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Feature Article

Kinetic modelling of temperature-programmed reduction of cobalt oxide by hydrogen

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ABSTRACT

The reduction activities and mechanisms of cobalt-based catalysts are of great interest to industry and researchers, due to their applications in Fischer–Tropsch synthesis. Here, we investigated the reduction of alumina-supported cobalt catalysts by hydrogen using temperature-programmed reduction. We propose a five-step reduction mechanism that incorporates both amorphous and crystalline Co_3O_4, and includes the interaction between CoO and the Al_2O_3 support. Based on our proposed mechanism, we developed a kinetic model of the reduction process. The modelling results of catalysts promoted with ruthenium and lanthanum in contrast with un-promoted catalyst clearly show that the promoter improves reducibility of the catalyst. The effect of Co_3O_4 crystallinity was also investigated by the reduction of fresh in comparison of pre-oxidised catalyst. We conclude that high crystallinity significantly increases the difficulty of reducing Co_3O_4. The interaction between CoO and Al_2O_3 under reduction conditions to form $CoAl_2O_4$ was quantitatively simulated. The kinetic modelling confirms that the support plays an important role in catalyst reduction via the interaction between the catalyst and the support. Those kinetic modelling results are supported by in situ X-ray diffraction studies of the reduction process.

1. Introduction

Cobalt-based catalysts are used in a range of catalytic processes [1], for example olefin polymerisation catalysed by Cr/SiO_2 [2,3], alkane dehydrogenation catalysed by Cr/Al_2O_3 [2,4,5], and reactions catalysed by Cr/ZSM-5 such as toluene disproportionation [6], combustion and oxidation of organic compounds [7–9], reactive sorption of chlorinated volatile organic compounds [10,11], reduction of nitrogen oxides [12,13], ethylene ammoxidation [14,15], and oxidative dehydrogenation of ethane with CO_2 [16]. Besides these processes, cobalt-based catalyst are of particular importance in the Fischer–Tropsch synthesis. This is due to their low water–gas shift activity, high degree of conversion, low rate of attrition, high selectivity for paraffin and high resistance to deactivation [17,18].

Temperature-programmed reduction (TPR) is a common characterisation method that provides useful information about the behaviour of metal oxide catalysts and catalyst precursors. TPR has been used extensively to study the reducibility of cobalt oxide materials, with or without promoters (typically other metal oxides) [19–31]. Arnoldy et al. [19] reduced pure cobalt oxides, CoO and Co_3O_4, separately. A single peak was found for the reduction of each oxide, possibly due to the high concentration of hydrogen (67% H_2 in argon). However, the peak for the reduction of Co_3O_4 was broader, which was deemed to be indicative of a two-stage reduction of Co_3O_4 to Co via CoO. Subsequently, Sexton et al. [20] described the TPR of Co_3O_4 on Co foil. The TPR profile consisted of two peaks: a low-temperature peak below 573 K, and a high-temperature peak between 573 and 973 K. They attributed the separate peaks to the reduction of Co_3O_4 to CoO and CoO to Co, and proposed the following two-stage process:

$$\text{R1}\ Co_3O_4 + H_2 \rightarrow 3CoO + H_2O$$

$$\text{R2}\ CoO + H_2 \rightarrow Co + H_2O$$

The temperature of each reduction step, and hence the peak position on the TPR profile, generally vary from one catalyst to

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Nomenclature

I_i	TCD signal intensity (a.u.) at time i
n_O	Amount of reducible oxygen anions (mol)
n_{RuO_2}	Amount of reducible RuO_2 (mol)
$n_{Co_3O_4}$	Amount of reducible Co_3O_4 (mol)
S_I	Obtained from integration of the TCD signal intensity after normalisation
β	Average heating rate in K/s
P_i and P_{H_2}	Hydrogen partial pressure (Pa) at time *i*
$Flow_i$	Flow rate (mol/s) calibrated by TCD at time *i*
$\overline{P}$	Average pressure (Pa)
T	Temperature (K)
ΔT	Temperature difference at each time increment (K)
t	Time (s)
k_i	Reaction constant for reaction *i*
A_i	Pre-exponential factor
E_i	Reaction activation energy (J/mol)
R	Universal gas constant (8.314 J/mol/K)
$[\text{Compound A}]_j$	Surface concentrations of Compound A (mol/m^2) at time *j*
$[Co_3O_4]_0$ and $[RuO_2]_0$	Initial surface concentrations (mol/m^2) of Co_3O_4 and RuO_2
RSS	The residual sum of squares
err	The standard deviation
x_i	The value of the i^{th} experiment
$\bar{x}$	The average value of total n experiments

another. This is largely due to differences in catalyst compositions. Examples include the metal loading, type of supports and promoters, preparation methods employed (wet impregnation or co-precipitation), and the conditions of preparation (pH of the solution during the impregnation step, precursor used to produce the catalyst, silica source, solvent used for impregnation, drying temperature and dwell time, and calcination temperature and atmosphere etc.) [28]. Arnoldy et al. [19] found that the calcination temperature of the catalyst during its preparation affects the conversion of the metal salts, and as a result, the reduction performance. Increasing the calcination temperature caused the reduction peaks shifting to higher temperatures, due to changes in particle sizes. Reduction of the remaining precursor, $Co(NO_3)_2$, was observed between 450 and 510 K by Steen et al. [28] when calcinations were performed below 523–573 K. Large differences in reduction profiles may also arise due to factors such as reduction temperature, particle/crystallite size, and choice of reducing agent.

Table 1 lists the characteristics of TPR profiles for cobalt catalysts described in the literature. Generally, two major peaks are observed: the first between 373 and 700 K, corresponding to the reduction of Co_3O_4 to CoO (R1), and the second between 550 and 1023 K, related to the reduction of CoO to Co (R2). Lin et al. [29] studied the reduction mechanism of Co_3O_4/SiO_2 by hydrogen, and simulated TPR profiles using kinetic modelling. They obtained activation energies of 94.4 and 83.0 kJ/mole for R1 and R2, respectively. In addition, a third peak is sometimes observed above 800 K and up to 1120 K [28]. Puskas et al. [21] assigned the third peak to the reduction of cobalt silicate or cobalt alumina, which formed from the reaction between CoO and the support at temperatures above 1173 K. Steen et al. [28] calculated the apparent activation energy for this peak at 47 kJ/mol. The implications of the presence of $CoAl_2O_4$ have not been thoroughly explored; however, some evidence suggests that it plays an important role in controlling the reduction kinetics of Co_3O_4.

Noble-metal promoters, such as Ru, Pt, Pd, Rh, and Re, are often employed to facilitate reduction and to generate more active surface sites on catalysts [22–25]. The addition of a noble metal to a cobalt-based catalyst can promote the reducibility and dispersion of Co_3O_4 [32], thus increasing the number of cobalt surface sites and improving catalyst activity. Noronha et al. [22] investigated the effect of Pd, Pt and Rh on Co_3O_4/Nb_2O_5, and found that the reduction peaks shifted to lower temperatures. While the promoters reduced the reduction temperature for both Co_3O_4 and CoO, the effect was more pronounced for Co_3O_4. Jacobs et al. [23,24] found that adding 0.5% Pt to Co/Al_2O_3 shifted both peaks to lower temperatures by ca 150 and 80 K, respectively. The peaks also narrowed significantly, and the higher-temperature peak at 973 K was no longer apparent. An X-ray analysis demonstrated that during reduction of Co_3O_4, the high-temperature transition of CoO to Co was incomplete, due to the interaction of cobalt species with the alumina support, which broadened the TPR profile. While Pt addition reduced this effect, it did not completely eliminate it. Blik et al. [25] studied the TPR of $Co\text{-}Rh/Al_2O_3$, and described a hydrogen spillover effect on the rhodium surface. According to their interpretation, the very first metallic rhodium species formed acted as nucleation centres, which dissociate hydrogen molecules into highly reducing hydrogen atoms. Chu et al. [26] calculated that the overall activation energies for the reduction of Co_3O_4/Al_2O_3 and $Co_3O_4\text{-}PtO_2/Al_2O_3$ were 130 and 60 kJ/mol, respectively. This demonstrated the effect of the noble metal promoter in reducing the reduction temperature. Ernst et al. [27] investigated the promotion effect of cerium oxide on the reduction of Co_3O_4. They found that the reduction of Co_3O_4 to metal Co was favoured when the amount of cerium was over 40 wt%. Three peaks (550–700, 700–800 K and 800–1150 K) were in the TPR profiles; the first two were assigned to the reduction of Co_3O_4, while the third peak was not identified.

The reduction parameters reflect the reducibility of catalysts. As mentioned above, they also provide information for optimising activation conditions before catalysts are used for reactions such as Fischer–Tropsch synthesis. Although TPR is a typical characterisation technique for metal oxide catalysts, studies of the reaction kinetics for the reduction of Co_3O_4 using TPR are rare. In the present study, we investigated the reduction of a Ru-promoted Co catalyst supported on alumina, because the well-known two-step reduction mechanism does not satisfy the experimental observations. Instead, a more complex mechanism may occur during the reduction of Co_3O_4/Al_2O_3. We therefore studied TPR of the catalyst to develop a kinetic model that describes the reduction process. Our aim was to gain a more comprehensive understanding of the reducibility of cobalt and the effect of noble-metal promoters, thus aiding future catalyst selection and activation.

2. Experimental

2.1. Materials

A commercial Co-based catalyst for the Fischer–Tropsch synthesis reactions was selected for this investigation. It was prepared using standard incipient wetness techniques based on the open literature [33], with nominal contents as 20 wt% Co, 0.5 wt% Ru, and 1 wt% La_2O_3 on γ-alumina (Puralox SBa 200). This catalyst is referred to as $Ru\text{-}Co\text{-}La/Al_2O_3$.

To investigate the promoting effect of individual metals, we prepared two catalysts, Co/Al_2O_3 containing 10 wt% Co, and $Ru\text{-}Co/Al_2O_3$ containing 0.25 wt% Ru and 10 wt% Co. A wet impregnation method was used to prepare these catalysts. In brief, the Co/Al_2O_3 was prepared by incipient impregnation of alumina with $Co(NO_3)_2{\cdot}6H_2O$ dissolved in acetone followed by drying and