# Reduction of supported cobalt catalysts by hydrogen

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The reduction of cobalt catalysts supported on $Al_2O_3$, $SiO_2$, and $TiO_2$ was investigated using a closed system filled with hydrogen gas. Effects of support and metal loading on the rate of reduction were also discussed. The activation energy of reduction increased in the following order: $Co/TiO_2 < Co/Al_2O_3 < Co/SiO_2$. For different metal loadings, it was found that the catalyst with the higher loading was more readily reducible than that with the lower metal loading. This was confirmed using the results from measurements of particle size, amount of CO adsorbed and activity.

**Keywords:** supported cobalt catalysts; rate of reduction

When supported metals or metal oxides are used as catalysts, it is of great interest to understand the nature of the exposed solid phase. One way to study the solid phase is to observe its rate of reaction with hydrogen in the reduction of a supported metal oxide. This reduction is a topochemical reaction and still capable of supplying a great deal of information. Reduction rates can give some information about the activity of a surface phase, the extent of interaction with the support, and the uniformity of metal oxide in the support surface. These factors may vary with the methods of catalyst preparation and have an important part in determining the activity of supported metal catalysts. This paper aims at reporting rates of reduction of supported cobalt oxides and attempts to understand the transformation of cobalt oxide to cobalt metal during reduction. Effects of different supports and preparative conditions on the rates of reduction were also studied. To accomplish these, measurements of reduction rates were made by observing the pressure change in a closed system which was filled with circulating hydrogen. This procedure was first reported by Hill and Selwood [1] and was used in a modified form in the reduction studies of supported metal-oxide catalysts in a previous investigation [2]. Sometimes these differential rates are used, since they are much more informative than integral reaction curves.

Supported cobalt catalysts were prepared by incipient wetness technique using $Co(NO_3)_2{\cdot}6H_2O$ obtained from the Ventron Corporation. The support materials used in this study were γ-$Al_2O_3$, $SiO_2$ (Ventron Corp.), and $TiO_2$ (Cabot Corp.). Surface areas of γ-$Al_2O_3$, $SiO_2$, and $TiO_2$ were 200, 600 and 50 $m^2/g$, respectively. Hydrogen (Matheson ultrahigh purity 99.9995%) was further purified before using Deoxo unit (Engelhard Ind.) and Molecular Sieve 5A (Linde) traps. After preparation, catalysts were dried at 383–393 K for 12 h and calcined in air at 773 K for 1 h. The catalyst was placed in a quartz tube that was heated in an electric furnace. The catalyst temperature was measured and controlled using a thermocouple (iron–constantan) and thermocontroller (Japan Ewha Co., Series RE-4), respectively. The total system volume was 40 $cm^3$ and the weight of catalyst was $\sim$ 0.2 g. Hydrogen was initially circulated in the system at about 600–760 mm using a circulation pump (Cole-Parmer C-7520-00). As the reduction proceeds, the pressure decreases. The gas circulation rate was 2.5 $\ell$/h so that the full circle was completed in less than 1 min.

One example of change of hydrogen pressure with time is shown in fig. 1. The pressure measurements at each temperature were made using a fresh catalyst. The pressure decreases represent the extent of reduction for equal increments of time, since the support was subtracted using the experimental results from employing the support itself. The pressure changes increase linearly with reduction time at each constant temperature, suggesting that the reduction reaction with hydrogen follows the zero-order kinetics. For some sample there was an induction period of accelerating rate. It can be also seen that the extent of reduction increased with increasing the reduction temperature. The different activation energies of reduction for 5 wt% cobalt catalysts supported on various supports were estimated using the Arrhenius plot (fig. 2) and increased in the following order: $Co/TiO_2 < Co/Al_2O_3 < Co/SiO_2$. Fig. 2 also shows the effect of metal loading on the extent of reduction for the $Co/Al_2O_3$ catalyst. It is known that the activation energy of reaction is directly related to the degree of reduction [3]. If this relation is applied to this study, the extent of reduction would be increasing in order of $Co/SiO_2 < Co/$

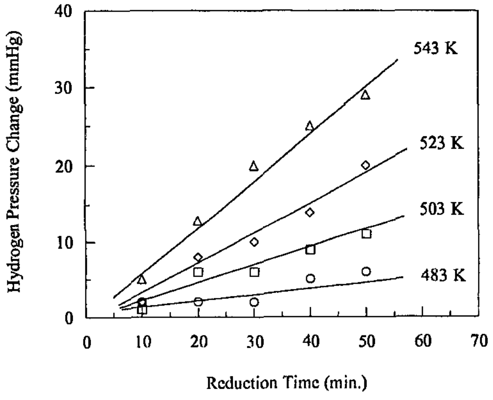

Fig. 1. Hydrogen pressure changes as a function of time at various temperatures for 5 wt% $Co/Al_2O_3$ catalysts.

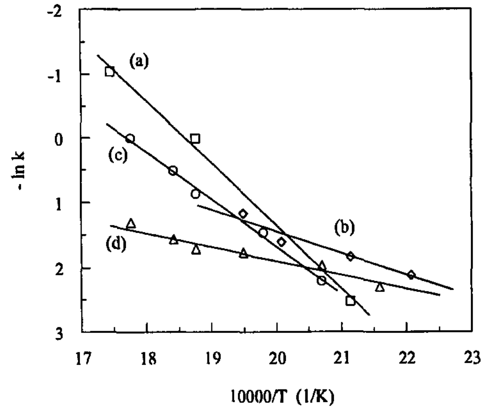

Fig. 2. Arrhenius plots for hydrogen reduction of supported cobalt catalysts: (a) 5 wt% $Co/SiO_2$, (b) 5 wt% $Co/TiO_2$, (c) 5 wt% $Co/Al_2O_3$, and (d) 12 wt% $Co/Al_2O_3$.

$Al_2O_3 < Co/TiO_2$. This is supported by the fact that, at two different loadings, the extents of reduction for $Co/TiO_2$ catalysts were higher than those for $Co/SiO_2$ catalysts, as discussed later (table 1). However, the thermal desorption results for CO adsorption indicated that the order for the extent of CO adsorbed was $Co/TiO_2 < Co/SiO_2 < Co/Al_2O_3$ (fig. 3). All the catalysts used for thermal desorption experiments were reduced at 800 K for 7 h in $H_2$ flow. One of the reasons for this difference is that the extent of reduction depends strongly on pretreatment conditions. In addition, the extent of reduction is relying on the preparative conditions such as different loadings, as can be seen in fig. 2 and table 1. In general, the catalyst with high metal loading is reduced more readily than that with low metal loading. Measurements of metal particle size can give one of the explanations for this metal loading effect on the reduction extent. In the case of $Co/Al_2O_3$, the particle sizes of 5 and 12 wt% catalysts were 90 and 135 Å, respectively. It was considered that the small particle (high percentage exposed) had stronger interaction between metal oxide and support than the large particle (low percentage exposed). Thus, the degree of interaction might be one of the reasons for different reducibility. Figs. 3a and 3b show the CO TPD spectra for 12 and 5 wt% $Co/Al_2O_3$ catalysts,

Table 1
Rate of hydrogen reduction at various temperatures for $Co/SiO_2$ and $Co/TiO_2$ catalysts

| Catalyst | Rate (μmol/s gram of Co) | | | | | | Relative total rate |
|---|---|---|---|---|---|---|---|
| | 373 K | 473 K | 573 K | 673 K | 773 K | 873 K | |
| 5 wt% $Co/SiO_2$ | 0.00 | 1.08 | 0.97 | 0.76 | 0.15 | 0.18 | 26 |
| 12 wt% $Co/SiO_2$ | 0.00 | 1.67 | 1.89 | 0.28 | 0.07 | 0.31 | 35 |
| 5 wt% $Co/TiO_2$ | 0.40 | 4.56 | 3.10 | 1.88 | 0.29 | 0.16 | 87 |
| 12 wt% $Co/TiO_2$ | 0.18 | 6.72 | 2.15 | 1.65 | 1.29 | 0.00 | 100 |

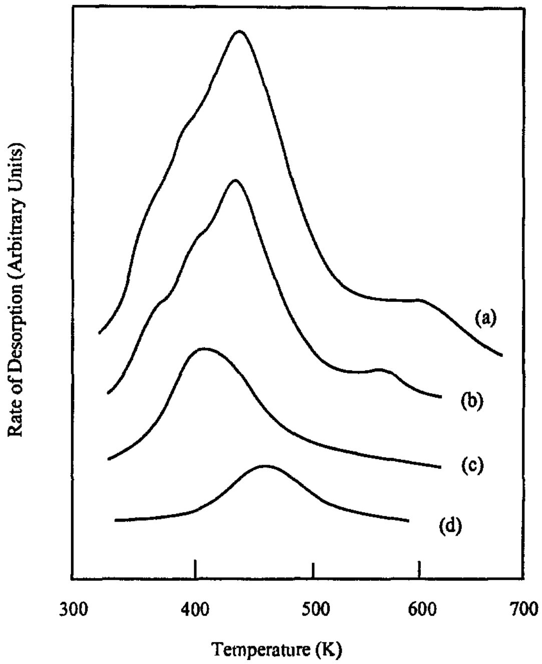

Fig. 3. TPD spectra of CO adsorbed on different Co catalysts: (a) 12 wt% $Co/Al_2O_3$, (b) 5 wt% $Co/Al_2O_3$, (c) 5 wt% $Co/SiO_2$, (d) 5 wt% $Co/TiO_2$. All the catalysts were reduced at 800 K for 7 h in $H_2$ flow.

respectively. The maximum desorption rate for 12 wt% $Co/Al_2O_3$ was much higher than that for 5 wt% $Co/Al_2O_3$. This result indicated that the 12 wt% cobalt surface had a greater CO saturation capacity than did the 5 wt% cobalt surface. Furthermore, some very preliminary flow reactor experiments indicated that the activity of 12 wt% $Co/Al_2O_3$ for CO hydrogenation was approximately 1.5 times higher than that of 5 wt% catalyst on a per gram basis. Therefore, it appears that the results from measurements of particle size, the amount of CO adsorbed and activity exhibit a relation between metal loading and the extent of reduction. The dependence on metal loadings can be found in other investigations. Zowtiak and Bartholomew [4] reported that for 3 wt% cobalt catalysts supported on various supports, the extent of reduction after treatment in $H_2$ at 673 K for 16 h increased with the following order: $Co/TiO_2 < Co/Al_2O_3 < Co/SiO_2$. The order for 10 wt% catalysts was $Co/Al_2O_3 < Co/TiO_2 < Co/SiO_2$. According to their results, it was clear that there was an effect of metal loading on the extent of reduction. In this study, since the experimental conditions such as loading, reduction time, and temperature, were very different from those of Zowtiak and Bartholomew, different results were obtained.

The rate of reduction was expressed as hydrogen consumption per second on a per gram of cobalt metal basis so that it was possible to compare the reduction rates for different catalysts (table 1). While the reduction temperature increased on a regular time schedule, the same catalyst was used. Reduction rate at each constant temperature was obtained by observing hydrogen consumption for 10 min. For $Co/SiO_2$ catalysts the reduction extent of 12 wt% catalyst increased 35%, while for $Co/TiO_2$ the reduction extent increased 15%. As the metal loading increased, the support effect was more eminent. Reuel and Bartholomew [5] reported that with the increase of metal loading from 3 to 10 wt%, the reduction extent of $Co/SiO_2$ increased 23%. Their results are close to those in this study. The plot of reduction rate with temperature suggests that the reaction mechanism for reduction of $Co/SiO_2$ and $Co/TiO_2$ catalysts follows two stages (fig. 4). A similar mechanism has been suggested by Sexton et al. [6]. This two-stage mechanism for the transformation of cobalt oxide to cobalt metal might be written as follows: $Co_3O_4 \rightarrow 3CoO + H_2O$ (first stage) $\rightarrow 3Co + 4H_2O$ (second stage). They also observed that the cobalt oxide $Co_3O_4$ was the dominant cobalt component on all air-calcined catalysts and was reduced rapidly to CoO at $\sim$ 573 K in hydrogen, but CoO was more slowly reduced to Co metal at $\sim$ 673 K. In this study, for $Co/Al_2O_3$ catalyst calcined at 773 K for 1 h in air, X-ray diffraction (XRD) patterns (Cu K$\alpha$ radiation) were characterized by two different peaks, the larger one being the (311) diffraction peak of $Co_3O_4$ and the smaller one the (220) diffraction peak of $CoAl_2O_4$. Maximum rates of reduction for $Co/SiO_2$ and $Co/TiO_2$ catalysts were observed at temperatures between 450 and 600 K, indicating that these temperatures were in the range of the first stage. Existence of reduction rate even after 600 K is related to the second stage forming the cobalt metal slowly from the cobalt oxide CoO.

Irrespective of metal loading the extent of reduction of $Co/SiO_2$ was about 3 times lower than that of $Co/TiO_2$. Even at the lowest temperature of 373 K, no reduction rates on $Co/SiO_2$ catalysts were observed while $Co/TiO_2$ catalysts exhibited some rates. These results suggested that $Co/SiO_2$ catalysts were reduced more slowly than $Co/TiO_2$ catalysts. Even though one of the $Co/TiO_2$ catalysts

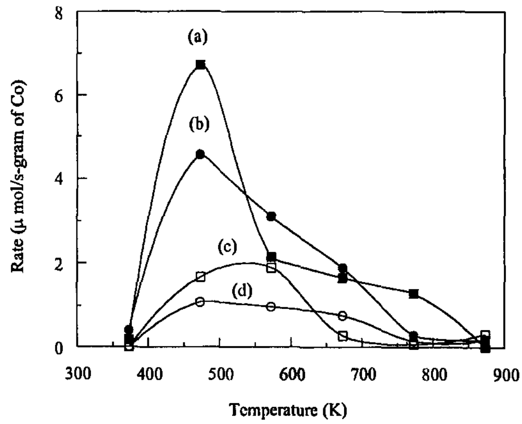

Fig. 4. Dependence of reduction rates on temperature over supported cobalt catalysts: (a) 12 wt% $Co/TiO_2$, (b) 5 wt% $Co/TiO_2$, (c) 12 wt% $Co/SiO_2$, and (d) 5 wt% $Co/SiO_2$

was completed to reduction at 873 K, the Co/$SiO_2$ catalysts still displayed the reduction rate. Strong resistance to reduction for Co/$SiO_2$ catalysts may be explained by the concept of strong oxide–oxide interaction (SOOI). Lund and Dumesic [7] proposed this SOOI concept from their observations on iron oxide supported on silica wherein they deduced the incorporation of $Si^{4+}$ ions in tetrahedral sites of $Fe_3O_4$ spinel lattice using the Mössbauer spectroscopy technique. Another study showed that silica stabilized $Fe^{2+}$ during the reduction of $Fe_3O_4$/ $SiO_2$ [8]. In this study, the stabilization of $Co^{2+}$ by $SiO_2$ may have resulted in retardation to reduction in the Co/$SiO_2$ catalyst.

## References

[1] F.N. Hill and P.W. Selwood, J. Am. Chem. Soc. 71 (1949) 2522.
[2] V.C.F. Holm and A. Clark, J. Catal. 11 (1968) 305.
[3] M. Boudart, *Kinetics of Chemical Processes* (Prentice-Hall, Englewood Cliffs, 1968).
[4] J.M. Zowtiak and C.H. Bartholomew, J. Catal. 83 (1983) 107.
[5] R.C. Reuel and C.H. Bartholomew, J. Catal. 85 (1984) 63.
[6] B.A. Sexton, A.E. Hughes and T.W. Turney, J. Catal. 97 (1986) 390.
[7] C.R.F. Lund and J.A. Dumesic, J. Phys. Chem. 85 (1982) 3175.
[8] J.W. Niemantsverdriet, A.M. Van Der Kraan and W.N. Delgass, J. Catal. 89 (1984) 138.