

Fischer–Tropsch synthesis on supported cobalt catalysts promoted by platinum and rhenium

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An investigation of the CO hydrogenation of Pt- or Re-promoted 8.7 wt% Co/Al₂O₃ (1.0 wt% Pt or 1.0 wt% Re) has been carried out at two different conditions: 473 K, 5 bar, H₂/CO = 2 and 493 K, 1 bar, H₂/CO = 7.3. The addition of Pt or Re significantly increases the CO hydrogenation rate (based on weight of Co), but the selectivity was not changed by the presence of Pt or Re. The results show that the observed increases in the reaction rates are caused by increased reducibility and increased number of surface exposed Co-atoms. Steady-state isotopic transient kinetic analysis (SSITKA) with carbon tracing was used to decouple the effects of the concentration of active surface intermediates and the average site reactivity of intermediates during steady-state CO hydrogenation. The SSITKA results show that the concentration of active surface intermediates leading to CH₄ increased as a result of the addition of a noble metal promoter. However, the average site activity was not significantly affected upon Re or Pt addition.

Keywords: Fischer–Tropsch; cobalt; rhenium; platinum; CO hydrogenation; SSITKA

1. Introduction

Methane has become an abundant hydrocarbon fuel and chemical feedstock. Utilizing this resource with minimum environmental impact is a major challenge to catalysis. The Fischer–Tropsch synthesis is an interesting and promising way of converting methane to liquid fuels and chemicals.

Recent developments in Fischer–Tropsch technology are focused on the production of high molecular, straight-chain waxes which in turn can be hydrocracked to products in the middle distillate range [1]. A key element in the modern Fischer–Tropsch processes is the development of an active cobalt catalyst. A Fischer–Tropsch catalyst for natural gas conversion usually consists of four parts: the cobalt metal, a second metal, oxide promoter(s) and the support [2]. The second metal is usually a noble metal such as Pt or Re.

The present study deals with the effect of Pt and Re on the behavior of alumina supported cobalt catalysts. The activity has been measured at steady-state as well as under transient conditions. By using isotopic transient methods it is possible to

separate the rate into contributions from the concentration of active surface intermediates and contributions due to average site activity [3–6].

2. Experimental

All the catalysts were prepared from the same, unpromoted catalyst in order to ensure similar Co particle size distributions. The 8.7 wt% Co/ γ -Al₂O₃ was prepared by impregnating γ -Al₂O₃ (Akzo, Alumina 000 –1½E) with an aqueous solution of Co(NO₃)₂·6H₂O using the incipient wetness technique. The sample was dried and calcined for 2 h at 573 K. Portions of the calcined base catalyst were then modified by impregnating with an aqueous solution of Pt(NH₃)₄(NO₃)₂ or Re₂O₇. After the second impregnation, the catalysts were calcined at 673 K for 2 h. The unpromoted catalyst was also calcined a second time at 673 K for 2 h to ensure the same treatment as the promoted catalysts.

CO adsorption isotherms were measured at 298 K in a standard volumetric glass apparatus. Before measurements, the catalysts were reduced in flowing H₂ for 14 h at 623 K after ramping at 2 K/min. The samples were evacuated for 0.5 h at 603 K before cooling to 298 K and the total adsorption isotherm was then measured between 10 and 300 Torr.

Temperature-programmed desorption (TPD) experiments were performed in a quartz microreactor heated by an electrical furnace. The sample was first pre-treated in Ar for 15 min at 748 K, after ramping at 20 K/min, and then cooled in flowing Ar to 303 K. The catalysts were reduced in flowing H₂ for 10 h at 623 K, after ramping at 1 K/min. After reduction, Ar was introduced at 623 K and the sample heated to 723 K and kept at this temperature for 1 h and cooled to 493 K. H₂ was introduced at 493 K and the reactor was cooled to 303 K and held at 303 K for 20 min. The reactor was then purged with Ar at 303 K for 80 min before the TPD measurements which involved heating of the sample to 748 K after ramping at 10 K/min and held at 748 K for 20 min. H₂ desorbed during TPD was detected by a thermal conductivity detector (TCD). The number of H-atoms desorbed during TPD were used to obtain the number of surface exposed Co (Co_s), making use of the assumption $H_{\text{total}}/Co_s = 1$ [7].

The extent of cobalt reduction was determined by O₂ titration of reduced samples at 673 K [8]. After reduction at the same standard conditions as for the CO adsorption isotherms, the catalysts were kept in flowing Ar at 673 K for 1 h to desorb any chemisorbed H₂. Calibrated pulses of O₂ were then added until no further consumption of O₂ could be detected by the TCD. The extent of reduction was calculated assuming stoichiometric conversion of metallic Co to Co₃O₄.

CO hydrogenation at 493 K, 1 bar and H₂/CO = 7.3 was carried out in a fixed-bed quartz microreactor. The feed composition was H₂/CO/Ar = 5.5/0.75/5 (ml/min). The catalysts were reduced at standard conditions (2 K/min, 623 K, 14 h), prior to reaction. The product gases were analyzed using a HP 5880 gas chro-

matograph equipped with TCD and flame ionization detector (FID). Ar (used as an internal standard), CO, CH₄ and CO₂ were analyzed on the TCD and separated by a Carbosieve packed column. C₁–C₄ hydrocarbons were separated by a 0.53 mm (i.d.) GS-Q capillary column and detected on the FID. GHSV (ml(H₂ + CO + Ar)/(g_{cat} h)) was varied between 4000 and 14000 h⁻¹ to give approximately constant conversion. Steady-state isotopic transient kinetic analysis (SSITKA) was performed at the same conditions as described above. The reaction was run for 3–6 h prior to an isotopic switch. The concentrations of Ar, Kr, ¹²CO, ¹³CO, ¹²CH₄ and ¹³CH₄ were continuously monitored by a mass spectrometer (Baltzers QMG 420). The surface residence time, τ , is determined as the area between the CH₄ transient and the inert transient (Ar or Kr), after correcting for the chromatographic effect on CO [4,5]. The chromatographic effect was used to determine the amount of CO adsorbed at reaction conditions and at non-reactive conditions. In the latter case, freshly reduced catalysts were cooled in flowing H₂ to 373 K and then exposed to the same reaction mixture as in the CO hydrogenation experiments.

CO hydrogenation at 473 K, 5 bar and H₂/CO = 2 was carried out in a fixed-bed stainless steel reactor. 0.3–1.0 g of catalyst and 3–5 g of inert (α -Al₂O₃) were mixed and placed between two layers of glass wool on a frit in the reactor. The particle size of both the catalyst and the diluent was 75–300 μ m. The GHSV was varied to obtain conversions in the range of 4–10%. The catalysts were reduced in flowing H₂ at 7 bar and 623 K for 16 h after ramping at 2 K/min to 603 K and 1 K/min from 603 to 623 K. After reduction the catalysts were cooled to 463 K in flowing H₂ before switching to synthesis gas and slowly increasing the reaction temperature to 473 K and adjusting the pressure to 5 bar. The products were analyzed on-line by a HP 5890 gas chromatograph equipped with FID (connected to a Megabore 30 m DB1, 5 μ m film from J&W Scientific) and TCD (connected to a Carbosieve-SII, 1/8" 110/120 from Supelco). N₂ was used as an internal standard.

3. Results and discussion

The properties of the unpromoted and the Pt- or Re-promoted catalysts are shown in table 1. The extent of reduction, as calculated from the reoxidation of reduced samples, is lower for the unpromoted catalyst compared to the promoted catalysts. Both Pt- and Re-promoted Co/Al₂O₃ catalysts show high extent of reduction, about 80% compared to 50% for the unpromoted Co/Al₂O₃. These results indicate that Pt and Re are promoting the reduction of cobalt oxide. Similar results have been reported for CoPt/Al₂O₃ [9], CoRh/Al₂O₃ [10], CoIr/Al₂O₃ [11], CoRu/CeO₂ [12], CoRu/TiO₂, CoRu/SiO₂ [13], CoPt/Al₂O₃ and CoPt/SiO₂ [14]. It has been proposed that noble metal components act as a source of hydrogen spillover to Co [2].

The amount of H₂ or CO chemisorbed is also strongly influenced by the pres-

Table 1
Properties of promoted and unpromoted Co/Al₂O₃ catalysts

Catalyst	Extent of reduction ^a (%)	H _{ads} : Co ^b	CO _{ads} : Co ^c	CO _{SSITKA} : Co ^d	Dispersion ^e (%)	Particle size ^f (nm)
8.7Co/Al ₂ O ₃	52	0.035	0.023	0.041	6.7	19
8.7Co1.0Pt/Al ₂ O ₃	79	0.110	0.065	0.080	13.9	14
8.7Co1.0Re/Al ₂ O ₃	78	0.129	0.061	–	16.5	19

^a Determined by reoxidation in O₂ at 673 K (pulse method).

^b Total H₂ chemisorption determined from TPD, assuming adsorption only on Co-atoms.

^c Total CO chemisorption at 298 K, assuming adsorption only on Co-atoms.

^d From ¹²CO/¹³CO transients at 373 K.

^e Cobalt metal dispersion, given as (H_{ads} : Co)/(fraction reduced), assuming adsorption on Co only.

^f Co₃O₄ particle size from XRD line broadening. Determined for calcined (unreduced) catalysts.

ence of Pt or Re as shown in table 1. The uptake of hydrogen increases about four times as a result of the addition of Pt or Re. The same trend is observed also for CO chemisorption but the amount of CO adsorbed is always less than for hydrogen. These results are confirmed by the SSITKA measurements (table 1).

In order to interpret the chemisorption results, the state of reduction of the catalysts has to be considered as well as the possibility of adsorption on Pt and Re. An obvious difficulty is to account for an unknown quantity of H₂ (or CO) adsorbed on Pt and Re. It is known that Re hardly adsorbs H₂ at these conditions [15], but Pt chemisorbs H₂. A reliable way of determining adsorption on Co and Pt or Re separately is not easily available. It is reasonable to assume that in the case of Co–Re, H₂ chemisorption determines only the Co surface area. We have chosen to report adsorbed amounts as if all H₂ or CO were adsorbed on Co.

The XRD results show that the particle size is not strongly affected by the addition of noble metal promoters. The calcined (unreduced) catalysts all showed Co₃O₄ particle sizes in the 14–19 nm range. In Al₂O₃-supported Co catalysts,

Table 2
CO hydrogenation characteristics^a

Catalyst	<i>T</i> (K)	<i>P</i> (bar)	H ₂ /CO	R _{CO} (μmol/gCo s)	TOF _{CO} ^c (10 ⁻³ s ⁻¹)	S-CH ₄ (%)
8.7Co/Al ₂ O ₃	473	5	2	19.1	32.2	8
8.7Co1.0Pt/Al ₂ O ₃	473	5	2	32.5	17.4	8
8.7Co/Al ₂ O ₃	493	1	7.3 ^b	18.4	31.0	76
8.7Co1.0Pt/Al ₂ O ₃	493	1	7.3 ^b	36.8	19.7	72
8.7Co1.0Re/Al ₂ O ₃	493	1	7.3 ^b	38.3	17.5	78

^a Co and Pt loadings are given as weight% of the metals for the catalysts in the unreduced state.

^b 44% inert in the feed.

^c Based on H₂ chemisorption calculated from TPD, assuming adsorption only on Co-atoms.

XRD will only detect the relatively large, crystalline Co_3O_4 particles [16]. We have previously suggested that the role of Pt in a $\text{CoPt}/\text{Al}_2\text{O}_3$ catalyst is to promote the reduction of amorphous surface oxides known to be present in $\text{Co}/\text{Al}_2\text{O}_3$ catalysts [14]. This explains the apparent discrepancy between XRD particle sizes and

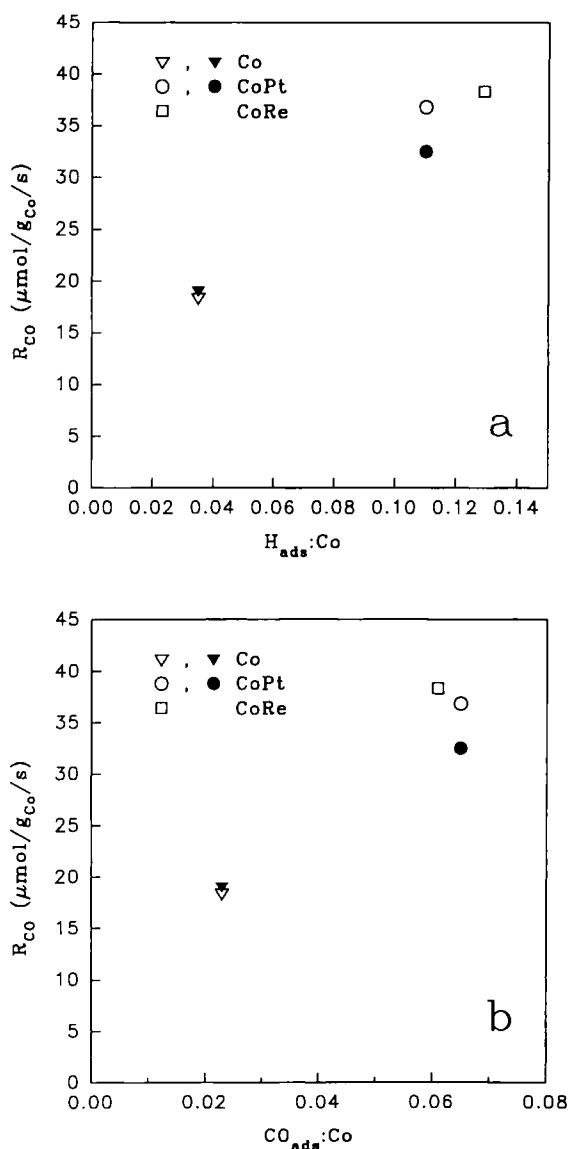


Fig. 1. Variation in the reaction rate with the amount of (a) H_2 adsorbed as calculated from TPD and (b) CO adsorbed as determined from volumetric chemisorption. Filled symbols denote CO hydrogenation at FT conditions ($T = 473 \text{ K}$, $\text{H}_2/\text{CO} = 2$ and $P = 5 \text{ bar}$) and open symbols denote CO hydrogenation at SSITKA conditions ($T = 493 \text{ K}$, $\text{H}_2/\text{CO} = 7.3$ and $P = 1 \text{ bar}$).

dispersion from H₂ or CO chemisorption. TPR results indicate a similar role for Re on CoRe/Al₂O₃ catalysts [17].

The catalytic effect of Pt or Re addition is shown in table 2. Based on weight of cobalt, the Pt- or Re-promoted catalysts are approximately twice more active than the unpromoted catalyst. It is also important to note that the selectivity for methane formation does not depend on the addition of promoters.

Plots of the reaction rate (based on weight of Co) as a function of adsorbed H₂ and CO (fig. 1) show that the reaction rate in general increases with the amount chemisorbed at a given set of reaction conditions. A straight line through the origin is expected if the turnover frequency is constant for all the catalysts, provided that H_{ads} : Co or CO_{ads} : Co determines the number of active sites correctly.

In order to decouple the effects of average site activity and the concentration of active surface intermediates leading to methane, the kinetics of methanation was studied by steady-state isotopic transient kinetic analysis (SSITKA), mainly developed by Happel et al. [6] and Biloen et al. [4]. Examples of normalized transients obtained by switching from ¹³CO to ¹²CO are displayed in fig. 2, and the results are summarized in table 3. It is obvious from table 3 that the increase in the reaction rate is accompanied by a similar increase in the surface concentration of active intermediates leading to CH₄ (denoted as N_{CH₄(t)}). This is a result of the essentially constant surface residence times (τ_{CH_4}) = 6–7 s for all the catalysts. It can be concluded from these results that the increase in the reaction rate for the Pt- or Re-promoted catalysts is caused by surface concentration effects and not by increased intrinsic reactivity. The average site activity, as given by 1/ τ_{CH_4} , is close to 0.15 s⁻¹ for all the catalysts used in this study. This result, together with the insignificant dif-

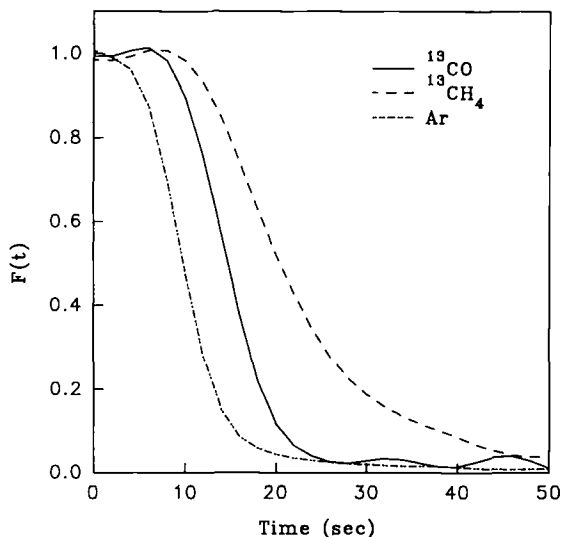


Fig. 2. Typical isotopic transients of Ar, ¹³CO and ¹³CH₄ corresponding to a switch from ¹³CO to ¹²CO.

Table 3
SSITKA results for CO hydrogenation on promoted and unpromoted Co/Al₂O₃^a

Catalyst	R_{CO} ($\mu\text{mol}/\text{g}_{\text{Co}}\text{ s}$)	$\text{TOF}_{\text{CO}} \times 10^3$ ^b (s^{-1})	S-CH ₄ (%)	τ_{CO} (s)	$\tau_{\text{CH}_{(4)}}$ (s)		
8.7Co/Al ₂ O ₃	18.4	31.0	76	8.3	6		
8.7Co1.0Pt/Al ₂ O ₃	36.8	19.7	72	11.6	7		
8.7Co1.0Re/Al ₂ O ₃	38.3	17.5	78	11.4	6		
	N_{CO} ($\mu\text{mol}/\text{g}_{\text{cat}}$)	$N_{\text{CH}_{(4)}}$ ($\mu\text{mol}/\text{g}_{\text{cat}}$)	Θ_{CO} ^b	$\Theta_{\text{CH}_{(4)}}$ ^b	Θ_{CO} ^c	$\Theta_{\text{CH}_{(4)}}$ ^c	
8.7Co/Al ₂ O ₃	30	8	0.58	0.15	0.50	0.13	
8.7Co1.0Pt/Al ₂ O ₃	83	16	0.51	0.10	0.70	0.14	
8.7Co1.0Re/Al ₂ O ₃	81	15	0.43	0.08	–	–	

^a CO/H₂/inert = 0.75/5.5/5 (ml/min), $T = 493$ K, $P = 1$ bar. CH₍₄₎ indicates surface intermediates leading to CH₄. τ_i : residence time of surface intermediates ($i = \text{CO}, \text{CH}_{(4)}$). N_i : concentration of surface intermediates ($i = \text{CO}, \text{CH}_{(4)}$). Θ_i : coverage of surface intermediates ($i = \text{CO}, \text{CH}_{(4)}$).

^b Based on H₂ chemisorption calculated from TPD, assuming adsorption only on Co-atoms.

^c Based on ¹²CO/¹³CO transients at 373 K (mol CO/mol Co), assuming adsorption only on Co-atoms.

ferences in selectivity, indicates that CO hydrogenation catalysis is not influenced by the presence of the noble metal in the systems which have been investigated.

The coverage of active surface intermediates leading to CH₄ ($\Theta_{\text{CH}_{(4)}}$) is low in all cases, corresponding to 8–15% of the available surface (based on H₂-TPD). The chromatographic effect indicates approximately 50% coverage of CO, independent of the presence of a noble metal promoter. The total coverage of surface species detected, $\Theta_{\text{CO}} + \Theta_{\text{CH}_{(4)}}$, is < 1.0 in all cases. It is difficult to conclude whether this indicates a large number of unoccupied sites or if the surface is blocked by some other unreactive compounds. However, some of these sites are obviously occupied by hydrogen and by intermediates which lead to higher hydrocarbons.

The lack of average site activity effects of Pt or Re has only been proved by SSITKA at methanation conditions. However, the similar bulk activity trends and the overall turnover frequency at Fischer–Tropsch conditions (5 bar, H₂/CO = 2) strongly suggest a similar role for Pt or Re also for the formation of higher hydrocarbons.

4. Conclusions

The addition of Pt or Re significantly increases the CO hydrogenation rate of Al₂O₃ supported Co catalysts. It has been shown that the increased reaction rates are caused by increased reducibility and increased number of surface exposed Co-atoms. Results obtained by steady-state isotopic transient kinetic analysis, SSITKA, indicate that the concentration of active surface intermediates leading to

CH₄ increases upon addition of a noble metal promoter. However, the average site activity was not affected upon addition of the promoters. This conclusion is also supported by the fact that the selectivity does not change as a result of Pt or Re addition.

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