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TPR study of the mechanism of rhenium promotion of alumina-supported cobalt Fischer–Tropsch catalysts

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The effect of small amounts of Re on the reduction properties of γ-alumina supported cobalt catalysts has been studied by temperature-programmed reduction (TPR). An intimate mixture of Co/Al_2O_3 and Re/Al_2O_3 catalysts showed a promoting effect of Re similar to that for coimpregnated $Co–Re/Al_2O_3$. A loose mixture of $Co/Al_2O_3 + Re/Al_2O_3$ did not show any effect of Re on the reduction of cobalt. However, when the loose mixture of $Co/Al_2O_3 + Re/Al_2O_3$ was pretreated with Ar saturated with water before the TPR, a promoting effect of Re on the reduction of Co was observed. It is suggested that Re promotes the reduction of cobalt oxide by hydrogen spillover, and that no direct contact between Re and Co seems to be necessary in order to obtain the promoting effect as observed by TPR. It is also shown that the presence of a high temperature TPR peak at 1200 K assigned to cobalt aluminate is mainly a result of Co-ion diffusion during the TPR and not during calcination.

Keywords: Fischer–Tropsch; cobalt; rhenium; alumina; promotion; reduction; spillover

1. Introduction

Supported cobalt catalysts are the preferred catalysts for the Fischer–Tropsch synthesis of long chain paraffins from natural gas. The classical cobalt catalysts used in the first German industrial plants had very low activity [1]. The development of cobalt catalysts with high activity and high selectivity towards long chain paraffins is important for utilizing the Fischer–Tropsch synthesis in natural gas conversion. One way of improving the activity is by adding small amounts of a second metal such as Pt or Re [2–5].

The addition of a second metal to supported cobalt catalysts is known to promote the reduction of cobalt oxide [2–7]. It has been shown previously [2,3] that the observed increase in CO hydrogenation rate for these bimetallic catalysts is caused mainly by increased reducibility resulting in an increased number of surface exposed cobalt atoms. It has also been shown [2] that the selectivity is not changed by the addition of Pt or Re. There have been suggestions of spillover as the cause of noble metal promotion in cobalt catalysts [7–9]. Hydrogen may adsorb on the reduced noble metal, dissociate and spill over to the cobalt, either on the support or directly from the noble metal to CoO_x, depending on the degree of contact between the components. Formation of bimetallic particles has been proposed by other authors [10–15] for Pt, Ru, Ir and Rh promoted cobalt catalysts. A crucial point is therefore to determine whether direct contact between Co and the noble metal is required for obtaining the promoting effect.

Mechanical mixtures of the individual catalyst components have been used in several cases to study the reduction behavior of bimetallic systems [10,16,17]. The experiments reported here are done with mechanical mixtures of supported cobalt and rhenium catalysts to study the possibility of hydrogen spillover as the cause of the increased reducibility of cobalt oxide in the presence of Re.

2. Experimental

Al_2O_3 supported catalysts (38–53 μm) containing 20 wt% Co and 20 wt% Co + 1 wt% Re were prepared by incipient wetness coimpregnation of the support with aqueous solutions of $Co(NO_3)_2{\cdot}6H_2O$ and $HReO_4$. The catalysts were dried in air overnight at 393 K and calcined in air at 573 K for 2 h. A Re/Al_2O_3 catalyst (53–106 μm) containing 1 wt% Re was also prepared. The sample was prepared by incipient wetness impregnation of the support with an aqueous solution of Re_2O_7. The catalyst was dried in air overnight at 393 K and calcined in air at 673 K for 2 h. The γ-Al_2O_3 support used for all the catalysts was Vista-B (from Vista Chemicals). A bulk Co_3O_4 catalyst was also prepared as a reference material. NH_3 was added to an aqueous solution of $Co(NO_3)_2{\cdot}6H_2O$ with continuous stirring until an excess of NH_3 was observed. The precipitate was washed several times in distilled water and dried overnight at 370 K before calcination in air at 643 K for 3 h.

Mechanical mixtures of $Co/Al_2O_3 + Re/Al_2O_3$ or $Co/Al_2O_3 + Al_2O_3$ were prepared in two different manners: either by gently mixing the two powders (denoted LM for loose mixture), or by mixing and gentle grinding followed by pressing the powders to a disk and regranulating to particles of 425–850 μm size (denoted IM for intimate mixture). In both cases a 1 : 1 ratio (by weight) was used to give the same Co/Re ratio as in the coimpregnated catalyst. Two different mixtures were made by both of these methods producing four different samples. These are listed in table 1.

Temperature-programmed reduction (TPR) experiments were performed at a heating rate of 10 K/min to 1203 K in a gas mixture consisting of 7% H_2 in Ar. The portion of the TPR curves above 1203 K signifies the consumption with time at 1203 K. Calibration was done by reduction of Ag_2O powder. The TPR apparatus has been described elsewhere [18]. The amount of cobalt in each sample was kept constant for all experiments, resulting in a doubled total sample mass for the mechanical mixtures. The gas flow rate was 30 ml(STP)/min for all experiments.

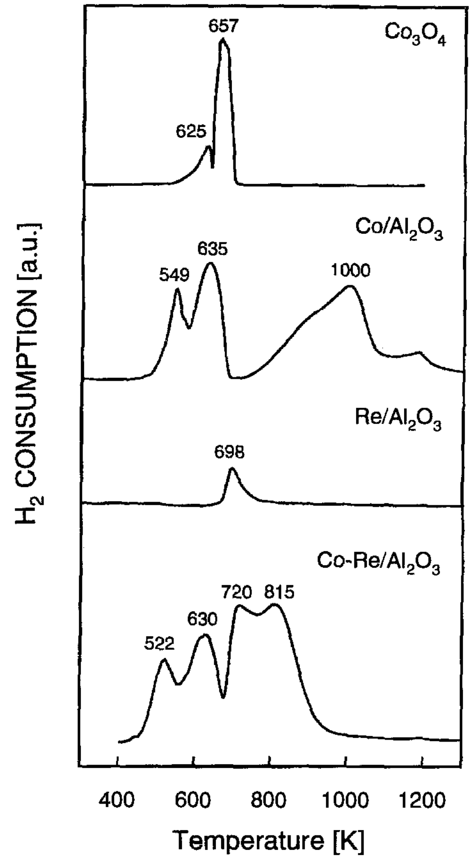

Fig. 1. TPR of Co/Al_2O_3, Re/Al_2O_3 and Co–Re/Al_2O_3 catalysts and unsupported Co_3O_4.

3. Results

Fig. 1 shows TPR curves for the different catalysts and bulk Co_3O_4. The reduction of bulk Co_3O_4 shows two TPR peaks at 625 and 657 K. The TPR curve for the Co/Al_2O_3 catalyst consists of several peaks ranging from 549 K to approximately 1200 K. The shape of the peak at 1200 K is somewhat modified due to the fact that the temperature reaches its final level at this point. The Re/Al_2O_3 catalyst shows a single TPR peak at 698 K. The Co–Re/Al_2O_3 catalyst shows several TPR peaks similar to the Co/Al_2O_3 catalyst. Comparison of the Co/Al_2O_3 and Co–Re/Al_2O_3 curves shows that the two low temperature peaks are not affected by the presence of rhenium. The peak at 1000 K for the unpromoted catalyst is shifted approximately 200 K to lower temperatures for the Re-promoted catalyst and is probably overlapping with the Re-reduction peak (720 K). The peak at 1200 K has almost disappeared in the TPR of the Re-promoted catalyst.

In order to investigate if the observed shift in the reduction temperature was caused by hydrogen spillover from Re to Co, and not dependent on a direct interaction of Re and Co, TPR of physical mixtures of Re/Al_2O_3 and Co/Al_2O_3 were performed. The total amount of sample was doubled for the physical mixtures, compared to the TPR samples of pure catalysts, but the specific flow rate (cm^3/g Co) was kept constant. The increased amount of sample may affect the TPR by changing the gas-flow pattern through the catalyst bed and the dilution may also change the temperature profile in the catalyst bed. Control experiments were therefore performed with physical mixtures of the Co-catalyst and the support. Fig. 2 shows TPR curves for Co/Al_2O_3 and $Co/Al_2O_3 + Al_2O_3$ (LM). The increase in the amount of sample led only to slight changes in the TPR curve with an increase in the starting reduction temperature for the peak at ca. 1000 K as the main result. Fig. 3 shows TPR curves for $Co/Al_2O_3 + Al_2O_3$ (LM) and $Co/Al_2O_3 + Re/Al_2O_3$ (LM). No effect of rhenium on the reduction of cobalt is observed and the resulting curve seems to be merely a superposition of the TPR curves for the two separate catalysts. The reduction of Re is visible as a separate peak at 720 K.

However, when the two catalysts are more intimately mixed (IM), a pronounced effect is observed on the

Table 1
Preparation of mixed samples

Catalyst mixture	Preparation
20% Co/γ-Al_2O_3 + γ-Al_2O_3	gently mixed powders (38–53 μm + 53–106 μm) (LM)
20% Co/γ-Al_2O_3 + 1% Re/γ-Al_2O_3	gently mixed powders (38–53 μm + 53–106 μm) (LM)
20% Co/γ-Al_2O_3+ γ-Al_2O_3	mixed, pressed and crushed to 425–850 μm particles (IM)
20% Co/γ-Al_2O_3 and 1% Re/γ-Al_2O_3	mixed, pressed and crushed to 425–850 μm particles (IM)

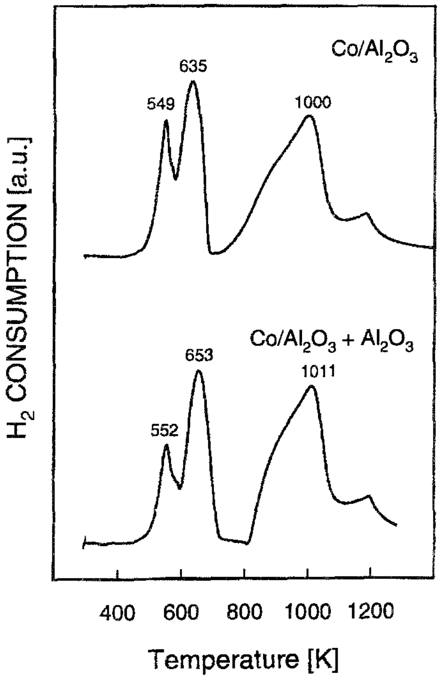

Fig. 2. TPR of Co/Al_2O_3 and $Co/Al_2O_3 + Al_2O_3$ (LM). (LM – loose mixture.)

reduction behavior (fig. 4). The peak at ca. 1000 K is shifted to lower temperatures by approximately 200 K and the peak at ca. 1200 K has almost disappeared, as was also observed for the coimpregnated $Co–Re/Al_2O_3$ catalyst. The intimately mixed (IM) samples consist of particles of 425–850 μm size compared to the 38–53 or 53–106 μm particle size for impregnated catalysts. It was therefore checked for possible intraparticle diffusion limitations in the large particles by performing TPR of Co-catalysts with different particle sizes (fig. 5). The two curves are virtually identical and indicate that there are no diffusion limitations for the large particles.

Fig. 6 shows TPR curves for loose mixtures (LM) of $Co/Al_2O_3 + Al_2O_3$ and $Co/Al_2O_3 + Re/Al_2O_3$. Both samples were pretreated with Ar saturated with water at 296 K for 30 min (equals exposure to ca. 1 mmol H_2O) before TPR. In the case of the $Co/Al_2O_3 + Re/Al_2O_3$ a

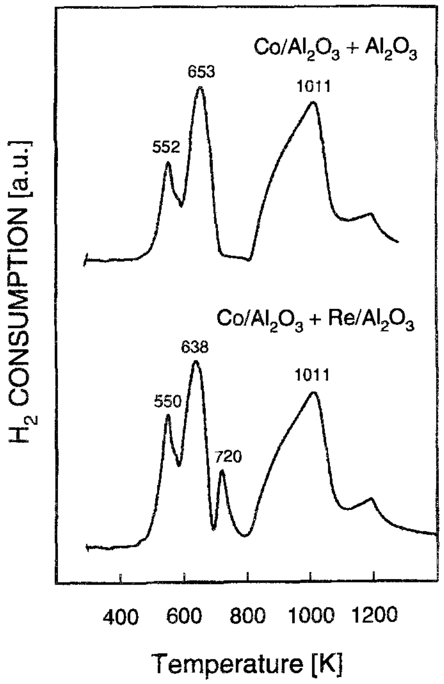

Fig. 3. TPR of $Co/Al_2O_3 + Al_2O_3$ (LM) and $Co/Al_2O_3 + Re/Al_2O_3$ (LM). (LM – loose mixture.)

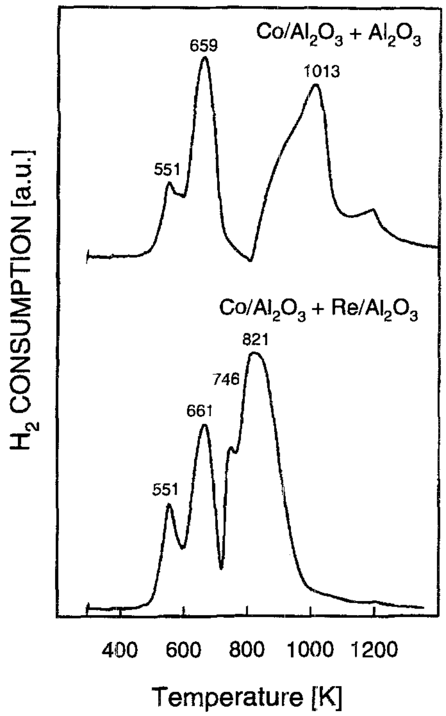

Fig. 4. TPR of $Co/Al_2O_3 + Al_2O_3$ (IM) and $Co/Al_2O_3 + Re/Al_2O_3$ (IM). (IM – intimate mixture.)

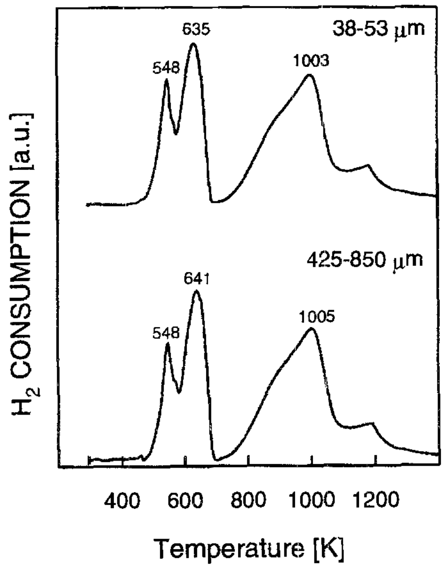

Fig. 5. TPR of Co/Al_2O_3 with particle size 38–53 and 425–850 μm.

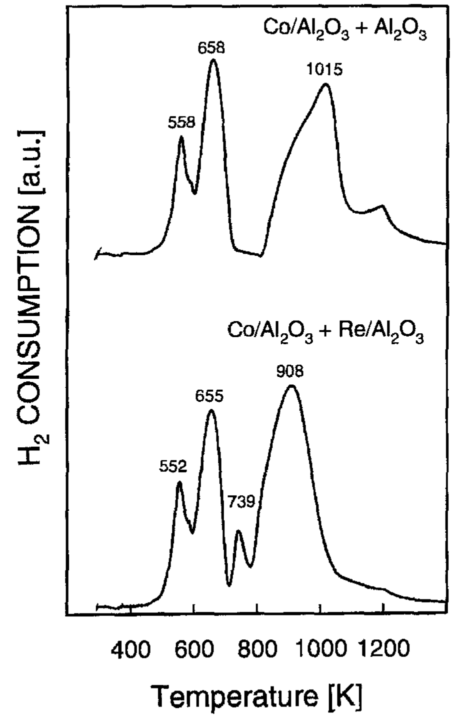

Fig. 6. TPR of Co/Al_2O_3 + Al_2O_3 (LM) and Co/Al_2O_3 + Re/Al_2O_3 (LM). Both samples have been exposed to Ar saturated with water at 296 K for 30 min prior to the TPR. (LM – loose mixture.)

significant effect on the reducibility is observed, although smaller than shown for the intimately mixed mixture (fig. 4). The peak at 1000 K is shifted approximately 100 K to lower temperatures, and also the peak at ca. 1200 K has decreased in size compared to the unpromoted Co-catalyst. The water pretreatment had no effect on the TPR curve for Co-catalyst mixed with pure support.

4. Discussion

The reduction of bulk Co_3O_4 shows two TPR peaks with a H_2-consumption corresponding to the stoichiometry of the two reduction steps involved ($Co^{3+} \rightarrow Co^{2+} \rightarrow Co^0$) (fig. 1). Reduction of Co_3O_4 has been observed as one or two TPR peaks, depending on whether the reduction sequence $Co^{3+} \rightarrow Co^{2+} \rightarrow Co^0$ is resolved or not [3,7,19–21]. Fig. 1 also contains a typical TPR curve for an alumina supported cobalt catalyst. The two-step reduction of Co_3O_4 is assumed to be unresolved in the case of Co/Al_2O_3 catalysts and the peaks have been ascribed to different oxide phases [3,19,22], except for the peak at 520–550 K which is due to reductive decomposition of cobalt nitrate remaining after calcination [7,19]. The peak at ca. 635 K is assigned to the reduction of large Co_3O_4 particles behaving similar to bulk Co_3O_4. The broad peak extending from 770 to 1070 K is due to the reduction of highly dispersed, amorphous surface phases. Spinel $CoAl_2O_4$, formed by diffusion of cobalt ions into the alumina lattice during calcination, is reduced around 1200 K. The reduction of the large Co_3O_4 particles and the reductive decomposition of cobalt nitrate are not affected by the presence of Re, but the reduction of the amorphous surface overlayers is shifted about 200 K to lower temperatures (fig. 1). It is likely that the promoting effect of Re requires that Re is in the reduced state. Only the Co-phases reduced at higher temperature than Re have their TPR peaks shifted to lower temperatures. It has been shown that Pt, which is reduced at lower temperatures, shifts the reduction temperature of both of the major cobalt oxide phases (Co_3O_4 and Co-surface phase) to lower temperatures [2,3,6]. Similar observations have been made for other noble metals [7]. Almost no cobalt aluminate is detected in the TPR of the Re-promoted Co-catalyst. This may be due to the decrease in the reduction temperature for the Co-surface phase, resulting in less Co-ions available at high temperature where cobalt aluminate can be formed during the TPR. The reduced cobalt aluminate peak area could also be a result of Re being present during calcination and in some way preventing the formation of cobalt aluminate at this stage.

It is a crucial point to know whether direct interaction of Co and Re is necessary for shifting the reduction temperature of the Co-surface phase and for decreasing the amount of cobalt aluminate. The loose mixture (LM) of Re/Al_2O_3 + Co/Al_2O_3 did not show any effect of Re on the reduction of Co (fig. 3). This is in agreement with results reported by Batley et al. [9], where no promoting effect of Pt in a mixture of cobalt oxide and supported Pt was observed. There will only be a very limited contact between the catalyst particles in a loose mixture and it is assumed that this is the reason for the absence of any effect of Re. This is confirmed by the large promoting effect observed when the catalyst particles are brought into more intimate contact (fig. 4). In the latter case, the magnitude of the shift in reduction temperature resembles that of the coimpregnated catalyst. This confirms that no direct contact between Re and Co is necessary for Re to promote the reduction of Co-oxide.

It has been suggested that some cobalt aluminate may be formed by solid-state diffusion of Co-ions during the TPR [19], which may affect the distribution of Co-phases as observed by TPR. Arnoldy et al. [19] observed that solid-state diffusion of Co^{2+}-ions occurs during calcination above 800 K. They found that the reduction of the Co-surface phase (and the more easily reducible phases) was not significantly affected by solid-state diffusion, and that TPR gives an essentially correct picture of the distribution of Co-phases. The decrease in the cobalt aluminate peak area for the Co/Al_2O_3 + Re/Al_2O_3 mixture (IM) as compared to the Co/Al_2O_3 catalyst shows that this peak is mainly a result of Co-ion diffusion during the TPR and is not formed during calcination. The two catalysts in the intimate mixture (IM) were calcined separately and the Co-oxide phases present in the IM before reduction should therefore be the same as in the unpromoted catalyst. It is reasonable to assume that the decrease in the reduction temperature for the Co-surface phase in the IM results in less Co-ions available for cobalt aluminate formation at high temperature.

It is known that water has a pronounced effect on hydrogen spillover when the degree of contact between acceptor and source is limited [25,26]. Water can enhance the ability of the support to transport spiltover hydrogen, probably via surface hydroxyl groups [27]. It can also act as a bridge between different phases [17,25] or it can decrease the energy barrier for hydrogen spillover by creating solvated protons [27,28]. Benson et al. [17] and Levy et al.[28] have shown the importance of water in the Pt-promoted reduction of WO_3 and Ambs et al. [29] have shown the effect of water in hydrogen spillover from Pt to alumina. The TPR curve for the water-pretreated loose mixture of $Co/Al_2O_3 + Re/Al_2O_3$ shows that the reduction of Co-oxide is promoted in this case, as opposed to the TPR results of the same mixture without water pretreatment (figs. 6 and 3). The absence of any shift in reduction temperatures for the water-pretreated mixture of $Co/Al_2O_3 + Al_2O_3$ (LM) shows that the observed promotion is not due to the presence of water alone. In spite of the limited contact between particles in the LM of $Co/Al_2O_3 + Re/Al_2O_3$, the addition of water evidently accelerates the diffusion of spillover hydrogen possibly by one of the mechanisms discussed above.

Our results suggest that the degree of promoting effect of Re depends on the efficiency of hydrogen transport from the reduced promoter to the cobalt oxide. Although formation of bimetallic particles cannot be excluded, the experiments confirm that no direct interaction between Re and Co is required for promoting the reduction as observed by TPR. It is also evident that most of the cobalt aluminate is formed during the TPR. This is supported by the TPR of the water-pretreated $Co/Al_2O_3 + Re/Al_2O_3$ (LM) where the Co-surface phase peak temperature is shifted less than for the corresponding IM, and the peak area for cobalt aluminate has also decreased less than for the IM.

Increased dispersion has been reported for Pt- and Re-promoted Co-catalysts compared to the unpromoted catalyst [2,3,7]. Further studies involving dispersion measurements on the mechanical mixtures, can reveal whether this is caused only by the additional reduction of highly dispersed Co-phases due to hydrogen spillover, or if Re has some direct effect on the Co-dispersion. Such studies and Fischer–Tropsch activity measurements are in progress.

5. Conclusions

It has been shown that Re promotes the reduction of cobalt oxide by hydrogen spillover, and that no direct contact between Re and Co particles seems to be necessary in order to obtain the promoting effect as observed by TPR. It has also been shown that the presence of a high temperature TPR peak at 1200 K assigned to cobalt aluminate is mainly a result of Co-ion diffusion during the TPR and not during calcination.

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