extent on the reduced materials. However, (see the bottom curves of

Figures 2 and 3), it adsorbed on the reoxidized materials as uni-dentate CO molecules (the peaks at  $2105 - 2108 \text{ cm}^{-1}$ ); some  $\text{CO}_2$  was also formed (the peaks at  $2338 - 2361 \text{ cm}^{-1}$ ). Furthermore, flushing with a nitrogen stream caused the amount of adsorbed CO on the non-promoted catalyst to decrease (Fig. 2), although there was still a significant amount of CO on the surface after 10 minutes. However, the amount of CO adsorbed on the material containing potassium was already so small after flushing for two minutes that the peak at  $2108 \text{ cm}^{-1}$  could hardly be distinguished from the background noise. Upon increasing the temperature up to  $100^\circ\text{C}$ , all the adsorbed CO disappeared from both samples. There was no evidence from the FTIR results of Figs. 1 and 2 for the cleavage or weakening of CO bonds or of the formation of different types of adsorbed CO species as a result of the addition of potassium to the catalyst. However a small band was evident at around  $1600 \text{ cm}^{-1}$ ; according to Edwards and Schrader [12], this band may correspond to an O-C-O species or possibly to an M-C-O species. In contrast to these results, preliminary FTIR experiments under the same conditions as used here with  $\text{CuCo/ZnO/Al}_2\text{O}_3$  catalysts (both with and without  $\text{K}_2\text{CO}_3$ ), materials which have been shown to give high selectivities to higher alcohols [16], gave evidence for weakening of the CO band [17]; in addition to the band corresponding to linearly adsorbed CO ( $2108 \text{ cm}^{-1}$ ), a band was found at about  $1970 \text{ cm}^{-1}$ , this being indicative of a bridged CO molecule lying flat on the surface.

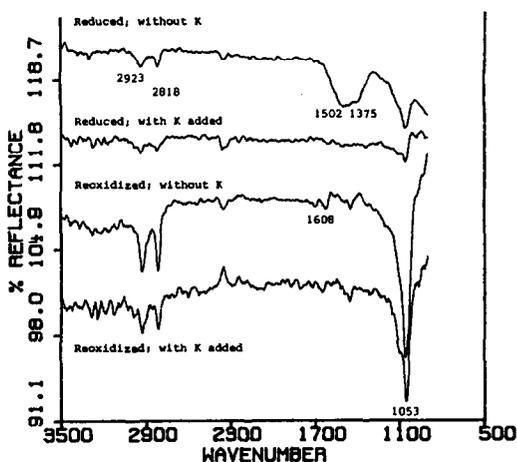


Fig. 4. Infrared spectra of methanol adsorbed on  $\text{Cu/ZnO/Al}_2\text{O}_3$  with or without  $\text{K}_2\text{CO}_3$ . Pretreatment, reduced or reduced and reoxidized, as indicated.

Figure 4 shows the results obtained with the unpromoted and promoted catalysts for the adsorption of methanol on the reduced and reoxidised surfaces; the upper two spectra correspond to the reduced catalysts and the two lower ones to the materials oxidized by  $\text{N}_2\text{O}$ . Adsorption bands were found at  $1053$ ,  $2818$  and  $2923 \text{ cm}^{-1}$  for each of the samples and these were due to the adsorbed methanol. In the case of the reduced sample without K, a peak centred

at  $1500\text{ cm}^{-1}$  appeared which was probably due to  $\text{CO}_3^{2-}$  formation; this contrasts with the material with K, with which no  $\text{CO}_3^{2-}$  was observed. The reoxidized materials did not show any  $\text{CO}_3^{2-}$ . Less methanol was adsorbed on the material with K, either reduced or re-oxidized, than on the materials without K; this may have been caused at least partially by the decrease in surface area upon addition of potassium.

Although it is not shown in the figures, it was observed that the formation of both (gas phase) methyl formate and  $\text{CO}_2$  took place during methanol adsorption at  $150\text{-}200\text{ }^\circ\text{C}$ . The catalyst with K gave rise to more of these products than did the catalyst without K. The selectivity measurements reported previously [10] showed that methyl formate was one of the minor products formed at a pressure of 40 bar.

When experiments were carried out with the  $\text{CO}+\text{H}_2$  mixture at long contact times (i.e. low flow rates) and high temperatures ( $300\text{ }^\circ\text{C}$ ), gaseous methanol and  $\text{CO}_2$  were both formed, infrared peaks due to adsorbed  $\text{HCOOH}$  (peaks in the range  $1580\text{-}1620\text{ cm}^{-1}$ ) and  $\text{H}_2\text{CO}$  (peaks in the range  $2600\text{-}2900\text{ cm}^{-1}$ ) species were found; the concentrations of these intermediates seemed to be higher at the surface of the promoted catalyst than at the surface of the non-promoted catalyst. There was, however, no evidence for the existence of intermediates consisting of more than one C-atom, i.e. species which could lead directly to higher alcohols instead of to methanol. Alcohols higher than methanol may have been produced as gaseous products in very low concentrations (weak bands in the region  $900\text{-}1500\text{ cm}^{-1}$ ). Further experiments of this type are in progress with the intention of identifying these species.

#### Activity and Selectivity Data

The detailed activities and selectivities were given elsewhere [10] and will therefore only be summarized here. It was found that the addition of about 0.5 wt%  $\text{K}_2\text{CO}_3$  gave the highest selectivity to higher alcohols; the synthesis of methanol was also promoted by this amount of  $\text{K}_2\text{CO}_3$ . At temperatures of  $280\text{ }^\circ\text{C}$  and above, significant quantities of  $\text{CO}_2$  and alkanes were produced in addition to higher alcohols. At  $280\text{ }^\circ\text{C}$ , the potassium-promoted catalyst produced more than 60% of methanol and 19% of higher alcohols; this is approximately the proportion of higher alcohols that is needed if this mixture were to be blended with petrol [18]. Due to equilibrium limitations, the amount of methanol formed at  $300\text{ }^\circ\text{C}$  was substantially lower than that formed at  $280\text{ }^\circ\text{C}$ .

Results showing the effect of the addition of Mn are presented in Table 1. At  $280\text{ }^\circ\text{C}$ , the selectivity to methanol was much higher than that of the unpromoted catalyst. Higher alcohols were only formed in significant amounts at  $300\text{ }^\circ\text{C}$ .

When, however, potassium was added to a Mn promoted catalyst, the selectivity to methanol increased significantly and the selectivity to higher alcohols (and also to  $\text{CO}_2$  and ethane) decreased further. It appeared that a synergy existed between K and Mn ions and that this helped in the selective formation of alcohols (mainly methanol).

Cerium-promoted catalysts were found to have a somewhat lower selectivity to methanol at temperatures up to  $280\text{ }^\circ\text{C}$ , but the selectivity to higher alcohols was significant; see the last column of Table 1. This cerium-promoted catalyst also produced somewhat more by-products ( $\text{CO}_2$ ,  $\text{CH}_4$ , ethane) compared to the unpromoted or the potassium-promoted catalyst [10]. It is

TABLE 1

The selectivities of promoted catalysts compared to those of a non-promoted catalyst at different temperatures. P = 40 bar; H<sub>2</sub>/CO = 1; 1 g. of catalyst; flow rate 1.92 l/h/ S<sub>tot</sub> gives the total selectivity to all alcohols ( including methanol) while S<sub>ha</sub> give the selectivity to higher alcohols.

	T(°C)	none	4%Mn	4%MN + 0.5%K	4%Ce
Act. (mmol/g/h)	260	7.2	6.7	5.3	7.1
	280	8.9	7.9	6.5	8.3
	300	9.9	9.2	6.9	-
S <sub>tot</sub> (C-atoms converted)	260	85.9	92.5	93.7	84.3
	280	74.4	77.4	84.1	68.2
	300	44.9	51.0	58.5	-
S <sub>ha</sub> (C-atoms converted)	260	5.5	4.9	1.1	6.6
	300	15.2	9.5	4.2	19.9
	300	14.2	17.0	13.7	-

of interest to note that in the case of 4% Ce addition, the alcohols formed were not equally distributed but that methanol, 1-propanol and iso-butanol were the main alcohols produced. Since iso-butanol in the alcohol mixture has many advantages compared to other alcohols [18], Ce appears to be a promising additive for further examination. The activity of this catalyst has not yet been measured at temperatures higher than 280 °C, but this will be done in the near future.

### CONCLUDING REMARKS

It can be concluded that the addition of K<sub>2</sub>CO<sub>3</sub>, MnO<sub>x</sub>, or CeO<sub>2</sub> to a Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst had an effect on the structural and textural properties of the material. The addition of K<sub>2</sub>CO<sub>3</sub> decreased the Cu surface area strongly. CeO<sub>2</sub> had the smallest influence on those physical properties which were examined. In spite of the decrease in Cu surface area, the total activity for the production of alcohols increased initially upon the addition of K<sub>2</sub>CO<sub>3</sub>.

Kochloefl et al. [3] have suggested that impregnating a CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> material with a solution of promoter decreases the pore size of the material; due to the longer residence time in these smaller pores, the chance of chain growth to give higher alcohols is significantly increased. As the pore size is probably unaffected with the Mn promoted catalysts (the copper surface area does not change), it might be expected that these will then produce smaller amounts of higher alcohols, which has indeed been established. When, however, potassium was added to a Mn-promoted catalyst, one would have expected the selectivity to higher alcohols to have

increased because of a decrease in pore size, but this was not the case. Ce addition, without the addition of K, also caused an increase in the formation of iso-butanol. We therefore conclude that the effect of addition of potassium, manganese or cerium ions is largely a surface effect: sites are created which favour the formation of either more methanol (Mn) or more higher alcohols (K, Ce).

Infrared measurements suggest that the reaction sequence leading to a mixture of alcohols is very closely related to that for methanol synthesis. To explain the effect of the addition of alkali metal ions, a number of mechanisms has been suggested in the literature. Klier et al. [8] proposed that a negatively charged  $\beta$ -keto alkoxide, stabilized by positive surface ions, was an intermediate. Mazanec [9] suggested that the most important intermediate species was an enolate, the role of the alkali being the same as in the mechanism of Klier et al. With our catalysts, the positive surface ion could be a  $K^+$ . In the materials without  $K_2CO_3$ , the variable valencies of the Mn and Ce ions (changing from the 4+ state to the 3+ state) could partly oxidize the Cu present in the Cu crystallites (or in the ZnO lattice) to  $Cu^+$  and these ions could then provide the necessary centres. Another possibility is that the Ce and Mn ions form the positive centres themselves by taking up the position of a Cu ion (with valency 2+) in the surface lattice, creating a positively charged lattice defect.

If such an explanation of the promoting effects is correct, we would expect to find similar behaviour for catalysts promoted by Mn and Ce. However, there was a significant difference in either reduction behaviour or in selectivity between these two promoted materials. We must therefore conclude that there is a distinct chemical difference between the effects of the Mn and Ce ions at the surface of the catalyst. There is no reason to believe that the promotion of the catalysts with different ions (K, Mn, Ce) leads to different reaction mechanisms. It is more likely that the rates of the various reaction steps in the same mechanism are influenced differently by the different additions.

Further experiments are currently being carried out in order to obtain a better understanding of the mechanism of the synthesis of higher alcohols over the differently promoted catalysts. Among these experiments is an investigation of the effect of the variation of contact time (W/F) for different catalysts, furthermore, infrared measurements with Ce promoted catalysts may reveal whether the same intermediates are to be found as with a K promoted catalyst. The surface effects of Ce ions is further being examined by incorporating the cerium by impregnation rather than by coprecipitation; impregnation should give a higher concentration of the cerium at the surface, in contrast to a more uniform distribution of the cerium through the bulk of the catalyst in the case of coprecipitation.

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