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The effect of water on cobalt Fischer–Tropsch catalysts studied by steady-state isotopic transient kinetic analysis (SSITKA)

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Abstract

The mechanism of deactivation due to water on the Fischer–Tropsch synthesis (FTS) over alumina supported cobalt catalysts has been studied using steady-state isotopic transient kinetic analysis (SSITKA). This method makes it possible to estimate the concentrations of adsorbed reaction intermediates as well as the time constants involved in the rate determining elementary reaction steps. Both Co/Al_2O_3 and Co/Re/Al_2O_3 showed similar deactivation when exposed to water vapour before or during CO hydrogenation reaction. The SSITKA results show that this deactivation is due to loss of active sites, whereas the specific site activity of the remaining active sites is unchanged by the water treatment. This can be explained by assuming that part of the cobalt metal surface is oxidized during the water treatment.

Keywords: Fischer–Tropsch synthesis; Cobalt catalyst; Deactivation; Rhenium; SSITKA

1. Introduction

The Fischer–Tropsch synthesis (FTS) is a promising pathway for the utilization of natural gas resources. Current developments aim at improved technologies for the production of high-molecular waxes followed by hydrogenation to liquid fuel products. In order to control the highly exothermic FTS at high conversions, slurry reactors are particularly useful due to their favorable heat transfer properties [1]. Furthermore, cobalt-based catalysts seem to be especially suitable due to their high activity and selectivity, low water-gas shift activity and a comparatively low price.

It has been reported that the catalytic properties of Co-based systems change significantly in the presence of water. Schulz et al. [2] found no changes in the activity of a Co/Zr/aerosil catalyst even at high water pressures but reported a decreasing selectivity to methane $S(CH_4)$, an increasing $S(C_5^+)$ and a higher olefin content in the products. Iglesia and co-workers [3] carried out experiments with water and ethene addition to a CO/H_2 feed over Ru and Co/TiO_2 catalysts and proposed that water inhibits the secondary hydrogenation, especially of α-olefins. Other results from the literature regarding the effect of water indicate an increasing chain-growth probability [2–4]

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which can be explained by the inhibiting effect of water on the termination of growing chains by hydrogen addition which is the predominant irreversible termination step. A deactivation of Co/Al_2O_3 and $Co/Re/Al_2O_3$ catalysts after feeding water was observed by Schanke et al. [5], which was explained by surface Co oxide formation.

The changes in the properties of Co catalysts in the presence of water have to be taken into account especially when the FTS is carried out in a slurry reactor where the concentration of water (as the main oxygen-containing product over Co catalysts) will be high throughout the whole reactor due to extensive back-mixing.

In the present work the effect of water on the FTS over Co/Al_2O_3 and $Co/Re/Al_2O_3$ catalysts was studied using steady-state isotopic transient kinetic analysis (SSITKA) and steady-state activity measurements. Due to its potential to distinguish between changes in site activity and site density, the application of the transient isotopic method is expected to give further information on the mechanism of deactivation.

2. Experimental

2.1. Apparatus

The experimental set-up consists of a catalytic microreactor dedicated to fast switching experiments. The on-line measurement of the transients was carried out using a Balzers QMG 420 quadrupole mass spectrometer while the catalytic activity was determined using a HP 5880 GC equipped with a GS-alumina column (J&W Scientific) connected to a FID detector. A separation of all hydrocarbons up to C_4 was possible while only negligible amounts of higher hydrocarbons (C_5^+) were detected. The water feeding system was based on a peristaltic pump used to introduce the water into the reactor through heated lines. For the duration of the water feed the reactor outlet was directly connected to the ventilation line and both GC and MS analysis lines were disconnected. All lines from the pump to the reactor outlet as well as the downstream lines were heated to 150°C to prevent condensation of water. For further details on the experimental set-up, see Refs. [6,7].

2.2. Catalyst preparation and characterization

Co(17.1 wt%)/Al_2O_3 (S_{BET}=138 m^2/g) and Co(17.2 wt%)/Re(1 wt%)/Al_2O_3 (138 m^2/g) were prepared by standard incipient wetness techniques using either $Co(NO_3)_2$ or co-impregnation of $Co(NO_3)_2$ and $HReO_4$ on the Al_2O_3 (Puralox, 174 m^2/g) support. The catalysts were dried overnight at 393 K followed by calcination in air for 2 h at 573 K. The cobalt dispersions were measured by hydrogen chemisorption and amounted to 4.9% (Co) and 9.3% (Co/Re). The catalysts used in the present study are identical to those applied by Schanke et al. [5].

The following gases and gas mixtures were used for the experiments: ^{13}CO (>99% ^{13}C, Cambridge Isotope Laboratories), $^{12}CO/Ar$ (24 : 1, Norsk Hydro), H_2 (99.995%, Norsk Hydro), He (99.998%, Norsk Hydro).

2.3. Experimental procedure

For most experiments 100 mg of catalyst were mixed with 200 mg of SiC of the same particle fraction 38–75 μm. One experiment was also carried out with 200 mg of Co/Al_2O_3 catalyst mixed with 100 mg of SiC.

The catalysts were reduced in a flow of 10 ml/min H_2 for 12 h at 753 K after ramping at 1 K/min from room temperature, followed by cooling in He to the reaction temperature of 473 K. Syngas was then fed at T=473 K, P=1.85 bar and flow rates of 78 ml/min He, 2 ml/min CO, 20 ml/min H_2 and 0.08 ml/min Ar (at standard conditions). Activity data were obtained after 3 h time on stream when a steady-state level was approached.

The first experiment was carried out by switching from $^{12}CO/H_2/Ar$ to $^{13}CO/H_2$ feed. After the concentrations for all components had reached a steady-state level, the opposite step change was performed.

After this, the catalyst was treated with a water-containing feed for 16 h at 473 K using the flow rates 17.7 ml/min He, 24.8 ml/min $H_2O(g)$, 2.48 ml/min H_2 for the runs with 100 mg catalyst and 35.4 ml/min He, 49.6 ml/min H_2O and 4.96 ml/min H_2 for the run with 200 mg of catalyst. Prior to the experiments the water was degassed by bubbling He for one day.

After the water treatment, the feed was changed back to syngas (flow rates as above) and another $^{12}CO \rightarrow {}^{13}CO \rightarrow {}^{12}CO$ switch was performed.

The transient concentration changes during the switches were monitored on-line by the mass spectrometer using the following atomic mass units (AMU) for the identification of the different compounds: H_2 (2), He (4), $^{12}CH_4$ (15), $^{13}CH_4$ (17), ^{12}CO (28), ^{13}CO (29), Ar (40).

The reactor was operated at low CO conversions (<15%) to achieve a pseudo-gradientless behavior in order to use the CSTR approximation for the mathematical treatment to simplify the mathematical analysis of the data (see below).

2.4. *Data treatment*

From basic SSITKA theory (see e.g. [8]) it can be derived that for an irreversible first order reaction with rate constant k, the residence time of reaction intermediates on the catalyst surfaces, τ, as obtained from the measured transients, is equal to $1/k$. Three different methods were applied in order to obtain $\tau(CH_4)$ from the $^{12}CO \rightarrow {}^{13}CO \rightarrow {}^{12}CO$ switches:

1. The surface residence time was determined from the transients as the area between the Ar transient and the $^{12}CH_4$, 1-$^{13}CH_4$, $^{13}CH_4$, or 1-$^{12}CH_4$ transients. The corresponding τ values are denoted as τ(INT) in the following text. The mean deviation of the τ values was estimated from the deviation of the time constants that were determined separately for all transients.
2. A single exponential function was fitted to the methane transient by minimizing the sum of absolute deviations between simulation and experiment as object function τ(EXP). The uncertainty for τ was obtained from the statistical deviations of all estimated time constants for the different fits.
3. To reduce the contribution of noise all transients at equal experimental conditions were averaged and the resulting average methane transient was fitted to an exponential function τ(SUM).

3. Results and discussion

3.1. *Catalyst deactivation*

The conversion of CO decreased after 16 h of water treatment to approximately 70% of the initial activity level for both catalysts (see Table 1). The deactivation of the Co/Al_2O_3 and the $Co/Re/Al_2O_3$ catalysts during water treatment is similar to that observed in previous work using identical catalysts [5]. Similar deactivation was observed for experiments with H_2O/H_2 feed prior to the catalytic experiments and with water addition to the syngas feed [5]. Satterfield et al. [9] also reported a deactivation of a Fe/FeO catalyst when water vapor was added to the reaction mixture. However, the deactivation was reversible. In contrast, Schulz et al. [2], who studied the FTS using a Co/Zr/Aerosil catalyst in a slurry reactor, found no change in the catalyst activity due to water addition. These experiments were carried out after one week of steady-state operation. It is possible that during this pre-run time the (lower) water concentration in the reaction mixture has already affected the catalyst activity which might have reached its final (deactivated) state before the actual water addition experiments were started.

3.2. *Product distribution*

In order to compare the product distributions of the fresh and water-treated catalyst one experiment with a catalyst load of 200 mg of the water-treated catalyst was carried out in order to achieve comparable conversions. The CO conversion and the product selectivities measured in this experiment are summarized in Table 2 together with the data for the fresh catalyst. From the results it can be derived that the water treatment leads to a moderate increase in the formation of olefins compared to the product distribution

Table 1
Comparison of CO conversions before and after treatment with water of Co/Al_2O_3 and $Co/Re/Al_2O_3$ catalysts (T=473 K, p=1.85 bar, H_2/CO=10)

	Co/Al_2O_3	$Co/Re/Al_2O_3$
Conversion before H_2O treatment	7.1	13.2
Conversion after H_2O treatment	5.4	9.4
Ratio (conversion after/conversion before)	0.76	0.71

Table 2

Comparison of the product selectivities in the conversion of syngas over Co/Al_2O_3: fresh catalyst ($X(CO)=7.1\%$, $m_{cat}=100$ mg) and water-treated catalyst ($X(CO)=9.3\%$, $m_{cat}=200$ mg) (conditions: $T=473$ K, $p=1.85$ bar, $H_2/CO=10$)

S (%)	CH_4	C_2H_6	C_2H_4	$C_2{=}/C_2$	ΣC_2	C_3H_8	C_3H_6	$C_3{=}/C_3$	ΣC_3	C_4H_{10}	$C_4{=}$	$C_4{=}/C_4$	ΣC_4	$\Sigma(C_{1-4}$-paraffins)	$\Sigma(C_{1-4}$-olefins)
Fresh catalyst	52.4	8.8	0.7	0.08	9.6	6.7	13.5	2.0	20.2	6.9	10.8	1.6	17.8	74.9	25.1
H_2O-treated catalyst	44.9	7.4	1.1	0.15	8.6	4.8	19.1	3.9	23.9	7.9	14.6	1.8	22.7	65.1	34.9

Table 3

Comparison of the product selectivities in the conversion of syngas over Co/Al_2O_3 ($X(CO)=9.3\%$, $m_{cat}=200$ mg) and $Co/Re/Al_2O_3$ ($X(CO)=9.4\%$, $m_{cat}=100$ mg) catalyst after treatment with water (conditions: $T=473$ K, $p=1.85$ bar, $H_2/CO=10$)

S (%)	CH_4	C_2H_6	C_2H_4	$C_2{=}/C_2$	ΣC_2	C_3H_8	C_3H_6	$C_3{=}/C_3$	ΣC_3	C_4H_{10}	$C_4{=}$	$C_4{=}/C_4$	ΣC_4	$\Sigma(C_{1-4}$-paraffins)	$\Sigma(C_{1-4}$-olefins)
Co/Al_2O_3	44.9	7.4	1.1	0.15	8.6	4.8	19.1	3.9	23.9	7.9	14.6	1.8	22.7	65.1	34.9
$Co/Re/Al_2O_3$	46.8	8.1	0.9	0.11	8.9	6.1	18.1	3.0	24.2	6.3	13.9	2.2	20.1	67.2	32.8

over the fresh catalyst. A similar effect was observed earlier [2,3] and explained by an inhibition of secondary hydrogenation reactions of olefins due to the water addition. It has to be noted, however, that in the present work the differences in olefin selectivity were still significant even after water addition. However, as reported by Schanke et al. [5] co-feeding of water to syngas under reaction conditions or a pretreatment of the Co catalysts with water prior to the reaction lead to similar results with respect to catalytic activity.

In the present work, the analytical restrictions due to the MS analysis necessary for the SSITKA experiments, limited the reaction conditions to a range where methane is the predominant product. Hence, no conclusions could be made regarding the effect of water on $S(C_5^+)$ or on the chain-growth probability which both have been reported to increase due to the presence of water [2–4].

3.3. *Effect of rhenium*

Table 3 summarizes the product distributions for the Co and Co/Re catalysts after water treatment at about identical CO conversion. There are only relatively minor differences in the selectivities, hence, it can be derived that doping with Re did not change the effect of water on selectivity for the catalysts.

3.4. *SSITKA results*

The application of the SSITKA method for the investigation of the deactivation after water treatment can yield more information concerning the origins of the water-induced changes in the catalyst activity due to the separate determination of site reactivity and the number of active sites. Because the evaluation of the MS data becomes increasingly difficult with increasing carbon number of the products (due to the extensive overlap of their fragmentation patterns), the evaluation is limited to the reaction of methane formation only.

Table 4 summarizes the results for the Co/Al_2O_3 and $Co/Re/Al_2O_3$ catalyst before and after water treatment. The responses for transient methane decay are compared in Fig. 1 for the $Co/Re/Al_2O_3$ catalyst. From the SSITKA results it is obvious that the decrease in the overall activity of both catalysts after water treatment is due to a decrease of the number of active surface intermediates, N^*, that can be hydrogenated to methane under steady-state conditions. The intrinsic site activity, $1/\tau(CH_4)$, however, remains unchanged within the given uncertainties. Furthermore, it seems that the decrease in the number of reactive intermediates leading to CH_4, N^*, and the decrease in the amount of sites for reversible CO adsorption under reaction conditions, $N(CO_{rev.ads.})$, are correlated (cf., Table 4). These results are in agreement with the assumption put forward by

Table 4
Influence of water treatment on CO conversion, $X(CO)$, the number of active surface species reacting to methane, N^* and their surface residence time, $\tau(CH_4)$, and the amount of reversibly adsorbed CO at 473 K, $N(CO_{rev.ads.})$ for Co/Al_2O_3 and $Co/Re/Al_2O_3$

Catalyst	$X(CO)$ (%)	N^{*a} (μmol/g_{cat})	$\tau(CH_4)$ (s)			$N(CO_{rev.ads.})$ (μmol/g_{cat})
			INT[b]	EXP[c]	SUM[d]	
Co/Al_2O_3						
Before H_2O	7.1	27.9	30.3±5.5	28.4±3.0	29.2	61.9
After H_2O	5.4	22.2	34.1±6.1	29.6±6.1	30.9	41.7
Ratio	0.76	0.79				0.67
$Co/Re/Al_2O_3$						
Before H_2O	13.2	47.8	27.2±2.8	26.9±2.1	26.8	115.7
After H_2O	9.4	38.8	29.9±6.2	30.3±7.6	30.7	79.4
Ratio	0.71	0.82				0.69

[a] Calculated using the SUM residence time for both catalysts.

[b] Determined by integration of the transient.

[c] Determined by fit of an exponential function to every single transient.

[d] Determined by fit of an exponential function to an averaged transient (see main text).

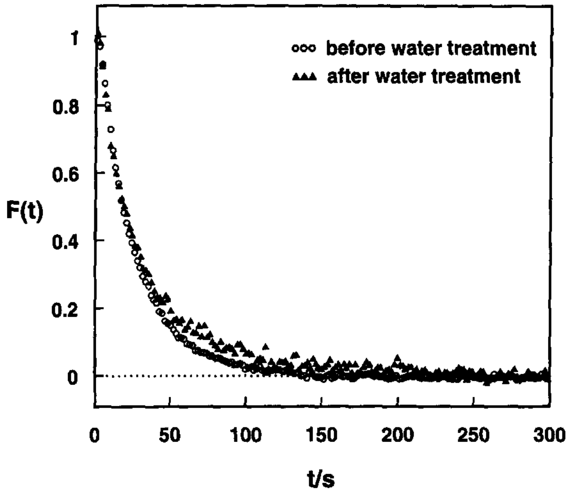

Fig. 1. Comparison of the averaged, normalized methane transients in a $^{12}CO/H_2 \rightarrow ^{13}CO/H_2$ switch over $Co/Re/Al_2O_3$ at 473 K before and after treatment of the catalyst with water (cf. Table 4 for results).

Schanke et al. [5] for explaining the observed deactivation: It was proposed that exposed Co sites are oxidized during the water treatment, decreasing the available active catalyst surface but leave the intrinsic activity of the remaining Co surface sites unchanged.

No differences were observed between the Co and $Co/Re/Al_2O_3$ catalysts with respect to the influence of water on the site activity, the number of active sites or the number of sites for reversible CO adsorption. For both catalysts the relative changes in N^* and $N(CO_{ads.})$ were comparable. The intrinsic activities $(1/\tau)$ were similar on Co/Al_2O_3 and $Co/Re/Al_2O_3$ before and after water treatment. This indicated that the doping with Re did neither change the Co site activity nor the properties of the catalyst for the interaction with water. Hence, Re seems not to be involved in the FTS itself but Re doping results in a catalyst with a higher Co dispersion, and thus a higher activity for syngas conversion (cf. Table 4).

4. Conclusions

After treatment with water, both the Co/Al_2O_3 and the $Co/Re/Al_2O_3$ catalysts showed a reduced activity with respect to the conversion of syngas. Furthermore, an increase of the olefin selectivity after water treatment was observed.

Based on SSITKA results, it can be stated that the catalyst surface available for methane formation and reversible CO adsorption decreases after water treatment, but the intrinsic catalytic behavior of the catalysts is not influenced with regard to the methane formation. These results can be explained assuming that the water treatment of the Co catalysts leads to an oxidation of exposed Co atoms, thus decreasing the available active surface but leaving the intrinsic site activity of each available surface Co atom unchanged.

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