Gd promotion of Co/SiO_2 Fischer–Tropsch synthesis catalysts

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Received 22 August 2000; accepted 20 March 2001

Addition of Gd to Co/SiO_2 Fischer–Tropsch synthesis catalysts (1) increases reducibility to Co metal, (2) decreases CH_4 selectivity, (3) increases activity for CO hydrogenation based on the mass of Co, and (4) causes carbon deposition at lower temperatures when compared to the unpromoted catalyst. The intrinsic activity, based on H_2 chemisorption surface area, is the same for both unpromoted and promoted catalysts.

KEY WORDS: gadolinium; Gd promotion; Fischer–Tropsch synthesis; CO hydrogenation; cobalt; promoter

1. Introduction

Addition of group VIIIA metals, including Ru, Rh, Pd and Pt, to Co Fischer–Tropsch synthesis (FTS) catalysts increases specific activity, dispersion, reducibility, and selectivity to higher hydrocarbons [1–10]. It is noteworthy that all of these promoters and many other catalytically active metals have ground state electronic configurations not predicted by the aufbau principle. Pursuing this line of reasoning, it follows that gadolinium (Gd, electron structure: [Xe] $4f_75d_16s_2$) also having a ground state electronic configuration not predicted from the aufbau principle, should therefore, possess catalytic activity. It is further emphasized that Gd oxide has chemical characteristics similar to other oxides of the lanthanide and actinide series used as FTS promoters; moreover, being considerably less expensive than other commonly used precious metal promoters (table 1), it should have potential to be an ideal FTS promoter.

A number of studies have addressed the role of rare earth oxides (REOs) as promoters in CO hydrogenation on group VIII metals [11–24]. Vannice and co-workers [14,16] found specific methanation activities of Pd/REO catalysts to be about ten times greater than for Pd/SiO_2. In their TPD/IR study of REO-promoted Pd/SiO_2, Rieck and Bell [17] suggested partially reduced REO decorates Pd crystallite surfaces and promotes CO dissociation by forming side-on CO species upon adsorption (Pd–C=O–REO). Indeed, several studies [11,14–18,23] provide evidence for (1) migration during reduction of partially reduced REO onto group VIII metal crystallites and (2) promotion of CO dissociation by these partially reduced REOs. Using H_2 and CO adsorption, XPS and TPR Viswanathan and Gopalakrishnan [19] found that ThO_2 promotion of Co/kieselguhr catalysts improved the reducibility of the cobalt by preventing silica encapsulation of the cobalt. On the other hand, Sexton *et al.* [18] observed no change in the extent of reduction when ThO_2 was added to cobalt–kieselguhr catalysts. ThO_2 and other basic oxides are claimed to lower the support acidity of cobalt FTS catalysts which causes an increase in the chain growth probability [12,13]. Addition of La to Co/Al_2O_3 apparently decreases its methane selectivity [24]. It has been claimed that lanthanide and actinide promoters (1) improve the thermal stability of Co/TiO_2 catalysts [20,21] and (2) enhance the selectivity of a Fe/Mn/K for light olefins [22].

Shido and Iwasawa [23] found that GdO_x enhances the rate of CO hydrogenation on Ni/SiO_2 by (1) promoting CO dissociation and (2) providing sites for H_2 storage. Its promoting effect was found to be larger than for several other REOs. Their work provides strong evidence that clusters of a GdO_x suboxide decorate the surfaces of nickel crystallites in Ni/SiO_2 catalysts. No previous studies known to the authors have addressed specifically the effect of Gd promotion of cobalt FTS catalysts. The purpose of this short work was to investigate the feasibility of using Gd as a promoter for Co/SiO_2 FTS catalysts.

2. Experimental

Three catalysts, containing 12 wt% Co, 2 wt% Gd plus 12 wt% Co and 2 wt% Gd, all supported on Cab-O-Sil (M-5) were prepared by a non-aqueous evaporative deposi-

Table 1
Cost of various noble metals used as FTS promoters.[a]

Metal	Year 2000 price (in US dollars per g of material)
Rh	65
Pt	17
Ru	3.8
Gd	0.5

[a] Sources: noble metal prices from platinum 2000 published by Johnson Matthey; price of Gd from the chemistry website of Netscape.

tion technique using acetone as the solvent [25]. The support was dried in a muffle furnace at 600 °C for 2–3 h. Reagent grade $Co(NO_3)_2{\cdot}6H_2O$ and $Gd(NO_3)_3{\cdot}6H_2O$ were added to reagent grade acetone, and this solution was quantitatively added dropwise to the dried support. The slurry was stirred for 0.5 h at room temperature with a magnetic stir bar in a Pyrex glass bowl. The acetone was slowly evaporated by flowing purified He gas over the slurry while stirring. When the consistency was that of a thick paste, the stir bar was removed and the contents were placed in an oven at 60 °C for 5 min, following which the contents were then restirred with a spatula. This short drying/stirring procedure was repeated until only a trace of acetone could be detected by smell. At this stage, the catalyst was dried at 25 °C under a 25 cmHg vacuum for 5 min, stirred, dried in a 64 cmHg vacuum for 30 min, restirred, and placed in a desiccator overnight. The catalyst was subsequently dried at 42 °C under a 64 cmHg vacuum for 1 h.

Prior to chemisorption measurements, catalysts were reduced *in situ* in 0.8 atm of pure H_2 flowing at a gas hourly space velocity (GHSV) of 3000 while heating at a temperature ramp of 1 °C/min from room temperature to 400 °C followed by a 12 h hold at 400 °C. Chemisorption measurements were conducted using a flow chemisorption method and apparatus described by Jones and Bartholomew [26]. All dispersions were calculated using only the fraction of reduced Co metal according to a method validated by Bartholomew and co-workers [27,28]. Prior to activity tests, Co/SiO$_2$ catalysts were reduced in a 1 : 1 mixture of H_2 and Ar at 11 atm flowing at a GHSV of 3000 while heating at a temperature ramp of approximately 10–15 °C/min to 400 °C followed by a 12 h hold at 400 °C. Activity tests were conducted in a fixed-bed reactor described elsewhere [29].

Temperature-programmed reduction (TPR), temperature-programmed heating in argon (TPAr), and temperature-programmed CO hydrogenation (TPCOH) were performed in a Perkin–Elmer thermogravimetric analyzer (TGA) model TG 7. TPCOH involved reacting the reduced catalysts in a 5 : 5 : 90 (mole ratio) mixture of CO/H_2/Ar at a GHSV of ∼500 000 and a ramp of 6 °C/min followed by a temperature hold at 500 °C. All other TGA runs were conducted at a ramp of 1 °C/min and a GHSV of ∼500 000. TPR experiments were carried out in a 10% mixture of H_2 in Ar. Prior to each TPR and TPAr experiment the catalyst was calcined *in situ* in 10% O_2 in Ar, at a GHSV of ∼500 000, and a ramp of 1 °C/min to 300 °C and held at 300 °C for 4 h. TPR of each calcined catalyst was conducted as described above, followed by a TPAr (in 100% Ar) of a different sample of the same catalyst. The area under the corrected TPR profile, obtained by subtracting the TPAr profile from the experimental TPR profile (thereby eliminating experimental artifacts such as buoyancy and/or loss of water from the support), was used to calculate the extent of reduction of cobalt to the metal; in making this calculation it was assumed that after calcination, all cobalt was present in the form of Co_3O_4.

3. Results and discussion

The corrected TPR spectra are shown in figure 1. The peaks below 350 °C correspond to the reduction of Co_3O_4 which takes place in two steps: first reduction of Co_3O_4 to CoO and second, reduction of CoO to metallic Co [9,30]. The peaks having maxima at 400–600 °C correspond to reduction of CoO species that are difficult to reduce because of a strong interaction with the support and those above 600 °C to Co-silicates. For 2 wt% Gd/SiO$_2$ no change in weight was observed, indicating that Gd does not reduce under these conditions. The areas of the TPR spectra for the unpromoted and Gd-promoted Co/SiO$_2$ from 100 to 800 °C catalysts are the same further indicating that Gd does not reduce under these conditions. Gd addition, however, causes all reduction peaks to be shifted to lower temperatures and decreases the amount of hard-to-reduce Co species. Indeed, the unpromoted and Gd-promoted Co/SiO$_2$ catalysts have extents of reduction at 400 °C of 45 and 65%, respectively (see table 2). This is a surprising result, given that Gd is present in the catalyst as oxides (*e.g.*, Gd_2O_3 and GdO_x) and that REOs are themselves not capable of dissociating H_2. Noble metal promoters, on the other hand, are readily reduced at temperatures much lower than base metals and, upon reduction to the metal, can dissociate molecular hydrogen to hydrogen atoms which can spillover to base metal oxide surfaces, facilitating their reduction at lower temperatures than possible in the absence of the noble metal promoters.

A different mechanism probably operates in the case of Gd-promoted cobalt. One possibility is that Gd inhibits sil-

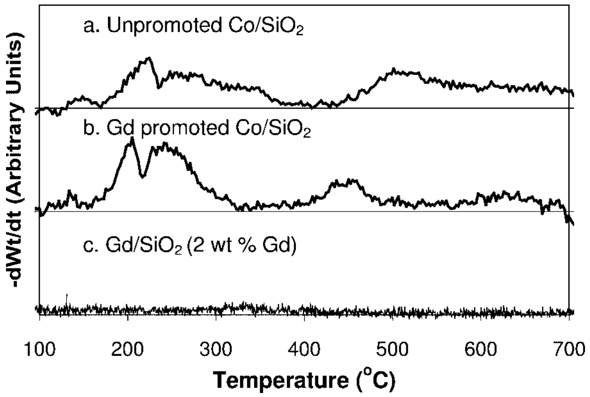

Figure 1. Effect of Gd on temperature-programmed reduction profile (heating ramp of 1 °C min^{-1}, 10% H_2 in Ar, GHSV = 500 000) of 12% Co/SiO$_2$, 12% Co/2% Gd/SiO$_2$, and 2% Gd/SiO$_2$.

Table 2

Effects of Gd on H_2 chemisorption, extent of reduction, and dispersion.[a]

Catalyst	Extent of reduction at 400 °C (%)	Uptake (μmol-H_2 g_{cat}^{-1})	Dispersion of Co (%)
Unpromoted	45	73.9 ± 5.1	17.0[b]
Gd-promoted	61	114.8 ± 2.7	15.6[c]

[a] Values of uptake are average of three runs.

[b] Cobalt dispersion based on reduced Co metal atoms only.

[c] Cobalt dispersion, assuming that GdO_x covers 20% of the cobalt surface.

ica migration, which otherwise encapsulates the Co metal. This hypothesis is consistent with that of Viswanathan and Gopalakrishnan [19], who observed that addition of ThO$_2$ inhibited silica migration onto the surface of cobalt oxide. Cab-O-Sil is a fumed silica consisting of non-porous, nanoscale primary particles that form free-to-migrate, long-chain aggregates [31–33]. These long chains in Cab-O-Sil are more likely to migrate onto cobalt metal crystallites than are primary particles in a silica gel which comprise more rigid structures [33,34]. Huber *et al.* [33,34] found evidence for considerable silica migration in Co/Cab-O-Sil especially in the presence of water, although Pt addition decreased the rate of silica migration. In the case of Gd-promoted Co/SiO$_2$, Gd oxide may be a textural promoter that largely prevents silica migration by either (1) "trapping" of otherwise mobile surface silanol groups or (2) increasing the rigidity of the silica surface, in either case, through formation of strong Gd oxide–Si oxide bonds.

Another possible scenario is a spillover mechanism involving first, reduction of cobalt oxides to metal atoms; second, dissociation of H$_2$ on cobalt metal surface atoms; followed by diffusion of H$_2$ atoms to Gd$_2$O$_3$ crystallites; and third, reduction of the neighboring Gd$_2$O$_3$ crystallites to GdO$_x$ clusters which migrate to the Co metal surface where they can assist the reduction process by extracting oxygen atoms from the cobalt oxide surface. As GdO$_x$ clusters accumulate on the cobalt surface they could store hydrogen atoms, increasing the overall hydrogen atom concentration and thereby increasing the rate of reduction. This result is consistent with that of Shido and Iwasawa [23], who concluded that GdO$_x$ provides sites for atomic hydrogen storage and for bonding to the oxygen end of CO when used as a promoter on Ni/SiO$_2$ catalysts.

The effects of Gd on chemisorption uptake, extent of reduction at 400 °C and dispersion are summarized in table 2. Extent of reduction and H$_2$ uptake are substantially higher for the Gd-promoted catalyst, while dispersions are the same within experimental error for the two catalysts. The dispersion of the Gd-promoted catalyst was calculated assuming that (1) reduced GdO$_x$ species are located on the surface of cobalt crystallites at a coverage of about 20% and (2) the adsorption stoichiometries are H/Co = H/Gd = 1. These assumptions are consistent with the adsorption data of Shido and Iwasawa [23] for 1.5% Ni/2% Gd/SiO$_2$ and with morphologies reported for REO promoters on silica-supported group VIII metals [11,14–18,23]. Nevertheless, the calculated dispersion is only approximate and might vary ±20%, depending on the assumptions made. Even so, within the limits of error of these assumptions, the dispersions of the Co/SiO$_2$ and Co–Gd/SiO$_2$ catalysts are not significantly different.

Activities and selectivities of the unpromoted and promoted catalysts are listed in table 3. The addition of Gd causes the CH$_4$ selectivity to decrease almost a factor of four and the CO hydrogenation rate based on weight of Co to increase about 50%. These results are similar to those reported by Huber *et al.* for Pt-promoted Co FTS catalysts [1]. The lower methane selectivity for Gd-promoted Co observed in this study could be due to a lowering of the acidity of the support due to addition of the Gd. The addition of other REOs to Co/Al$_2$O$_3$ FTS catalysts has been observed to decrease methane selectivity, and it has been postulated that this is due to a lowering of support acidity [12,13].

Table 3
Summary of activities and selectivities for unpromoted and Gd-promoted catalysts in a fixed-bed reactor.[a]

Catalyst	X_{CO} (%)	GHSV	Rate (mol-CO converted min^{-1} g$_{Co}^{-1}$)	Molar CH$_4$ selectivity (%)	TOF × 10^3 (s^{-1})
Unpromoted	13.8	1310	2.12	7.1	27.1
Gd-promoted	19.8	1330	3.23	1.9	26.5

[a] Catalysts reduced at 11 atm and 400 °C for 24 h at a GHSV of 1000; reaction conditions: $y_{CO} = 0.2$, $y_{H_2} = 0.4$, $y_{Ar} = 0.4$, 20 atm, 200 °C.

The TOF or site time yield, based on total chemisorption uptake, for Co/SiO$_2$ and Co–Gd/SiO$_2$ catalysts are similar indicating that Gd does not affect the intrinsic activity. Shido and Iwasawa [23] reported the TOF, based on irreversible adsorption of H$_2$ at room temperature, to be a strong function of Gd concentration. However, the validity of these results [23] must be questioned given (1) the low metal loading of their catalyst (1.5 wt% Ni) which typically complicates measurement of H$_2$ uptake due to decoration of metal crystallites by the support, thereby blocking H$_2$ adsorption sites [35] and (2) the use of irreversible H$_2$ adsorption capacities at room temperature to estimate TOF, since it has been demonstrated that irreversible H$_2$ adsorption undercounts the number of metal surface atoms [35]. On the other hand, Vada *et al.* [24] showed that addition of La to Co/Al$_2$O$_3$ at a La/Co atomic ratio of 0.10 does not affect the TOF based on H$_2$ adsorption at 298 K, while the TOF for a La/Co atomic ratio of 0.05 was only slightly higher, *i.e.*, double the TOF of the unpromoted catalysts. Other studies provide evidence that addition of precious metal promoters to Co FTS catalysts does not affect the intrinsic catalytic activity [1,8,10]. However, it is not possible on the basis of the data of this study to determine if Gd participates in the reaction or if Co is the only surface species, since the rate could be constant in either case when based on total H$_2$ chemisorption uptake and the assumptions discussed above (*e.g.*, adsorption on GdO$_x$ with H/Gd = 1), although it is clear that GdO$_x$ without Co is not active for either H$_2$ adsorption or the FT reaction.

Ribeiro *et al.* [36] (in a compilation of twelve studies of CO hydrogenation over Co on Al$_2$O$_3$, SiO$_2$, TiO$_2$, and other supports) and Zennaro *et al.* [29] (in a kinetic study of CO hydrogenation on Co/TiO$_2$) reported TOFs of 17 ± 14 and $15.4 \pm 7.4 \times 10^3$ s^{-1}, respectively, for supported cobalt, for which the data were normalized to $P_{H_2} = 6.67$ bar, $P_{CO} = 3.33$ bar and a temperature of 200 °C. When our data are normalized to these conditions, using reaction orders of 0.7 and −0.2 for H$_2$ and CO [29], the TOFs are 24.2 and 24.7×10^3 s^{-1} for Gd-promoted and unpromoted Co/silica, respectively. Thus, the TOF data for our catalysts fall within

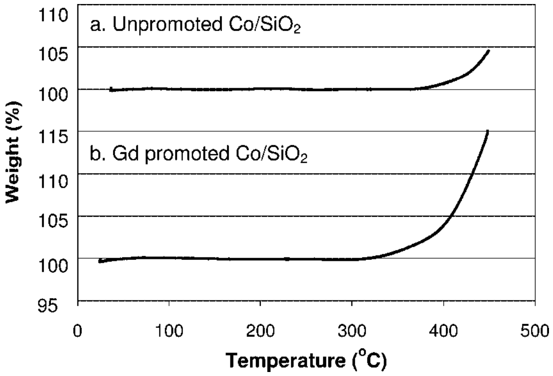

Figure 2. Effect of Gd on rate of carbon deposition during TPCOH. (Reduced catalysts, heating ramp of 6 °C min^{-1}, 5% H_2 and 5% CO in Ar, GHSV = 500 000.)

the range of TOF data for supported cobalt from previous studies. This good agreement suggests further that Gd does not significantly affect the specific activity of Co/SiO_2.

Temperature-programmed CO hydrogenation (TPCOH) in a 1 : 1 CO/H_2 mixture (see figure 2) causes significant carbon formation on the promoted and unpromoted catalyst, starting at temperatures of 320 and 380 °C, respectively. Thus, addition of Gd causes carbon to form at a lower temperature relative to the unpromoted catalyst. These results suggest that Gd provides sites for CO dissociation on Co catalysts as reported for Ni catalysts [23]. The effects of Gd on the carbon deposition rate are opposite to those for Ru-promoted Co/TiO_2 reported by Iglesia *et al.* [6] and for Pt-promoted Co/SiO_2 catalysts reported by Huber *et al.* [1]. Thus, Pt and Ru appear to have an advantage relative to Gd because they decrease the rate of carbon deposition, while Gd promotes carbon deposition due to its ability to dissociate CO. However, the results of this accelerated deactivation test do not necessarily imply that at typical reaction conditions (temperatures of 190–240 °C) carbon deposition is more likely to occur on the Gd catalysts.

4. Conclusions

In summary, we observe four effects of Gd promotion: (1) increased reducibility of Co to the metal, (2) decreased CH_4 selectivity possibly due to decreased support acidity, (3) increased activity based on the mass of Co, and (4) carbon deposition at lower temperatures. The increased reducibility, activity and decreased CH_4 selectivity on Co FTS catalysts are similar to the promotional effects of other rare earth oxides promoted Co FTS catalysts [11–13,19], while the higher carbon forming potential at lower reaction temperatures is opposite to that of Pt and Ru promoters [1,6,33,37].

Acknowledgement

The authors gratefully acknowledge financial support from ExxonMobil Research and Engineering, Mobil Technology, and Brigham Young University as well as technical assistance by Jenny Case, Daniel M. Bennett, and Ethan A. Mastny.

References

[1] G.W. Huber, T.L. Conrad, K.W. Woolley, C.G. Guymon and C.H. Bartholomew, Prepr. Petr. Chem. Am. Chem. Soc. 45 (2000) 260.
[2] A.R. Belambe, R. Oukaci and J.G. Goodwin, J. Catal. 166 (1997) 8.
[3] H.F.J. van't Blik, D.C. Koningsberger and R. Prins, J. Catal. 97 (1986) 210.
[4] L.A. Bruce, M. Hoang, A.E. Hughes and T.W. Turney, Appl. Catal. A 100 (1993) 51.
[5] L. Guczi, R. Sundararajan, Z. Kippany, Z. Zsoldos, Z. Schay, F. Mizukami and S. Niwa, J. Catal. 167 (1997) 482.
[6] E. Iglesia, S.L. Soled, R.A. Fiato and G.H. Via, J. Catal. 143 (1993) 345.
[7] E. Iglesia, S.L. Soled and R.A. Fiato, J. Catal. 137 (1992) 212.
[8] A. Kogelbauer, J.G. Goodwin and R. Oukaci, J. Catal. 160 (1996) 125.
[9] D. Schanke, S. Vada, E.A. Blekkan, A.M. Hilmen, A. Hoff and A. Holmen, J. Catal. 156 (1995) 85.
[10] S. Vada, A. Hoff, E. Adnanes, D. Schanke and A. Holmen, Topics Catal. 2 (1995) 155.
[11] C.H. Bartholomew, in: *New Trends in CO Activation*, Stud. Surf. Sci. Catal., Vol. 64, ed. L. Guczi (Elsevier, Amsterdam, 1991) p. 158.
[12] H. Beuther, C.L. Kibby, T.P. Kobylinski and R.B. Pannell, US Patent 4399234 (1983), assigned to Gulf Research and Development Company.
[13] H. Beuther, C.L. Kibby, T.P. Kobylinski and R.B. Pannell, US Patent 4413064 (1983), assigned to Gulf Research and Development Company.
[14] M.D. Mitchel and M.A. Vannice, Ind. Eng. Chem. Fundam. 23 (1984) 88.
[15] R.F. Hicks and A.T. Bell, J. Catal. 91 (1984) 104.
[16] C. Sudhakar and M.A. Vannice, J. Catal. 95 (1985) 227.
[17] J.S. Rieck and A.T. Bell, J. Catal. 99 (1986) 278.
[18] B.A. Sexton, A.E. Hughes and T.W. Turney, J. Catal. 97 (1986) 390.
[19] B. Viswanathan and R. Gopalakrishnan, J. Catal. 99 (1986) 342.
[20] C.H. Mauldin, S.M. Davis and K.B. Arcuri, US Patent 4719240 (1988), assigned to Exxon Research and Engineering Co.
[21] C.H. Mauldin, S.M. Davis and K.B. Arcuri, US Patent 4762959 (1988), assigned to Exxon Research and Engineering Co.
[22] R.A. Fiato, R. Bar-Gadda and S. Miseo, US Patent 4719240 (1988), assigned to Exxon Research and Engineering Co.
[23] T. Shido and Y. Iwasawa, J. Catal. 137 (1992) 267.
[24] S. Vada, B. Chen and J.G. Goodwin, J. Catal. 153 (1995) 224.
[25] G.W. Huber, C.C. Guymon and C.H. Bartholomew, in preparation (2001).
[26] R.D. Jones and C.H. Bartholomew, Appl. Catal. 39 (1988) 77.
[27] R.C. Reuel and C.H. Bartholomew, J. Catal. 85 (1980) 63.
[28] C.H. Bartholomew and R.B. Panell, J. Catal. 65 (1980) 390.
[29] R. Zennaro, M. Tagliabue and C.H. Bartholomew, Catal. Today 58 (2000) 309.
[30] A.Y. Khodakov, J. Lynch, D. Bazin, B. Rebours, N. Zanier, B. Moisson and P. Chaumette, J. Catal. 168 (1997) 16.
[31] K.C. Vranken, K. Possemiers, P.V.D. Voort and E.F. Vansant, Colloids Surf. A 98 (1995) 235.
[32] C.C. Liu and G.E. Maciel, J. Am. Chem. Soc. 118 (1996) 5103.
[33] G.W. Huber, Masters thesis, Brigham Young University (2000).
[34] G.W. Huber, C.G. Guymon, B.C. Stephenson and C.H. Bartholomew, in preparation (2001).
[35] C.H. Bartholomew, Catal. Lett. 7 (1990) 27.
[36] F.H. Ribeiro, A.E.S. von Wittenau, C.H. Bartholomew and G.A. Somorjai, Catal. Rev. Sci. Technol. 39 (1997) 49.
[37] C.H. Bartholomew, G.D. Weatherbee and G.A. Jarvi, Chem. Eng. Commun. 5 (1980) 125.