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Fischer–Tropsch synthesis over cobalt catalysts supported on zirconia-modified alumina

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Abstract

The effect of adding zirconia to the alumina support on supported cobalt Fischer–Tropsch catalysts has been studied. At 5 bar and H_2:CO ratio 9:1 zirconia addition to the support leads to a significant increase in both activity and selectivity to higher hydrocarbons as compared to the unmodified catalysts. Reducibility and cobalt dispersion on the other hand are not improved by the presence of zirconia compared to the unmodified catalysts. SSITKA measurements have been performed in order to determine the intrinsic activity per active site. At constant temperature, zirconia-modified and unmodified catalysts showed basically the same intrinsic activity. Similar results were obtained with a noble metal (Pt) promoted catalyst. The promoting effect appears to be mainly due to coverage effects rather than a change in the intrinsic activity of the active sites. The turnover frequencies were found to be independent of pressure but strongly temperature dependent. However, the increase in turnover frequency did not account for the entire increase in reaction rate with temperature. This indicates that also the coverage of reactive intermediates increases with increasing temperature. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Fischer–Tropsch synthesis; Cobalt; Support

1. Introduction

Supported cobalt catalysts are the preferred catalysts for the Fischer–Tropsch synthesis of long-chain paraffins from syngas made from natural gas. Alumina is often used as a support for cobalt catalysts due to favourable mechanical properties, but cobalt supported on alumina has a limited reducibility due to a strong interaction between the support and the cobalt oxides [1–3]. This can be overcome, to a certain extent, by promotion with easily reducible metal promoters like Pt or Re [2,4].

The Fischer–Tropsch synthesis is generally believed to be structure insensitive and the specific activities in terms of intrinsic turnover frequencies at practical conditions are reported to be independent of the support and promoter [5].

In the present work we focus on zirconia which is reported to be a promoter for Fischer–Tropsch synthesis over Co/SiO_2 [6], where addition of Zr leads to improved activity. We have investigated the possibility of changing the support interaction between cobalt and alumina by adding zirconia to the alumina support and studying the changes in the catalytic properties of cobalt supported on this new material. The use of steady state isotopic transient kinetic analysis (SSITKA) [7–9] allows the measurement of intrinsic turnover frequencies as well as the surface coverage with reaction intermediates at steady state conditions. The determination of the origin of an effect leading to a change in the activity of the catalyst is then possible.

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2. Experimental

A range of supported cobalt catalysts based on zirconia-modified and unmodified alumina has been prepared. All catalysts were prepared by sequential impregnation or co-impregnation, applying the incipient wetness technique. Cobalt catalyst promoted (the terms modifying or promoting are used indiscriminantly) with zirconia were prepared by means of sequential impregnation of the alumina support with solutions of the cobalt and zirconia precursors, respectively. The zirconia impregnation was always carried out first. The samples were dried (80°C for 24 h in air) and calcined (350°C for 2 h in air) after each impregnation step. Different Co and zirconia loadings were achieved by varying the concentration of the precursor solutions. In the case of the samples with the highest zirconia loading the zirconia impregnation had to be carried out in two steps due to limited solubility of the zirconia precursor. As the starting material for the support commercial Al_2O_3 (boehemite-phase) from Kaiser Chemicals was used. An organic solution of Zr^{IV}-isopropoxide was chosen for the zirconia impregnation. The solvent used was a mixture of toluene, acetylacetone and isopropanol (1:1:1), all reagent grade qualities. Cobalt impregnation was carried out with an aqueous solution of Co^{II}-nitrate. The zirconia promoted catalysts were compared with noble metal promoted cobalt catalysts as well as unpromoted catalysts. The noble metal containing catalysts were prepared by co-impregnation of the alumina support with an aqueous solution of cobalt nitrate and the noble metal precursor. The drying and calcination procedure was as given above. The unpromoted catalysts were prepared using the same procedure as the one used for the zirconia promoted catalysts but with the promotion step omitted.

To specify the particular samples the following notation will be used: a catalyst containing 12 wt.% cobalt and 10 wt.% zirconia supported on alumina will be denoted 12Co10Zr. An unpromoted catalyst of the type x wt.% cobalt/Al_2O_3 catalyst will be denoted xCo (e.g. 12Co). A noble metal promoted cobalt catalyst containing 1 wt.% Pt and 12 wt.% cobalt supported on alumina will be denoted 1Pt12Co.

The CO-hydrogenation was studied in a fixed-bed microreactor. Under the chosen conditions (H_2:CO= 9:1; T=245°C; total pressure=5 bar; catalyst loading= 100 mg calcined catalyst; and feed-rate=250 ml/min) methane is the main reaction product and a steady state is attained rapidly. Although these conditions deviate from the industrial reaction conditions comparative experiments done as a part of this work showed that activity comparisons at these conditions favouring methanation give a fair assessment of the relative activities under process conditions closer to those used in the industry. Prior to the activity measurements the catalysts were reduced for 16 h in flowing hydrogen at 350°C and 1 bar pressure. Product analysis was performed online with a HP 5880 GC equipped with TCD and FID detection, allowing for the analysis of CO, CO_2, CH_4 and hydrocarbons up to C_9.

Different analytical techniques such as measurements of the BET surface, TPD and hydrogen chemisorption measurements were used to characterise the catalysts. The reducibility was estimated by means of temperature programmed reduction (TPR). The experiments were performed on the calcined samples without any further pre-treatment. All TPR-measurements involved heating the catalysts at a rate of 10 K/min to 900°C with a feed gas consisting of 7% hydrogen diluted in argon. Hydrogen consumption was measured as a function of sample temperature using a Shimadzu GC-8A gas chromatograph. Quantitative calibration of the TPR-signal was carried out by a reference experiment on Ag_2O, which is fully reducible under the conditions reported here.

BET measurements were carried out in a Coulter SA 3100 surface analysis unit. Prior to the nitrogen adsorption the calcined catalysts were evacuated at 250°C for 30 min. Hydrogen chemisorption measurements were employed to investigate the cobalt dispersion. The H_2-isotherms were recorded using a Micromeritics ASAP 2010 volumetric glass apparatus. Prior to the measurements the catalysts were reduced in hydrogen at 350°C for 16 h. Subsequently, the samples were outgassed in vacuum at 350°C for 30 min. The total adsorption isotherm was then measured at 100°C between 0.2 and 1 bar pressure.

SSITKA measurements were performed in order to determine the coverage with reactive intermediates and the intrinsic turnover frequency under steady state conditions [7–9]. The measurements were carried out in a separate experimental unit using a differential quartz microreactor. Reduction was carried out in situ using the standard reduction conditions reported above. A mixture of syngas gas (H_2:CO ratio 10:1) diluted in helium at 1.8 bar total pressure was used as the reaction gas feed. In order to investigate the influence of the syngas partial pressure different He/synthesis gas ratios between 2:1 and 4:1 were employed while keeping the total pressure constant. The total feed rate was varied between 60 and 100 ml/min. Different reaction temperatures ranging from 210 to 240°C were chosen. The CO-feed was switched between an isotopically labelled (^{13}CO) and unlabelled supply (^{12}CO). The isotopic composition of the product stream was monitored as a function of time with a Balzers QMG 420 mass spectrometer allowing for a time resolution of about 1 s.

3. Results and discussion

3.1. Catalyst activity and selectivity

Catalysts with varying contents of cobalt and zirconia were prepared and screened. Activity data obtained at T=245°C, 5 bar and H_2:CO=9:1 are presented in Fig. 1 where the catalyst activity is depicted as a function of the cobalt loading for three different zirconia loadings, and compared to unpromoted catalysts. A summary of all of the activity measurements at 5 bar is given in Table 1. For the promoted samples the activity increases with zirconia loading at constant cobalt amount. While the relative activity enhancing effect is not so evident at low cobalt loading due to low conversions it is becoming increasingly more apparent at higher cobalt loadings.

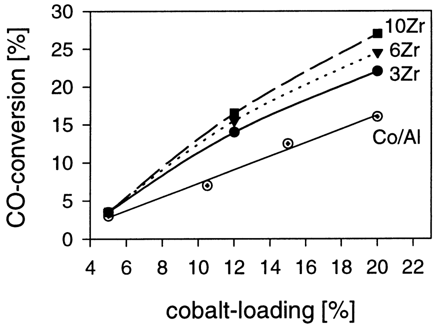

Fig. 1. CO-hydrogenation activity in terms of CO-conversion for different catalysts as a function of cobalt-loading. Conditions: H_2:CO=9:1; T=245°C; total pressure=5 bar; catalyst loading=100 mg calcined catalyst; and feed-rate=250 ml/min.

For constant zirconia loading the activity also increases with cobalt loading. However, the rise is not linear and levels out for high cobalt loadings. This is different for the unmodified system which shows a linear increase in activity even beyond the range of Co loadings presented here (25% Co). Promotion with zirconia also influences the product selectivity. The yield of the C5+ fraction of the hydrocarbon product spectrum increases for all of the zirconia promoted samples (Fig. 2) compared to the unpromoted catalysts. However, the specific amount of Zr does not seem to lead to any major differences for the three different Zr loadings we investigated.

Table 1
Results from characterisation and activity measurements at 5 bars

Catalyst	S_{BET} (m^2/g)	Dispersion (%)	$r_{CO} \times 10^{-5}$ (mol/g s)	TOF (s^{-1})	S_{CH4} (%)	S_{C5+} (%)
5Co3Zr	271	0.5	0.7	1.7	34	27
12Co3Zr	238	1.6	2.6	0.8	24	30
20Co3Zr	215	1.5	3.9	0.8	22	30
5Co6Zr	273	0.8	0.7	1.1	40	26
12Co6Zr	247	2.6	2.9	0.5	23	34
20Co6Zr	221	2.2	4.3	0.6	18	37
5Co10Zr	271	0.6	0.7	1.4	36	28
12Co10Zr	239	1.9	3.0	0.8	22	33
20Co10Zr	218	1.8	4.5	0.8	19	37
10.5Co	NM	2.5	1.4	0.3	37	15
15Co	NM	2.5	2.4	0.4	40	12
20Co	NM	2.7	2.9	0.3	37	15

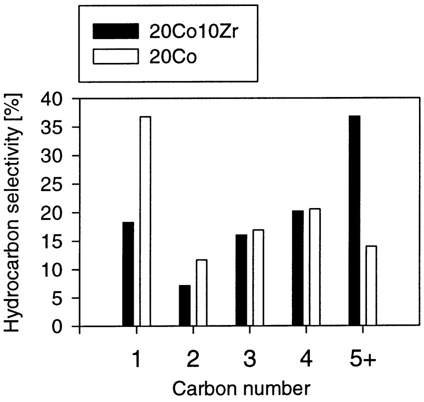

Fig. 2. Effect of promotion with zirconia on the hydrocarbon selectivity.

3.2. Chemisorption and BET measurements

Total surface areas and hydrogen chemisorption data are reported in Table 1. There is no significant dependency of the surface area on Zr loading for a given Co loading. However the cobalt addition in increasing amounts leads to a reduction in the total surface area for all Zr loadings. Promotion with Zr does not lead to an increase in cobalt dispersion compared to the unmodified system. For most modified samples the observed hydrogen chemisorption values are slightly lower. For the three different Zr loadings the cobalt dispersion is highest for the 12% Zr samples, this sample gives a H:Co ratio similar to that of unmodified catalysts with similar cobalt loading.

3.3. Reducibility

The TPR-data reveals that zirconia modification influences the reduction behaviour of the catalyst. In Fig. 3 TPR-profiles are shown for the catalysts 12Co10Zr, 12Co and for the modified support (10 wt.%Zr) without cobalt. Both Co catalysts show corresponding peaks but with different relative intensity. While the 12Co10Zr catalyst shows a sharp low temperature peak around 550 K (peak a) the unmodified catalysts only has a weak shoulder in that region. On the modified support 10Zr this feature is absent. The peak decreases sharply with increasing calcination temperature and duration. It is assigned to nitrate that is still present on the catalyst after calcination, as also proposed elsewhere [10,11]. However, the modified catalysts seem to have a higher affinity to nitrate reflected by the more pronounced nitrate peak compared to the unmodified catalysts calcined under identical conditions. The reason for this is not clear at the moment.

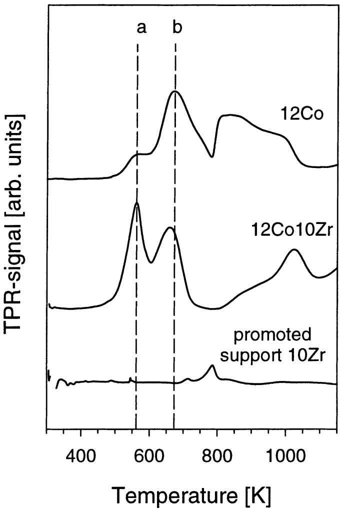

Fig. 3. TPR-data for the catalysts 12Co, 12Co10Zr and for zirconia-modified alumina 10Zr.

The broad peak around 660 K (peak b) is attributed to bulk-like cobalt oxide (Co_3O_4). The two different oxidation states of the cobalt ions are not resolved. Zirconia promotion leaves this peak nearly unchanged. The broad feature between 750 and 1000 K is generally agreed to be a cobalt oxide surface species interacting strongly with the support [10]. Zirconia modification leads to a substantial redistribution of the TPR-signal in this region. Basically the TPR-signal seems to shift to higher temperature for the promoted catalysts. A quantitative analysis of the peak area shows that the total area under the TPR-curve and thus the degree of reduction is nearly independent of promotion with zirconia. The activity enhancing effect of zirconia is therefore not due to an increase in the cobalt reducibility.

On the basis of thermodynamic calculations Zr is expected to be present as the oxide also on the reduced catalyst. The TPR-data recorded for the modified support alone confirms this and indicates close to zero reducibility (see Fig. 3). However, reduction of the zirconia on the cobalt-containing sample cannot be fully excluded since the metal could act as a reduction promoter.

3.4. Turnover frequencies

The calculated reaction rates and turnover frequencies (TOF) from the activity measurements at 5 bar are shown in Table 1. The reaction rates measured at each cobalt loading are close, independent of zirconia modification. Due to the lower chemisorption capacity the zirconia-modified catalysts show higher TOFs. The 5% cobalt catalysts show particularly high TOFs, but this is probably an artefact linked with very low chemisorption capacities and not very useful due to the very low chemisorption capacity and hence very low reaction rates.

3.5. SSITKA measurements

To obtain further knowledge of these systems SSITKA measurements were performed. SSITKA measurements allow the separation of the apparent TOF values into the intrinsic TOF frequency per active site and the fraction of the surface metal atoms covered with reactive intermediates. The “intrinsic TOF” can also be interpreted as a first order rate constant Eq. (1).

$$\text{TOF} = \text{“iTOF”}\theta = k\theta = \frac{1}{\tau}\theta \tag{1}$$

where iTOF is the intrinsic TOF [s^{-1}]; θ the surface coverage of active intermediates; k the first order rate constant [s]; and t the measured time constant.

The method involves the assumption that the catalyst surface can be modelled as a CSTR. It is widely accepted that the rate determining step in CO-hydrogenation over Co catalyst is the hydrogenation of an activated carbon species [12,13]. We assume that this elementary step is first order in the activated carbon species. These assumptions yield expected methane transients in the form of exponential functions. A typical transient is shown in Fig. 4. The transients could in all cases be satisfactorily fit with one exponential function, thus corroborating the validity of the model. The intrinsic TOF values are given by the time constant of the exponential function. SSITKA measurements were performed for the catalysts 12Co, 20Co10Zr and 1Pt12Co in order to investigate the influence of promotion on the intrinsic activity of the catalyst.

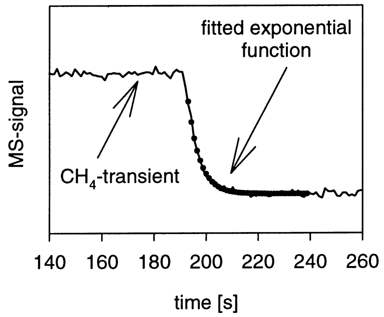

Fig. 4. Typical methane transient in SSITKA experiment. The intrinsic TOF values are extracted by fitting an exponential function to the transient.

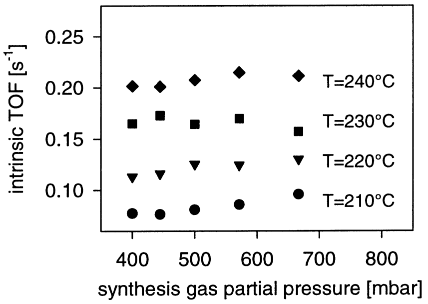

Fig. 5. Intrinsic TOF values for the catalyst 1Pt12Co as a function of reaction temperature and syngas partial pressure.

For a given temperature the measured intrinsic TOF values were independent of the partial pressure of the syngas as depicted in Fig. 5 for the platinum promoted catalyst 1Pt12Co. The same holds for the other catalysts investigated. Intrinsic TOF values as a function of temperature are reported in Table 2. Similar values were found for all catalysts at a given temperature,

Table 2
Results from SSITKA measurements

	Intrinsic TOF values [s^{-1}] at different temperatures T (°C)			
	210	220	230	240
1Pt12Co	0.08	0.12	0.17	0.21
12Co	0.10	0.13	0.19	0.27
20Co10Zr	–	0.14	0.21	0.22

indicating that the intrinsic activity per active site is the same for all catalysts tested. The difference in the activity is therefore due to different degrees of coverage with reactive intermediates. The action of the modifier can then be linked with the tendency to form strongly adsorbed deposits on the active cobalt sites. However, a similar effect has been observed for Ru-promoted Co catalysts [5], where it was suggested that the Ru acted through inhibition of the oxidation of reduced Co surface atoms. It has previously been demonstrated that oxidation of surface cobalt atoms is an important cause of loss of activity for supported cobalt catalysts [14], and an alternative explanation to the results observed here could be that the zirconia somehow helps to protect the cobalt from oxidation. If that was the case a difference in deactivation with time-on-stream between the zirconia-modified and unmodified catalysts would be expected. As no such difference was observed this explanation can clearly be ruled out.

TPR and chemisorption results clearly show that zirconia does not increase the number of metallic cobalt atoms on the reduced catalyst because both cobalt dispersion and reducibility are not improved by the presence of the promoter. These findings are in line with results obtained on zirconia promoted silica supported cobalt FT catalysts [6]. The SSITKA results indicate that the intrinsic activity of the cobalt atom is basically the same for all catalysts investigated and is independent of the nature of the promoter. This is in line with the widely accepted opinion that the FT synthesis over supported cobalt catalysts is structure insensitive. Different explanations for the effect of transition metal oxide promotion on CO-hydrogenation have been discussed in the literature. Based on the principles of metal/semiconductor interfaces some authors proposed a change in the electronic properties of the metal caused by the metal oxide [15,16]. Others attributed promoting effects to cation or anion vacancies at the edge of the metal oxide moieties [17–19]. Cation vacancies facilitate the rupture of the CO bond by a Lewis acid–base type interaction with the oxygen end of the CO. Bell [20] could relate the activity ranking in CO and CO_2 hydrogenation on Rh to the Lewis acidity of the metal oxide. He could furthermore show that the activity passed a maximum for the metal/metal oxide ratio where the number of interface sites is highest. At higher metal oxide contents the oxide encapsulates the catalytic active metal thus reducing the number of available reactive sites on the catalyst. Many of the findings of our study are in line with that explanation. The SSITKA results show that different catalytic activities are due to differences in the coverage with reactive intermediates. The intrinsic TOF values give no evidence of changes in the intrinsic activity of the surface cobalt atom. This would be likely if the electronic properties of the cobalt atoms were altered by the metal oxide. However, some changes in the adsorption properties are likely, since the surface coverage of reactive intermediates is influenced by modifying the support with zirconia.

As Fig. 5 and Table 2 show, both reaction rates under SSITKA conditions and intrinsic TOF values increase with temperature. However, the increase in the intrinsic TOF values is not large enough to account for the entire increase in reaction rate. This is a surprising result because it suggests that the coverage with reactive intermediates increases with increasing reaction temperature. A possible explanation could be that there is a competition between reactive carbon-containing species and other adsorbed species. The relative coverage of species leading to methane could then increase as the coverage of other species (e.g. H_2 or CO) is reduced with increasing temperature.

3.6. Effect of total pressure

The results reported so far have been obtained at conditions far from those employed in the industry, where total pressures are higher and the hydrocarbons are mainly long-chained paraffins. It is therefore of some interest to see if the low-pressure screening results can be extrapolated to conditions closer to those used in industry. Fig. 6 shows activity results obtained at various conditions denoted I–IV in Figs. 6–8. Reaction temperature, syngas ratio, pressure and space velocities were varied to progressively move from methanation condition to reaction conditions resembling the industrial process. The conditions applied were T=245°C, p=5 bar, H_2:CO=9:1 for condition I, T=245°C, p=5 bar, H_2:CO=2:1 for condition II, T=235°C, p=5 bar, H_2:CO=2:1 for condition III and T=220°C, p=20 bar, H_2:CO=2:1 for condition IV. For experiments I–III the space velocity was fixed and chosen to give around 10% CO-conversion for the unpromoted catalyst. For experiment IV the space velocity was individually set to obtain CO-conversion

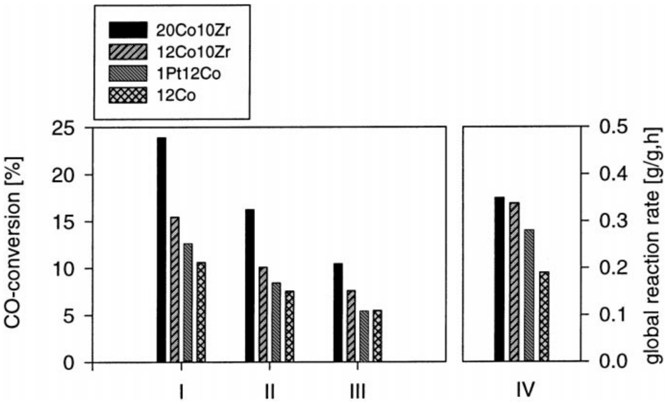

Fig. 6. CO-hydrogenation activity at four different reaction conditions (denoted I, II, III, IV) for four different catalysts. The exact reaction parameters are given in the text.

of 50% for all catalysts. Four different catalysts were tested at each of these different conditions. Fig. 6 shows that the order of activities is maintained throughout the testing series. However, the exact activity ratios differ. Compared with industrial like conditions the methanation reaction seems to exaggerate the activity differences of the four catalysts. Fig. 7 reports C_{5+} selectivities for the different conditions. Again, the order of selectivities for the four catalysts is basically the same at the various testing conditions, whereas differences are more pronounced at methanation conditions. Fig. 8 presents olefin/paraffin selectivity ratios of for the C_2 and C_3 hydrocarbons. Despite some minor differences the pattern of olefin/paraffin ratios is very similar through all experiments.

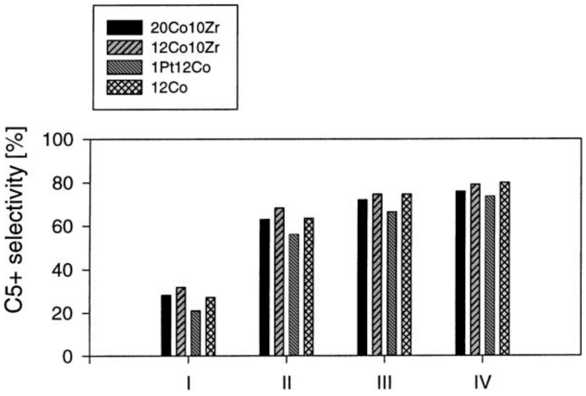

Fig. 7. Selectivities to the C_{5+} hydrocarbon product fraction at different reaction conditions. Catalysts and conditions as in Fig. 6.

The comparison experiments show, that for the type of catalysts investigated here methanation gives a fair assessment of the catalysts activity and selectivity under industrial FT conditions. However the relative differences in activity and selectivity decrease gradually when moving towards industrial reaction conditions.

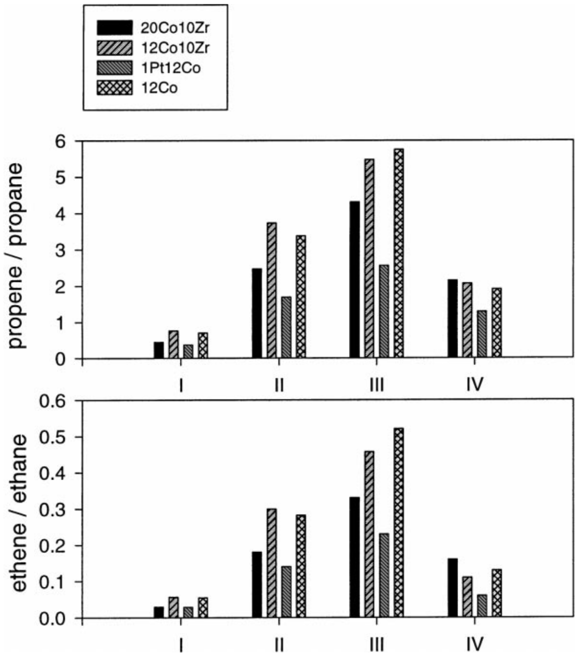

Fig. 8. Olefin/paraffin ratios at four different reaction conditions for four different catalysts. Catalysts and conditions as in Fig. 6.

3.7. Summary and conclusions

Addition of zirconia to the alumina support does not lead to improved reducibility or cobalt dispersion. However, at CO-hydrogenation at low pressure conditions a marked increase in activity and C_{5+} selectivity is observed. This effect has been studied with SSITKA, and can be attributed to changes in the surface coverage of reactive intermediates, not to a change in the intrinsic activity. The SSITKA experiments also revealed unexpectedly an increase in the surface coverage of reactive intermediates with increasing temperature. The low-pressure CO-hydrogenation experiments have been found to exaggerate differences in activity and selectivity between catalyst compared to industrial conditions.

Acknowledgements

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